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## SEPARATION OF HOMOLOGOUS ALKYL BENZENESULPHONATES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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### SUMMARY

Homologous series of linear alkylbenzenesulphonates (LAS) were separated by high-performance liquid chromatography, employing a porous micro-spherical poly(styrene-divinylbenzene) gel as the stationary phase with 0.5 M perchloric acid in methanol as the mobile phase. A mixture of even-carbon-numbered LAS (C<sub>10</sub>-, C<sub>12</sub>- and C<sub>14</sub>-LAS) and odd-carbon-numbered LAS (C<sub>11</sub>-, C<sub>13</sub>- and C<sub>15</sub>-LAS) was well resolved according to the alkyl chain length and the positional isomers were partly separated. The logarithm of the capacity factor of each isomer was directly proportional to the alkyl chain length.

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### INTRODUCTION

Linear alkylbenzenesulphonates (LAS), anionic surface-active agents, have been widely used as raw materials for synthetic detergents. Commercial LAS are usually mixtures of homologous series of C<sub>10</sub>-C<sub>14</sub> alkyl compounds and each homologous series contains positional isomers derived from Friedel-Craft alkylation.

The determination of the composition of homologous series of LAS has been carried out by gas chromatography. This method, however, requires their conversion into volatile derivatives before analysis. Knight and House<sup>1</sup> formed alkylbenzenes from detergent-range alkylbenzenesulphonates by desulphonation with hot orthophosphoric acid. Later, micro-scale and rapid desulphonation methods were also reported<sup>2,3</sup>. Nishi<sup>4</sup> reported that an alkali fusion of alkylbenzenesulphonates provided alkylphenols, the gas chromatographic patterns of which corresponded to those of original alkylbenzenes. Watanabe *et al.*<sup>5</sup> determined LAS by gas chromatography after conversion into the sulphonyl chlorides by the reaction with phosphorus pentachloride. Imaida *et al.*<sup>6</sup> described the gas chromatography of trace amounts of LAS as methylsulphonates obtained by sulphonylation followed by methylation, using a flame photometric detector. Liddicoet and Smithson<sup>7</sup> devised a pyrolysis-gas chromatographic method for the rapid analysis of surface-active agents either alone, in

synthetic mixtures or in commercial products. Lew<sup>8,9</sup> developed an "acid" pyrolysis-capillary gas chromatographic method for anionic and non-ionic surface-active agents. The "acid" pyrolysis of C<sub>11</sub>-C<sub>14</sub> LAS produced a chromatogram that was almost identical with that of the original alkylbenzenes.

In a previous paper<sup>10</sup>, we reported the separation of homologous alkylbenzyl-dimethylammonium chlorides and alkylpyridinium halides by high-performance liquid chromatography without pre-treatment of the samples and also showed that this method may be applicable to other surface-active agents. This paper is concerned with the application of high-performance liquid chromatography to the separation of homologous series of LAS.

## EXPERIMENTAL

### *Apparatus*

The liquid chromatograph used was the same as that described previously<sup>10</sup>. A Pyrex glass separation column (500 mm × 5 mm I.D.) was used, with a water-jacket for temperature control.

### *Reagents and samples*

The column packing material was Hitachi Gel 3011, which consists of porous micro-spherical particles of a copolymer of styrene and divinylbenzene of average particle diameter 10–15 μm.

LAS with C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub>, C<sub>13</sub>, C<sub>14</sub> and C<sub>15</sub> alkyl groups were obtained by alkylating benzene with the corresponding α-olefins, sulphonating the alkylbenzene with chlorosulphonic acid and neutralizing the sulphonic acid mixture with sodium hydroxide. Sodium (1-methylnonyl)benzenesulphonate (C<sub>10</sub>-LAS 2ϕ), (1-methylundecyl)benzenesulphonate (C<sub>12</sub>-LAS 2ϕ) and (1-methyltridecyl)benzenesulphonate (C<sub>14</sub>-LAS 2ϕ) were obtained by sulphonating the corresponding (1-methylalkyl)benzene with chlorosulphonic acid, which was isolated from the alkylbenzene by preparative gas chromatography, and neutralizing the sulphonic acid with sodium hydroxide. The sulphonates prepared were dissolved in 50% aqueous ethanol and extracted with light petroleum to remove unreacted substances. The ethanolic solution was evaporated to dryness and the residue was re-dissolved in ethanol. The ethanol solution was filtered to remove sodium chloride and sulphate, and the filtrate was evaporated to dryness under reduced pressure.

