(iii) The comparison of the results of surface tension determination with the anionic detergent sodium dodecyl benzene sulphonate shows that the products obtained have a pronounced surface activity.

REFERENCES

1. Schönfeldt, N., *Surface Active Ethylene Oxide Adducts*, Pergamon Press, Oxford, 1969, p. 633.
2. Rom. patent 58,048 (1975); *Chem. Abstracts 85*:23042 (1976).
3. Habib, O.M.O., A.M. Badawy and S.G.A. El-Sayed, *Tenside Detergents 18*:89 (1981).
4. Hager, W., and H. Schief, *Chem. Tech. 6*:456 (1954).
5. Van Nes, K., and H.A. Van Westen, *Aspects of the Constitutions of Mineral Oils*, Elsevier Co., New York (1951), p. 461–469.
6. UOP, Laboratory test method for petroleum and its products (1959).
7. *Manual chemistului*, Bucuresti 2:2117 (1948).
8. Marei, A., and S.A. Fam, *J. Chem. UAR 12*:129 (1969).
9. Zeinalov, B.K., V.S. Leikakh and E.N. Shagidanov, *Dokl Akad Nauk. Azerb. SSR. 18*:24 (1962); *Chem. Abstracts 58*:12437 (1963).
10. Tanchuk, Yu V., P.A. Demchenko and S.A. Samodymov, *Nefteperal. Neftkhim 9*:73 (1973); *Chem. Abstracts 80*:82186 (1974).
11. Relaston, A.W., C.W. Hoerr and W.D. Pool, *J. Org. Chem. 8*:473 (1943).
12. Wrigley, A.N., F.D. Smith and A.J. Striton, *J. Amer. Oil Chem. Soc. 34*:39 (1957).
13. Padgett, A.R., and ED.F. Degring, *Ind. Eng. Chem. 32*:204 (1940).
14. U.S. patent 3004056 (1959); *Chem. Abstracts 56*:3585 (1962).
15. Findlay, A., *Practical Physical Chemistry*, Longmans, London, 6th ed., p. 101 (1963).
16. Ross, J., and G.D. Miles, *Oil and Soap*, 99 (1941).
17. Harris, J.C., and E.L. Brown, *J. Amer. Oil Chem. Soc. 27*:564 (1950).

♣ Isotachophoretic Analysis of Surfactants

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The qualitative and quantitative determination of anionic surfactants (sodium and lithium alkylsulfate, sodium dodecylbenzenesulfonate, sodium di-2-ethylhexyl sulfosuccinate, sodium and lithium perfluoroalkylcarboxylate, and lithium perfluorooctanesulfonate) were investigated by a capillary tube isotachophoresis using a potential gradient detector. The leading electrolyte solution was the mixture of acetonitrile and aqueous solution of histidine buffer containing calcium chloride. The terminating electrolyte solution was the aqueous solution of sodium octanoate. These electrolytes were effective for the analysis of the mixtures of strongly acidic surfactants.

The quantitative determination of surfactants usually has been performed by gas chromatography, high performance liquid chromatography and other widely used methods (1,2). However, most methods are elaborate and rather time consuming. The isotachophoretic method has a large field of application of the analysis of ionic species (2-7). Many difficulties were involved in the isotachophoretic analysis of surfactant mixtures, i.e., the simultaneous separation of individual surfactants from each other and from their respective homologs. In general, the isotachophoretic separation of ionic species was achieved based on the difference in the absolute mobility or the difference in the degree of dissociation of ionic species. If an ionic species had a similar dissociation constant, the effects of addition of counterion and organic solvent usually were examined.

In this paper, we study the separation and quantifica-

tion of various ionic surfactants. A rapid and simple procedure for determination of surfactant homologs was examined by isotachophoresis.

EXPERIMENTAL

Materials. Sodium perfluorooctanoate, lithium perfluorooctanesulfonate and alkylsulfate salt were the same samples as those used in the previous work (8,9). Sodium dodecylbenzenesulfonate (Kanto Chemical Co. Inc., Tokyo, Japan) and sodium di-2-ethylhexyl sulfosuccinate (Wako Pure Chemical Industries Ltd., Tokyo, Japan) were used without further purification. Lithium perfluorononanoate (Asahi Glass Co., Tokyo, Japan) was prepared by a procedure similar to that of Kunieda and Shinoda (10). Their chemical structures and abbreviations used in this study are illustrated in Table 1. All other reagents were of guaranteed grade.

