cellulose is reversed when SDS is added to the environment at high concentration.

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⚓Separation and Estimation of Anionic Surfactants by Thin Layer Chromatography: I. Mixtures of Sodium Dodecylbenzenesulfonate, Sodium Dodecyl Sulfate and Sodium Dodecanesulfonate

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ABSTRACT

The conditions for separation and quantitative determination of anionic surfactants such as sodium dodecylbenzenesulfonate, sodium dodecanesulfonate and sodium dodecyl sulfate by thin layer chromatography (TLC) were investigated. Analytical results for mixtures of 2 or 3 components under optimal TLC conditions were in satisfactory agreement with known values. The absolute errors and variation coefficients both were within ca. 4%.

INTRODUCTION

Microscale analytical methods using colorimetric analysis have been described by Abbott (1), Longwell and Maniece (2) and others. Analytical results from these methods show only the total content of methylene blue active substances (MBAS) and, therefore, the values of individual substances are not obtained.

In this paper, the conditions for separation and quantitative determination of sodium dodecylbenzenesulfonate (LAS), sodium dodecanesulfonate (SAS) and sodium dodecyl sulfate (LS-Na) by TLC were investigated. Quantitation of mixtures of 2 or 3 components was done under optimal conditions.

EXPERIMENTAL

Preparation of Sodium Dodecylbenzenesulfonate

Forty g of n-dodecylbenzene (purity = 99.4%) was placed in a 300-mL, 4-necked, round-bottomed flask equipped with a stirrer, a separatory funnel, a thermometer and a glass tube connected to an aspirator. Twenty percent oleum (60 g) was added under vigorous stirring, keeping the reaction temperature at 20 C. After the temperature had been raised to 50 C in a water bath, the mixture was stirred for 10 min and neutralized with 30% sodium hydroxide. The product obtained was dried and extracted with 95% ethyl alcohol and petroleum ether repeatedly to remove inorganic salts and nonreactive oily materials. By 2 repetitions of recrystallization from ethyl alcohol, white crystals of sodium dodecylbenzenesulfonate (6.0 g) were obtained. The purity of the crystals using the p-toluidine method was 97.5%. The IR spectrum of the LAS, which was run in potassium bromide, is shown in Figure 1.

Preparation of Sodium Dodecyl Sulfate

Dodecyl alcohol, 46.6 g (purity = 98.5%) was placed in a 3-necked flask fitted with a stirrer, a thermometer and a separatory funnel. Concentrated sulfuric acid (49.0 g) was added by drops from the funnel under vigorous stirring at temperatures below 30 C. After the reaction was complete, the product was neutralized with 35% aqueous sodium hydroxide. After drying, the product was extracted with 95% ethyl alcohol, then with petroleum ether to remove inorganic salts and nonreactive oily materials. White, scaly crystals of sodium dodecyl sulfate (9.2 g) were obtained by repeated recrystallization from ethyl alcohol. The purity of the crystals using the p-toluidine method was 98.6% .The IR spectrum of the LS-Na, which was run in potassium bromide, is shown in Figure 2.

Preparation of Sodium Dodecanesulfonate

A procedure similar to the method of Reed and Tartar (3) was done and the purity of the product by p-toluidine method was 97.9%. The IR spectrum of the SAS in potassium bromide is shown in Figure 3.

Thin Layer Chromatography

Preparation of TLC plates. A slurry of the adsorbent was applied to a glass plate (5 × 20 cm, 20 × 20 cm) resulting in an application of 0.25 mm thickness. The adsorbent layers were placed in a well-ventilated oven, activated by heating and stored over silica gel in a desicator before use.