Commercial LAS and branched alkylbenzenesulphonates (ABS) were obtained from Kao Soap Co. Ltd. (Tokyo, Japan).

All other reagents were of analytical-reagent grade.

### *Procedure*

The column packing material, dispersed in methanol-water (8:2, v/v), was packed into the glass column under high pressure (about 120 kg/cm<sup>2</sup>) by the slurry packing procedure. The packed column was treated with methanol before use.

A mixture of even-carbon-numbered LAS (C<sub>10</sub>-, C<sub>12</sub>- and C<sub>14</sub>-LAS), odd-carbon-numbered LAS (C<sub>11</sub>-, C<sub>13</sub>- and C<sub>15</sub>-LAS), and (1-methylalkyl)benzenesulphonates (C<sub>10</sub>-, C<sub>12</sub>- and C<sub>14</sub>-LAS 2ϕ) was dissolved in methanol. Commercial LAS and ABS were also dissolved in methanol. These samples were injected into the column

with a microsyringe through a septum injector. The column effluents were monitored at 225 nm.

## RESULTS AND DISCUSSION

In liquid chromatography with poly(styrene-divinylbenzene) gel as the stationary phase, a polar solvent, such as methanol or methanol-water (9:1), is usually used as the mobile phase. These chromatographic systems, however, are not suitable for the separation of homologous series of LAS, because LAS are eluted at the solvent front.

In previous work<sup>10</sup>, homologous alkylbenzyltrimethylammonium chlorides and alkylpyridinium halides were separated completely by using a methanolic solution of inorganic acids or their salts as the mobile phase. In this study, similar chromatographic systems were applied to the separation of homologous series of LAS. The results are given in Table I.

TABLE I  
CAPACITY FACTORS OF ALKYL BENZENESULPHONATES

$R-CH-R'$		Compound:	R'		
			R-CH-C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> Na		
$R'$	Abbreviation	Mobile phase*			
		0.5 M HClO <sub>4</sub>	0.5 M NaClO <sub>4</sub>	0.5 M LiCl	
C <sub>10</sub> H <sub>21</sub>	C <sub>2</sub> H <sub>5</sub> -C <sub>4</sub> H <sub>9</sub>	(C <sub>10</sub> -LAS 3 Ø-5 Ø)	0.79	0.58	0.53
	CH <sub>3</sub>	(C <sub>10</sub> -LAS 2 Ø)	0.95	0.70	0.63
C <sub>11</sub> H <sub>23</sub>	C <sub>2</sub> H <sub>5</sub> -C <sub>5</sub> H <sub>11</sub>	(C <sub>11</sub> -LAS 3 Ø-6 Ø)	0.98	0.73	0.62
	CH <sub>3</sub>	(C <sub>11</sub> -LAS 2 Ø)	1.27	0.91	0.76
C <sub>12</sub> H <sub>25</sub>	C <sub>3</sub> H <sub>7</sub> -C <sub>5</sub> H <sub>11</sub>	(C <sub>12</sub> -LAS 4 Ø-6 Ø)	1.23	0.89**	0.79**
	C <sub>2</sub> H <sub>5</sub>	(C <sub>12</sub> -LAS 3 Ø)	1.37		
	CH <sub>3</sub>	(C <sub>12</sub> -LAS 2 Ø)	1.64	1.18	0.99
C <sub>13</sub> H <sub>27</sub>	C <sub>3</sub> H <sub>7</sub> -C <sub>6</sub> H <sub>13</sub>	(C <sub>13</sub> -LAS 4 Ø-7 Ø)	1.58	1.13	0.94
	C <sub>2</sub> H <sub>5</sub>	(C <sub>13</sub> -LAS 3 Ø)	1.85	1.29	1.04
	CH <sub>3</sub>	(C <sub>13</sub> -LAS 2 Ø)	2.16	1.51	1.24
C <sub>14</sub> H <sub>29</sub>	C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>13</sub>	(C <sub>14</sub> -LAS 5 Ø-7 Ø)	2.00	1.40**	1.18**
	C <sub>3</sub> H <sub>7</sub>	(C <sub>14</sub> -LAS 4 Ø)	2.16		
	C <sub>2</sub> H <sub>5</sub>	(C <sub>14</sub> -LAS 3 Ø)	2.37	1.65	1.35
	CH <sub>3</sub>	(C <sub>14</sub> -LAS 2 Ø)	2.80	1.94	1.59
C <sub>15</sub> H <sub>31</sub>	C <sub>4</sub> H <sub>9</sub> -C <sub>7</sub> H <sub>15</sub>	(C <sub>15</sub> -LAS 5 Ø-8 Ø)	2.56	1.75	1.40**
	C <sub>3</sub> H <sub>7</sub>	(C <sub>15</sub> -LAS 4 Ø)	2.86	1.92	
	C <sub>2</sub> H <sub>5</sub>	(C <sub>15</sub> -LAS 3 Ø)	3.12	2.14	1.70
	CH <sub>3</sub>	(C <sub>15</sub> -LAS 2 Ø)	3.71	2.51	1.99