Isotachophoresis. Isotachophoregrams were recorded on a Shimadzu IP-2A equipped with a potential gradient detector. The capillary tube used consisted of a main column (150 × 0.5 mm I.D.) and a pre-column (40 × 1.0 mm I.D.) and was thermostated at 15 C. The leading electrolyte solution was prepared as follows. An aqueous solution containing 8.33 mM histidine monohydrochloride, 12.5 mM histidine and 8.33 mM calcium chloride was mixed with acetonitrile (1:1, v/v). Then the solution was degassed in vacuo. The terminating electrolyte solution was 10 mM aqueous sodium octanoate solution. The migration current was 200 μA after 250 μA for 7 min. All the sample solutions were prepared to the surfactant concentrations of 1-5 mM.

RESULTS AND DISCUSSION

Yagi used 50% acetone aqueous solution of histidine-HCl as a leading electrolyte for the analysis of

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Table 1

PU and R_E Values of Surfactants

Surfactants			PU	R_E
$C_{10}H_{21}SO_4Li$	(LiDeS)	lithium decylsulfate	0.48	1.88
$C_{12}H_{25}SO_4Li$	(LiDS)	lithium dodecylsulfate	0.54	1.99
$C_{14}H_{29}SO_4Li$	(LiTS)	lithium tetradecylsulfate	0.60	2.11
$C_{16}H_{33}SO_4Li$	(LiHS)	lithium hexadecylsulfate	0.66	2.30
$C_{10}H_{21}SO_4Na$	(SDeS)	sodium decylsulfate	0.48	1.88
$C_{12}H_{25}SO_4Na$	(SDS)	sodium dodecylsulfate	0.54	1.99
$C_{12}H_{25}C_6H_4SO_3Na$	(SDBS)	sodium dodecylbenzenesulfonate	0.63	2.12
$C_8H_{17}COOCH_2$ | $C_8H_{17}COOCHSO_3Na$	(AOT)	sodium di-2-ethylhexyl sulfosuccinate	0.67	2.35
$C_7F_{15}COONa$	(SPFO)	sodium perfluorooctanoate	0.42	1.78
$C_8F_{17}COOLi$	(LiPFN)	lithium perfluorononanoate	0.47	1.87
$C_8F_{17}SO_3Li$	(LiFOS)	lithium perfluorooctanesulfonate	0.43	1.81

surfactants (2). However, this leading electrolyte was not suitable for the separation of the mixture of strong ionic surfactant, e.g., homologous series of alkylsulfate. In general, the choice of pH of a leading electrolyte solution is of decisive importance for an optimal separation. With respect to the separation of strong ionic species with similar absolute mobilities, it is necessary to change the relative mobilities of ionic species. It is known that the addition of complexing agents and organic solvent affect the relative mobilities of ionic species (5). Therefore, these factors necessitate that conditions be optimized.

We examined the effects of pH of the buffer solution by controlling both concentration and mixing ratio of histidine and histidine-HCl in aqueous organic solvent, e.g. methanol, acetone and acetonitrile. A mixture of acetonitrile and aqueous solution of histidine buffer was suitable for separating the surfactant homologs. As the acetonitrile content was increased, the difference among relative mobilities of alkylsulfates increased to result in improved separation of the homologs of alkylsulfate. Addition of calcium chloride gave good separation and good reproducibility. In this study, the results indicate that not only pH but also the acetonitrile content and the complexing agents (calcium chloride) affect the separation. The optimized conditions are shown in Table 2.

The qualitative indexes, PU and R_E, can be expressed as (2):

$$PU = \frac{PG_S - PG_L}{PG_T - PG_L} \qquad [1]$$

$$R_E = \frac{PG_S}{PG_L} \qquad [2]$$

where PG_L, PG_T and PG_S are the potential gradients of the leading, terminating and sample ion, respectively. The PU value is useful for identification of ionic species with good reproducibility based on the difference in effective mobility (11). The R_E value is the ratio of the effective mobility of the sample ion to that of the leading ion. The obtained values of PU and R_E are tabulated in Table 1. As the chain length of alkylsulfate increased,