Samples were weighed precisely and dissolved in ethyl alcohol/water (1/1, v/v) to prepare 0.50% solutions. The solutions (0.6-3.0 μL) were applied using a microsyringe
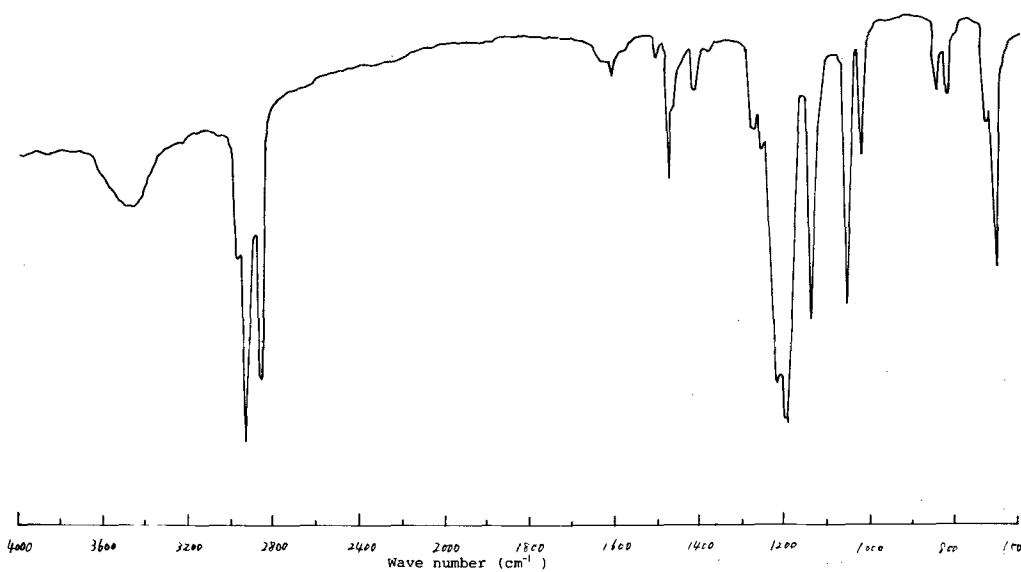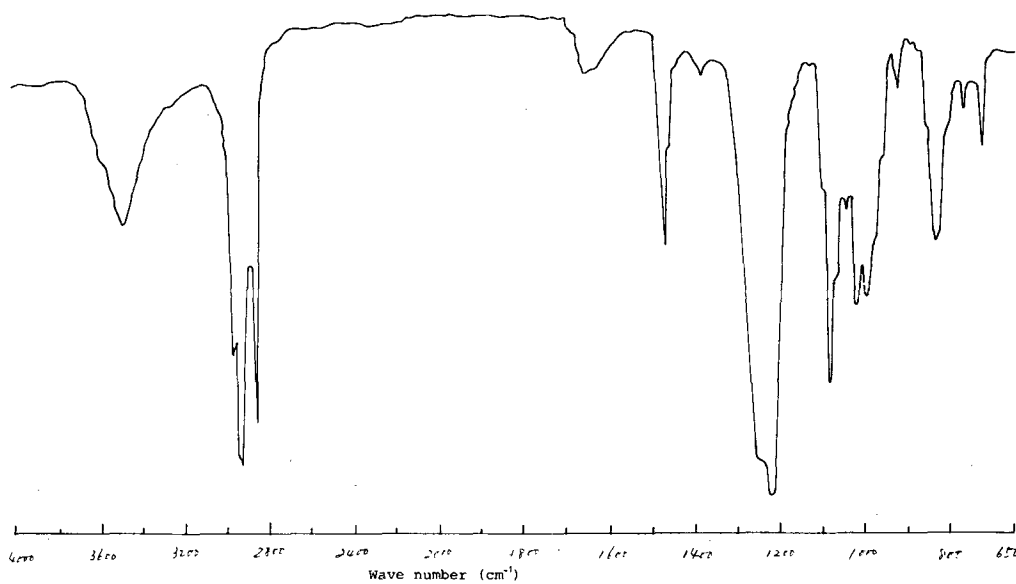
FIG. 1. IR spectrum of LAS (in KBr).
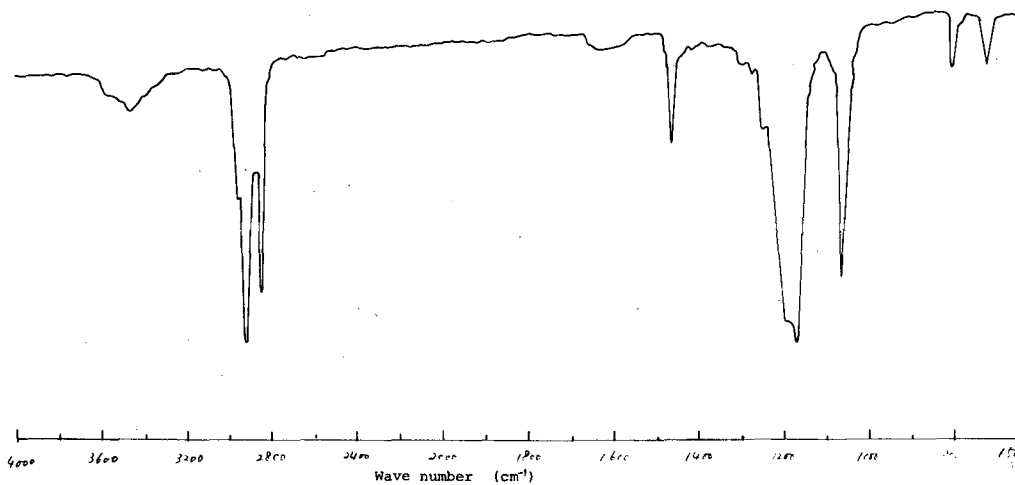
FIG. 2. IR spectrum of LS-Na (in KBr).