\* In methanol.

\*\* Unresolved.

The order of elution of LAS follows the order of increasing alkyl chain length or, for the same alkyl chain length, the order of decreasing distance of the substituent phenyl group from the end of the alkyl chain. The capacity factors of LAS with 0.5 M perchloric acid in methanol as the mobile phase were higher than those with 0.5 M

sodium perchlorate and 0.5 *M* lithium chloride in methanol. The difference in the capacity factors is presumed to be due to the difference in the solubilities in the stationary phase of the alkylbenzenesulphonic acids and their sodium and lithium salts, which were formed by exchange of the counter ion of the samples with that in the mobile phase. With 0.5 *M* perchloric acid in methanol as the mobile phase, the mixture of even-carbon-numbered LAS ( $C_{10}$ -,  $C_{12}$ - and  $C_{14}$ -LAS) was well resolved according to the alkyl chain length. Further, partial separations of positional isomers of LAS were obtained, as shown in Fig. 1. Fig. 2 shows the chromatogram of the mixture of odd-carbon-numbered LAS ( $C_{11}$ -,  $C_{13}$ - and  $C_{15}$ -LAS). With (1-methyl-alkyl)benzenesulphonates, a simpler chromatogram compared with those for the even- and odd-carbon-numbered LAS was obtained owing to the absence of positional isomers (Fig. 3).