Table 2

Migration Conditions for Capillary Type Isotachophoresis

Leading electrolyte	8.33 mM histidine—HCl 12.5 mM histidine 8.33 mM $CaCl_2$ 50% acetonitrile/50% water
Terminating electrolyte	10 mM sodium octanoate
Migration current	250 µA (7 min)—200 µA
Migration tube	pre-column 40× 1.0 mm I.D. main-column 150 × 0.5 mm I.D.
Chart speed	40 mm/min
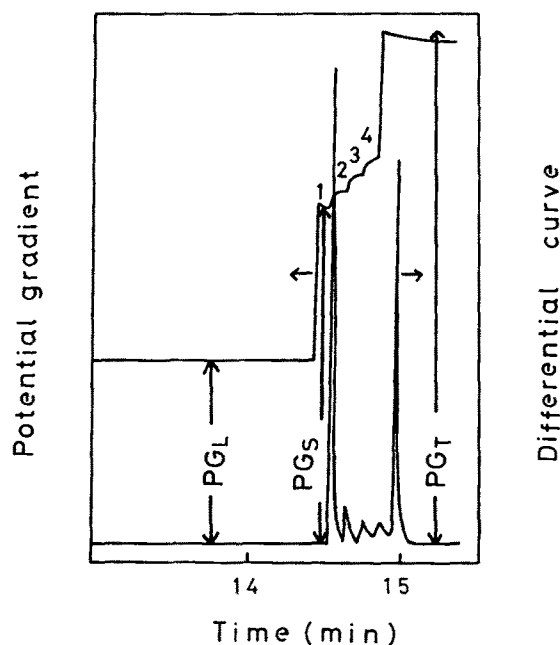
FIG. 1. Isotachophoregram of a mixture of LiDeS, LiDS, LiTS and LiHS. (1) LiDeS, (2) LiDS, (3) LiTS, (4) LiHS.
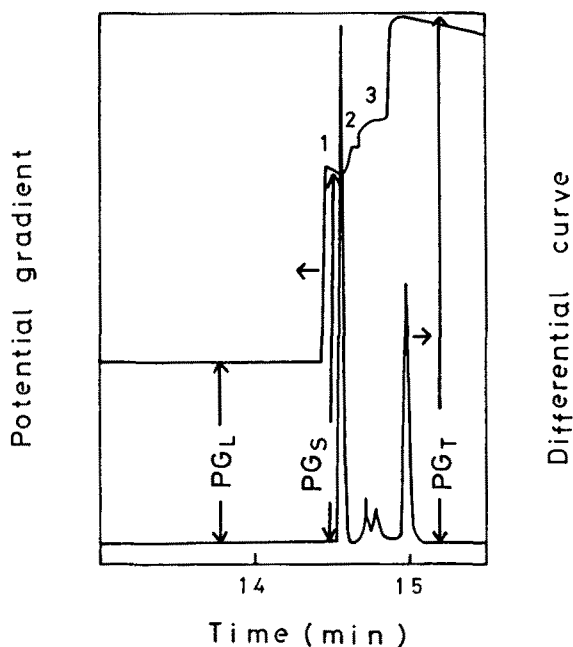
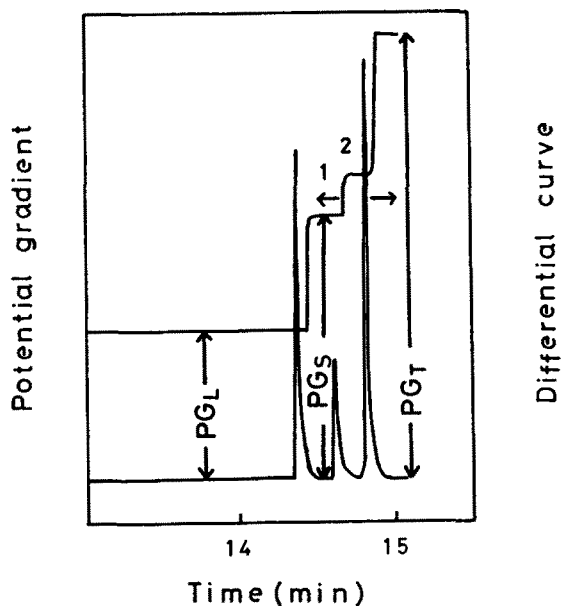FIG. 2. Isotachophoregram of a mixture of SDS, SDBS and AOT.
(1) SDS, (2) SDBS, (3) AOT.

FIG. 3. Isotachophoregram of a mixture of LiFOS and LiTS. (1)
LiFOS, (2) LiTS.

FIG. 4. Calibration curves for ionic surfactants. (●)LiFOS; (▲),
SPFO; (■),LiPFN; (O), LiDeS. The correlation coefficients are
0.9994, 0.9998, 0.9997 and 0.9998, respectively.

FIG. 5. Relation between the mole fraction of SPFO (LiFOS) and
the fraction of zone length of SPFO (LiFOS). (●), SPFO-SDS;
(O), LiFOS-LiDS; (■), LiFOS-LiTS. The correlation coefficients are
0.9996, 0.9964 and 0.9999, respectively.

the values of PU and R_E increased. This result means a
decrease of the relative mobility in that order. In
general, the mobility decreased as molecular weight of
ionic surfactant increased. The relation between the
mobility and molecular weight can be expressed by (11):