FIG. 3. IR spectrum of SAS (in KBr).

TABLE I

R_f Values of LAS, LS-Na and SAS Developed with Various Solvents

No.	Developing solvent	R_f value[a] LAS	R_f value[a] LS-Na	R_f value[b] LAS	R_f value[b] LS-Na	R_f value[b] SAS
1	Chloroform/methyl alcohol-aq. sulfuric acid[c] (8:2)[d]	0.61	0.55	0.68	0.60	0.56
2	2-Butanone/benzene, ethyl alcohol/water (3:3:3:1)	0.60	0.55	0.75	0.81	0.70
3	2-Methyl-4-pentanone/benzene/ethyl alcohol/0.1 N acetic acid (6:6:6:1.4)	0.65	0.54	0.55	0.58	0.43
4	Methyl acetate/benzene/ethyl alcohol (1:1:1)	0.96	0.95	0.97	0.84	0.74
5	Acetone/benzene/ethyl alcohol (1:1:1)	0.94	0.92	0.95	0.95	0.94
6	Carbon tetrachloride/benzene/ethyl alcohol (1:1:1)	0.78	0.75	0.60	0.55	0.61
7	Chloroform/benzene/ethyl alcohol (1:1:1)	0.74	0.70	0.50	0.52	0.37
8	2-Methyl-1,4-pentanone/methylene chloride/4-hydroxy-4-methyl-2-pentanone (1:1:1)	0.19	0.30	0.16	0.25	0.07
9	2-Methyl-4-pentanone/propyl alcohol/0.1 N acetic acid/acetonitrile (20:6:1.6:1)	—	—	0.37	0.45	0.23

[a]Developing distance = 10 cm.
[b]Developing distance = 15 cm.
[c]Methyl alcohol containing 5% of 0.1 N sulfuric acid.
[d]Volume ratio.
Stationary phase; Silica Gel G impregnated with 10% ammonium sulfate.

(Terumo, MS-10). Chromatoplates were developed in the selected solvents by the ascending technique at room temperatures to a height of 10 or 15 cm. After being removed from a running chamber, the plates were air-dried to evaporate solvents. The plates were then sprayed with a solution of 5% phosphomolybdic acid in ethyl alcohol, and charred by heating to obtain black spots. The spot areas were measured by a densitometer using a slit opening of 1 × 10 mm with a 500-nm filter.

RESULTS AND DISCUSSION

Preliminary examinations were done to select the TLC conditions for the separation of anionic surfactants (LAS, SAS, LS-Na).

Developing Solvents

With Silica Gel G impregnated with ammonium sulfate, separation conditions for mixtures of 2 or 3 components were examined. The relationship between various developing solvents and the R_f values of the spots is shown in Table I.

With a mixture of 2 components (LAS and LS-Na), satisfactory separation was obtained with a mixed solvent of 2-methyl-4-pentanone/4-hydroxy-4-methyl-2-pentanone/methylene chloride (1:1:1, vol. ratio). However, other mixed solvents, such as the chloroform/methyl alcohol/aq. sulfuric acid used by Mutter (4) for separation of alkane sulfonates, were unsuitable for separation of individual components (Table I). Using 3 components (LAS, LS-Na and SAS) developed to 15 cm with the solvent system shown in Table I, no. 8, R_f values for LS-Na, LAS and SAS were 0.25, 0.16 and 0.07, respectively. However, the solvent system was unsuitable because of a tailing phenomenon near the origin of the SAS spot. A solvent system composed of 2-methyl-4-pentanone/propyl alcohol/0.1 N acetic acid/acetonitrile (20:6:1.6:1, vol. ratio) was suitable for complete separation. Samples consisting of 2

components, such as LAS and LS-Na, LAS and SAS, and of 3 components (LAS, LS-Na, SAS) were completely separated from each other. The shape of the spots was nearly round, as shown in Figure 4. A solvent consisting of 2-methyl-4-pentanone/propyl alcohol/0.1 N acetic acid/acetonitrile was suitable for separation, but the other 7 developing solvents given in Table I were unsuitable, for practical reasons, because 3-component systems were not separated.