Fig. 4 summarizes the retention volumes of the LAS in order to clarify the

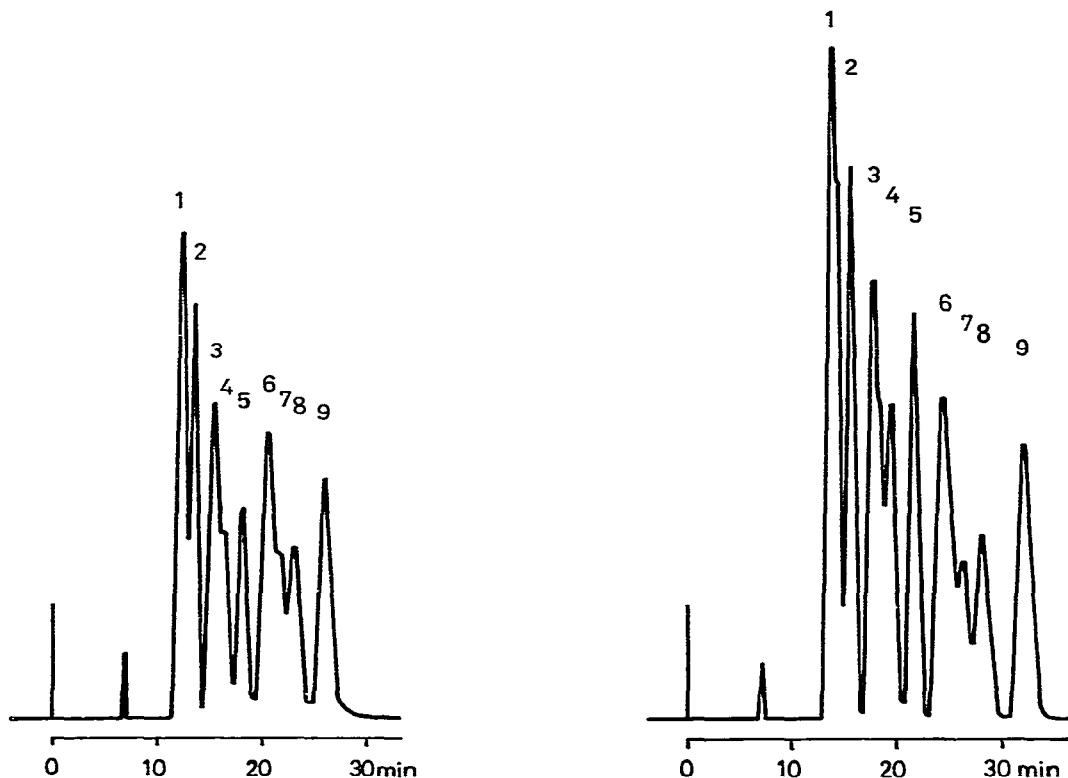


Fig. 1. Chromatogram of decyl-, dodecyl- and tetradecylbenzenesulphonates. Column: Hitachi Gel 3011, 500 mm  $\times$  5 mm I.D. Mobile phase: 0.5 *M* perchloric acid in methanol. Flow-rate: 1.2 ml/min. Pressure: 52 kg/cm<sup>2</sup>. Column temperature: 30°. Detector: UV, 225 nm, 0.5 a.u.f.s. Peaks: 1 =  $C_{10}$ -LAS 3 $\phi$ -5 $\phi$ ; 2 =  $C_{10}$ -LAS 2 $\phi$ ; 3 =  $C_{12}$ -LAS 4 $\phi$ -6 $\phi$ ; 4 =  $C_{12}$ -LAS 3 $\phi$ ; 5 =  $C_{12}$ -LAS 2 $\phi$ ; 6 =  $C_{14}$ -LAS 5 $\phi$ -7 $\phi$ ; 7 =  $C_{14}$ -LAS 4 $\phi$ ; 8 =  $C_{14}$ -LAS 3 $\phi$ ; 9 =  $C_{14}$ -LAS 2 $\phi$ .

Fig. 2. Chromatogram of undecyl-, tridecyl- and pentadecylbenzenesulphonates. Conditions as in Fig. 1. Peaks: 1 =  $C_{11}$ -LAS 3 $\phi$ -6 $\phi$ ; 2 =  $C_{11}$ -LAS 2 $\phi$ ; 3 =  $C_{13}$ -LAS 4 $\phi$ -7 $\phi$ ; 4 =  $C_{13}$ -LAS 3 $\phi$ ; 5 =  $C_{13}$ -LAS 2 $\phi$ ; 6 =  $C_{15}$ -LAS 5 $\phi$ -8 $\phi$ ; 7 =  $C_{15}$ -LAS 4 $\phi$ ; 8 =  $C_{15}$ -LAS 3 $\phi$ ; 9 =  $C_{15}$ -LAS 2 $\phi$ .

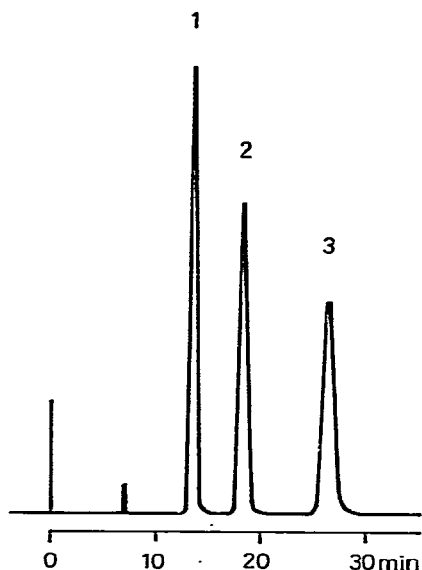


Fig. 3. Chromatogram of (1-methylnonyl)-, (1-methylundecyl)- and (1-methyltridecyl)benzenesulphonates. Conditions as in Fig. 1. Peaks: 1 =  $C_{10}$ -LAS 2 $\emptyset$ ; 2 =  $C_{12}$ -LAS 2 $\emptyset$ ; 3 =  $C_{14}$ -LAS 2 $\emptyset$ .