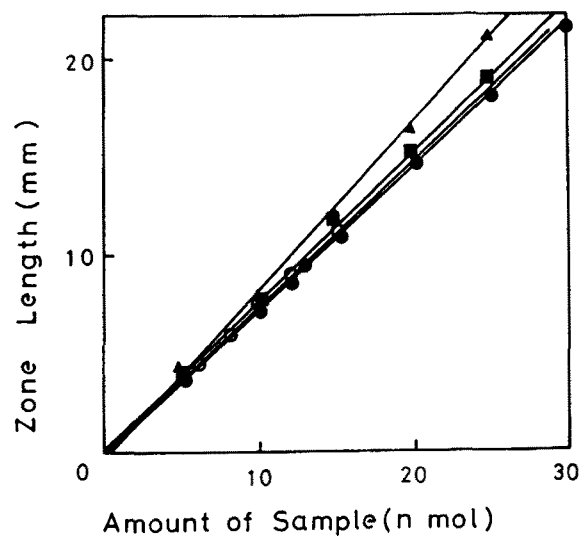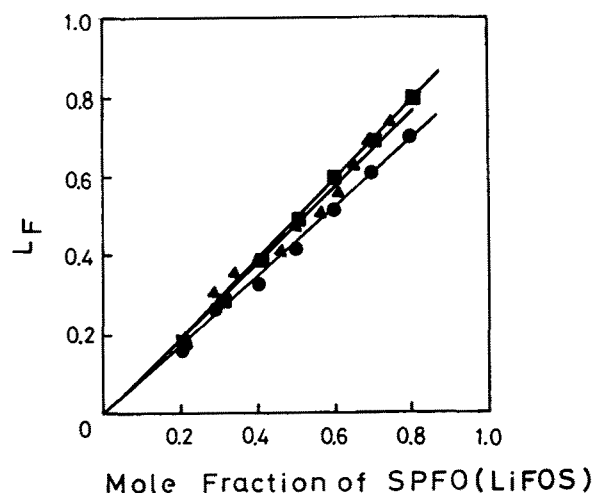$$\frac{1}{PU} = A \cdot Z \cdot M^{-2/3} + B \qquad [3]$$

where Z is the number of charge, A and B are constant
and M is molecular weight. The PU value of the
alkylsulfates obeyed Equation 3 with A = 125 and B =
−1.18. We used the molecular weight which does not
contain the counterion of surfactant, because the
difference of counterions was not observed as to the
mobility of surfactant (Table 1). The perfluorinated
surfactants had larger mobilities than the others because
the perfluorinated surfactants are salts of stronger acid.
For example, the mobility of sodium perfluorooctanoate
was about two times larger than that of sodium
octanoate, which was used as the terminating ion
(PU_{SPFO} = 0.42, PU_{SO} = 1).

Figures 1-3 show the typical isotachophoregrams of
mixed surfactants. We can distinguish each component
of the alkylsulfate homologs, and can separate them on

the basis of the difference in effective mobility. The difference in PU value had to be larger than 6% to distinguish the separated surfactants. The simultaneous determination requires more than 20% difference in PU value.

Figure 4 shows that a linear relation exists between the injected sample and a zone length. But the zone lengths were shorter than those expected in the case of injecting a large amount of sample. This may be derived from the formation of micelles resulting in the concentration effect. This will be the subject of a future study.

Figure 5 shows the relation between the mole fraction of component 1 and L_F ($= l_1/(l_1+l_2)$, l_i; zone length of component i). The surfactants are determined simultaneously by the results of Figures 4 and 5. The zone length per mole of a leading sample ion (SPFO) was always shorter than that of a following one (SDS) (Fig. 5).

Each component in the surfactant homolog could be distinguished by isotachophoresis. HPLC was also applicable to the determination of a small amount of surfactant. However, a large amount of organic solvent was required as an eluent. The present method is also effective for quantitative determination when samples contain certain amounts of the other ion, such as sodium chloride, etc. The isotachophoretic technique is favorable for separating a mixture of strong ionic species with respect to both low running cost and without pretreatment of sample.

REFERENCES

1. Nakamura, K., and Y. Morikawa, *J. Amer. Oil Chem. Soc. 59*:64 (1982).
2. Yagi, T., *Yukagaku 31*:2 (1982).
3. Mikkers, R.E.P., F.M. Everaerts and J.A.F. Peek, *J. Chromatogr. 168*:293 (1979).
4. Mikkers, F.E.P., F.M. Everaerts and J.A.F. Peek, *Ibid. 168*:317 (1979).
5. Hirokawa, T., and Y. Kiso, *Ibid. 242*:227 (1982).
6. Hirokawa, T., and Y. Kiso, *Ibid. 260*:225 (1983).
7. Motooka, I., H. Nariai and K. Nakazaki, *Ibid. 260*:377 (1983).
8. Asakawa, T., S. Miyagishi and M. Nishida, *J. Colloid Interface Sci. 104*:279 (1985).
9. Asakawa, T., K. Johten, S. Miyagishi and M. Nishida, *Langmuir 1*:347 (1985).
10. Kunieda, H., and K. Shinoda, *J. Phys. Chem. 80*:2468 91976).
11. Miyazaki, H., and K. Katoh, *J. Chromatogr. 119*:381 (1976).

[Received February 24, 1986]