Adsorbent

The solvent 2-methyl-4-pentanone/propyl alcohol/0.1 N acetic acid/acetonitrile was selected as a suitable solvent for the separation of 3 components, and adsorbents such as Alumina G, diatomaceous earth, Silica Gel G and Silica Gel
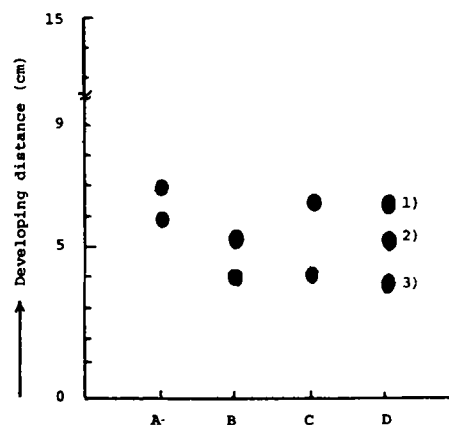
FIG. 4. TLC of mixtures of LAS, LS-Na and SAS. Sample A: LS-Na and LAS mixture; sample B: LAS and SAS mixture; sample C: LS-Na and SAS mixture; sample D: LS-Na, LAS ans SAS mixture (1, LS-Na; 2, LAS; 3, SAS). Developing solvent: 2-methyl-4-pentanone/propyl alcohol/0.1 N acetic acid/acetonitrile (20:6:1.6:1, v/v/v/v). Other conditions were the same as in Table III.

TABLE II

Rf Values of LAS, LS-Na and SAS When
Various Adsorbents Were Used

No.	Stationary phase	Rf value		
		LAS	LS-Na	SAS
1	Silica Gel G	0.21	0.25	0.14
2	Silica Gel G impregnated with boric acid	0.26	0.28	0.16
3	Silica Gel G impregnated with sulfuric acid	0.78	0.85	0.81
4	Silica Gel G impregnated with silver nitrate	0.40	0.47	0.33
5	Diatomaceous earth	0.83	0.88	0.82
6	Alumina G	0	0	0
7	Silica Gel G impregnated with ammonium sulfate	0.37	0.45	0.32

Conditions as listed in Table III except for stationary phases.

TABLE III

Optimal Separating and Estimating Conditions
for LAS, LS-Na and SAS

Stationary phase	Silica Gel G impregnated with 10% ammonium sulfate
Activating temperature and time	110 C, 80 min
Developing solvent	2-Methyl-4-pentanone/propyl alcohol/0.1 N-acetic acid/ acetonitrile (vol. ratio, 20:6:1.6:1)
Detection reagent	None used
Charring temperature and time	250 C, 15 min

G impregnated with boric acid were examined. The Rf values for LAS, LS-Na and SAS are shown in Table II. From the Rf values in Table II, ammonium-sulfate-impregnated Silica Gel G was found to be the most suitable adsorbent.

Detection Reagents, Charring Temperatures and Times

Detection reagents were examined using LS-Na. Chromatograms were developed with 2-methyl-4-pentanone/propyl alcohol/0.1 N acetic acid/acetonitrile (20:6:1.6:1). Spots were located by charring at 250 C after spraying with 2-5% phosphomolybdic acid in ethanol or by charring unsprayed. Peak areas were measured by a densitometer and calculated by the triangle method. The relationship between charring time and peak area is shown in Figure 5. Charring temperatures at 190-250 C were examined without spray reagents with a 15-min char. This relationship between peak area and charring temperature is shown in Figure 6. Spots charred at 250 C showed maximal values even without spray reagents.

Optimal Conditions

Suitable conditions for TLC separation and quantitative determination of the 3 components, LAS, LS-Na and SAS, are summarized in Table III. Mixtures of 2 or 3 components, such as LAS and LS-Na, LAS and SAS, LS-Na and SAS, LAS LS-Na and SAS, were separated completely