separations.  $C_{10}$ -,  $C_{12}$ - and  $C_{14}$ -LAS were well resolved as groups according to their individual alkyl chain lengths and  $C_{10}$ -LAS 2 $\emptyset$  was separated from  $C_{10}$ -LAS 3 $\emptyset$ -5 $\emptyset$ .  $C_{14}$ -LAS 2 $\emptyset$ , 3 $\emptyset$  and 4 $\emptyset$  were also separated from  $C_{14}$ -LAS 5 $\emptyset$ -7 $\emptyset$ . The elution bands of  $C_{10}$ -LAS 2 $\emptyset$  and  $C_{11}$ -LAS 3 $\emptyset$ -6 $\emptyset$ , as well as those of  $C_{11}$ -LAS 2 $\emptyset$  and  $C_{12}$ -LAS 4 $\emptyset$ -6 $\emptyset$ , overlapped with each other. The elution band of LAS that have the same alkyl chain length is very broad because of the presence of several positional isomers. Consequently,  $C_{10}$ -,  $C_{11}$ -,  $C_{12}$ -,  $C_{13}$ - and  $C_{14}$ -LAS were not separated as groups according to their individual alkyl chain lengths using this chromatographic system.

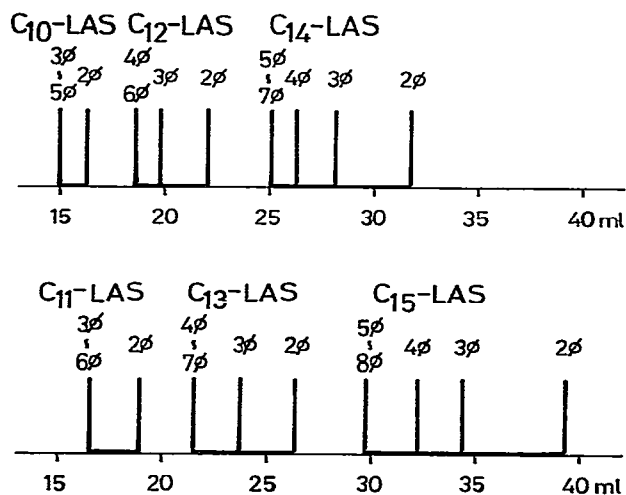


Fig. 4. Retention volumes of alkylbenzenesulphonates.

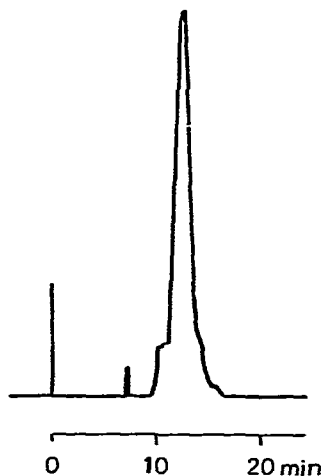
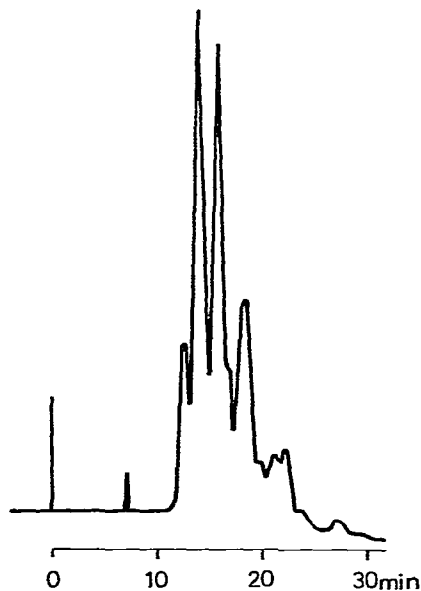


Fig. 5. Chromatogram of commercial linear alkylbenzenesulphonates. Conditions as in Fig. 1.

Fig. 6. Chromatogram of commercial branched alkylbenzenesulphonates. Conditions as in Fig. 1.

