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Note

Homologous distribution analysis of imidazoline type cationic surfactants by high-performance liquid chromatography

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Imidazoline-type cationic surfactants, examples of which are shown in Fig. 1, are used as softeners. The separation of homologous series of these surfactants has not been carried out using chromatographic methods. However, for the determination of average molecular weights, it is essential to measure distribution analyses; hitherto this distribution has been calculated only from the composition of the original fatty acids as determined by gas chromatography. For the analysis of commercial products containing imidazoline-type cationic surfactants, the composition of the fatty acids was determined by hydrolysis of the imidazoline ring, as described by Takano and Tsuji[1], but only when other fatty acids derived from foreign substances, such as glycerides, were not present in the formulations.

In this paper, we report the analysis of a homologous series of imidazoline-type cationic surfactants by high-performance liquid chromatography (HPLC) without any pre-treatment of samples.

EXPERIMENTAL

Apparatus

The HPLC equipment consisted of a Hitachi Model 655 pump, a Reodyne 7125 sample injector, a Haarke D1L water-bath for column temperature controlling (40°C) and a Hitachi 655 UV detector (detection at 240 nm). A Shimadzu CR1A Chromatopak was used for the calculation of the peak areas.

The column-packing materials, Develosil ODS-3 (3 μm, Nomura Chemical, Seto, Japan) was slurry packed in 150 × 4.6 mm I.D. columns.

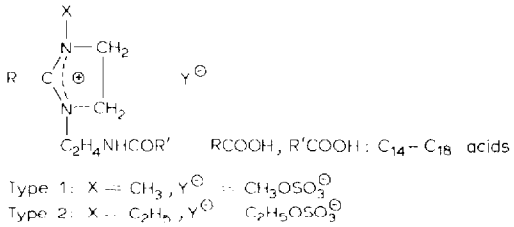

Fig. 1. Structures of imidazoline-type cationic surfactants.

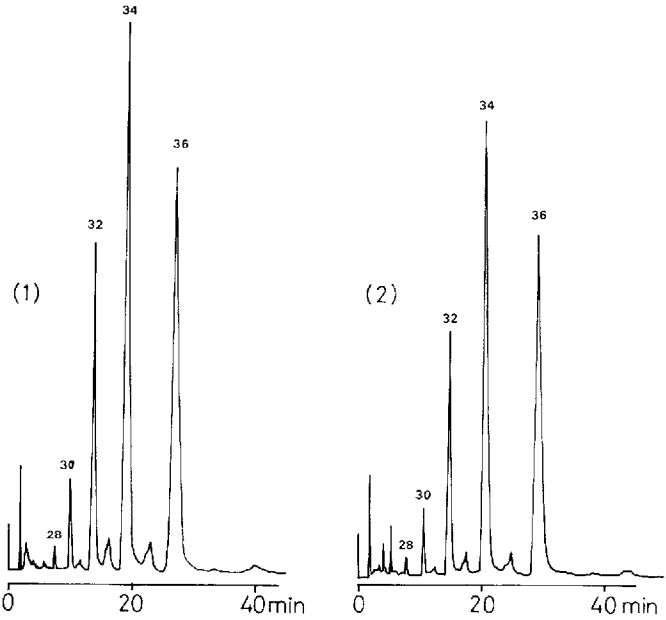

Fig. 2. Liquid chromatograms of imidazoline-type cationic surfactants : 1, type 1 ; 2, type 2. Total alkyl chain lengths of fatty acids (R_1 + R_2) are indicated on the peaks.

TABLE I

DETERMINATION OF DISTRIBUTIONS OF HOMOLOGUES

Alkyl chain length	*mol (%)*	*Molar distribution (%)*			
		*Type 1**		*Type 2**	
		*GC***	*HPLC*	*GC*	*HPLC*
C_{14}	*a*	3.82	—	3.80	—
C_{16}	*b*	32.39	—	31.23	—
C_{18}	*c*	63.79	—	64.97	—
Total alkyl chain length of fatty acids, R_1+R_2	*mol (%)*	*GC (calc.)*	*HPLC*** (obs.)*	*GC (calc.)*	*HPLC*** (obs.)*
28	$a^2/100$	0.14	0.53	0.14	0.66
30	$2ab/100$	2.47	2.90	2.37	3.07
32	$(b^2+2ac)/100$	15.36	14.60	14.69	13.92
34	$2bc/100$	41.32	40.38	40.58	38.96
36	$c^2/100$	40.69	41.60	42.21	43.39
Average molecular weight		720.45	720.86	749.55	749.34

* Types 1 and 2 are as shown in Fig. 1.
** Determined by GC.
*** Determined by the proposed method.

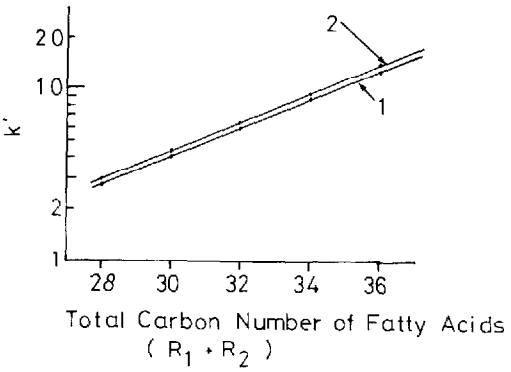

Fig. 3. Relationships between the capacity factors (k') and the total alkyl chain lengths of fatty acids (R_1 + R_2) of imidazoline-type cationic surfactants: 1, type 1; 2, type 2.

Materials

The imidazoline-type cationic surfactants listed in Fig. 1 were prepared from the appropriate fatty acids, diethylenetriamine and electrophilic reactants of dimethyl sulphate and/or diethyl sulphate in our laboratories. All other reagents were of analytical-reagent grade.

RESULTS AND DISCUSSION

Imidazoline-type cationic surfactants were separated on reversed-phase liquid chromatography. The recommended eluent was 0.1 *M* sodium perchlorate in methanol–acetonitrile–deionized water (60:60:5). Representative chromatograms are shown in Fig. 2. The chromatograms distinguish both the electrophilic reactant used for the preparation and the distribution of the surfactant homologues.

The relationship between the capacity factors (k') of each homologous series and their total alkyl chain lengths of the fatty acids (R_1 + R_2) are shown in Fig. 3. The logarithms of the capacity factors are directly proportional to the total alkyl chain lengths. Thus, the peaks for both homologous series can be identified from this relationship.

In the proposed method, the distribution of the homologues was determined from the peak areas detected at 240 nm and the results were compared with those obtained by conventional gas chromatographic methods involving hydrolysis of the imidazoline ring (Table I). In the gas chromatographic analysis, the distributions of the homologues were calculated from the compositions of the fatty acids as indicated in Table I. Agreement between the methods is good and distributions can be determined directly by the proposed method without pre-treatment of the samples. Furthermore, the method can be used for high-sensitivity analysis of commercial products.

REFERENCE

1 S. Takano and K. Tsuji, *J. Amer. Oil Chem. Soc.*, 60 (1983) 870.