However, if a high-efficiency column comparable to a capillary column in gas chromatography could be developed, these separations would become feasible. Figs. 5 and 6 show the chromatograms of commercial LAS with an alkyl chain length of  $C_{10}$ - $C_{14}$  and ABS of the propylene tetramer type. As discussed above, commercial LAS gave a complicated chromatogram, but commercial ABS gave one peak because ABS have only a small alkyl chain distribution and many positional isomers. There-

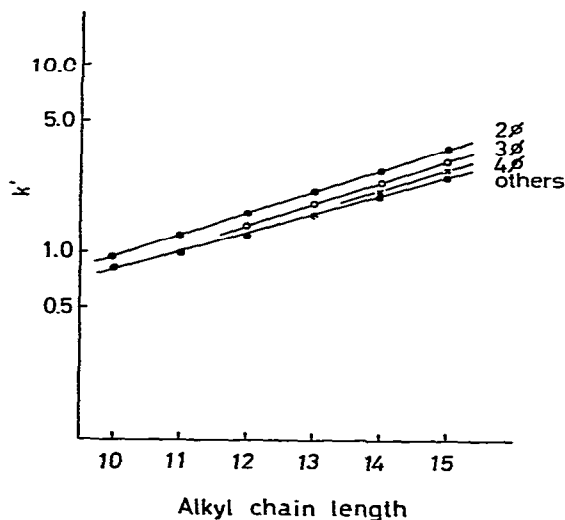


Fig. 7. Relationships between the capacity factors and the alkyl chain lengths of alkylbenzenesulphonates.

fore, LAS and ABS were easily distinguished by comparison of their chromatograms.

The relationships between the capacity factors of LAS and their alkyl chain lengths are shown in Fig. 7. The logarithms of the capacity factors of 2 $\emptyset$  isomers in LAS were directly proportional to their alkyl chain lengths, and similar linear relationships for individual isomers of LAS were found. In liquid-liquid partition chromatography, the dependence of the number of carbon atoms,  $n$ , in a homologous organic compound solute on the capacity factor is given by

$$\ln k' = a' + bn$$

where  $a'$  and  $b$  are constants<sup>10</sup>. These chromatographic systems might be explained in terms of the theory of liquid-liquid partition chromatography. Using these linear relationships, the elution peaks can be identified and the position of the phenyl group can be estimated.

A synthetic mixture prepared from C<sub>10</sub>-, C<sub>12</sub>- and C<sub>14</sub>-LAS was analysed in order to test the reproducibility and accuracy of the method. The results are given in Table II. The estimated relative standard deviations for each element were small, showing that the reproducibility of the method was good. The peak-area percentages of C<sub>10</sub>-, C<sub>12</sub>- and C<sub>14</sub>-LAS as measured by high-performance liquid chromatography agreed with the molar percentages in the synthetic mixture, the molar absorptivities being identical; a spectrophotometric detector was used for the detection of LAS in the column effluent.

TABLE II

ANALYSIS OF SYNTHETIC MIXTURE OF DECYL-, DODECYL- AND TETRADECYL-BENZENESULPHONATES

Compound	Present (mole-%)	Found (peak area, %)							Relative standard deviation	
		Isomer composition	1	2	3	4	5	Mean Total mean		
C <sub>10</sub> -LAS	23.6	3 $\emptyset$ -5 $\emptyset$	15.1	15.0	14.8	14.8	15.0	14.9	23.9	0.89
		2 $\emptyset$	9.0	9.1	9.0	9.0	9.1	9.0	9.0	0.60
C <sub>12</sub> -LAS	26.7	4 $\emptyset$ -6 $\emptyset$	14.4	14.4	14.5	14.6	14.7	14.5	26.9	0.89
		3 $\emptyset$	4.8	5.0	4.8	4.9	4.9	4.9	4.9	1.71
		2 $\emptyset$	7.4	7.5	7.5	7.7	7.4	7.5	7.5	1.63
C <sub>14</sub> -LAS	49.7	5 $\emptyset$ -7 $\emptyset$	18.8	19.0	19.0	19.1	19.3	19.1	49.2	0.95
		4 $\emptyset$	5.8	5.7	6.0	5.9	5.9	5.9	5.9	1.94
		3 $\emptyset$	9.3	9.3	9.4	9.4	9.0	9.3	9.3	1.77
		2 $\emptyset$	15.4	15.0	15.0	14.6	14.7	14.9	14.9	2.09

These chromatographic systems might be applicable to the separation of other surface-active agents such as alkylsulphates and  $\alpha$ -olefinsulphonates.

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