FIG. 5. Relationship between detecting agent, charring time and peak area. o—o 5% phosphomolybdic acid in ethanol; •—• 2% phosphomolybdic acid in ethanol; △—△ no charring agent. Charring temp., 250 C; sample, LS-Na. Other conditions were the same as in Table III.
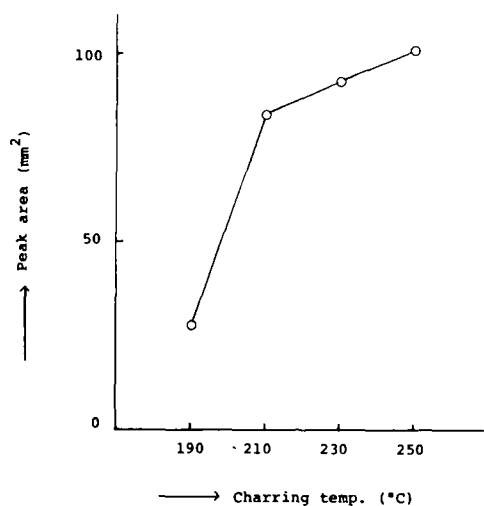
FIG. 6. Relationship between charring temperatures and peak areas. Samples, LS-Na charring time, 15 min; no detecting reagent was used. Other conditions were the same as in Table III.

FIG. 7. Calibration curves for LAS, LS-Na and SAS.

TABLE IV

TLC Analysis of Mixtures of LAS, LS-Na and SAS

No.	Sample	Known content (mg)	Known ratio (%)	No. 1 Content (µg)	No. 1 Ratio (%)	No. 2 Content (µg)	No. 2 Ratio (%)	No. 3 Content (µg)	No. 3 Ratio (%)	Average Content (µg)	Average Ratio (%)	Mean error (%)	Std. Dev.	CV (%)
1	LAS	10.4	68.0	10.7	9.6	9.7	64.4	9.7	64.2	10.0	64.6	± 3.4	0.43	0.67
	LS-Na	4.9	32.0	5.7	34.8	5.3	35.6	5.4	35.8	5.5	35.4			
2	LAS	5.2	47.3	5.0	46.7	5.0	46.7	5.2	48.6	5.1	47.3	± 0.0	0.90	1.90
	LS-Na	5.8	52.7	5.7	53.3	5.7	53.3	5.5	51.4	5.6	52.7			1.71
3	LAS	5.2	35.4	4.8	32.4	4.4	30.8	4.7	30.1	4.6	31.1	± 4.3	0.96	3.09
	LS-Na	9.1	64.6	10.0	67.6	9.9	69.2	10.9	69.9	10.3	68.9			1.39
4	LAS	9.0	67.2	8.1	61.8	8.6	63.7	8.5	63.0	8.4	62.8	± 4.4	0.79	1.26
	SAS	4.4	32.8	5.0	38.2	4.9	36.3	5.0	37.0	5.0	37.2			2.12
5	LAS	6.4	49.6	6.4	47.4	6.7	49.3	6.9	50.7	6.7	49.1	± 0.5	1.35	2.74
	SAS	6.5	50.4	7.1	52.6	6.9	50.7	6.7	49.3	6.9	50.9			2.65
6	LAS	4.9	38.6	4.4	37.5	4.4	34.4	4.3	34.7	4.4	35.5	± 3.1	1.40	3.94
	SAS	7.8	61.4	8.0	62.5	8.4	65.6	8.1	65.3	8.2	64.5			2.17
7	LS-Na	7.8	62.9	7.9	62.2	8.0	63.0	8.2	62.6	8.0	62.6	± 0.3	0.33	0.53
	SAS	4.6	37.1	4.8	37.8	4.7	37.0	4.9	37.4	4.8	37.4			0.88
8	LS-Na	5.2	50.0	5.7	50.0	5.5	51.4	5.3	51.5	5.5	51.0	± 1.0	0.69	1.35
	SAS	5.2	50.0	5.7	50.0	5.2	48.6	5.0	48.5	5.3	49.0			1.41
9	LS-Na	4.4	33.3	4.7	35.3	4.7	35.1	4.6	35.4	4.7	35.3	± 2.0	0.13	0.37
	SAS	8.8	66.7	8.6	64.7	8.7	64.9	8.4	64.6	8.6	64.7			0.20
10	LAS	5.2	33.3	4.8	31.8	4.3	29.7	4.3	29.1	4.5	30.2	-3.1	1.16	3.84
	LS-Na	5.6	35.9	5.8	38.4	5.8	39.2	5.8	39.2	5.8	39.2	+3.3	0.65	1.66
	SAS	4.8	30.8	4.5	29.8	4.4	30.3	4.7	31.8	4.5	30.6	-0.2	0.85	1.78
11	LAS	7.2	48.0	6.6	43.7	6.7	44.7	6.6	44.3	6.6	44.2	-3.8	0.41	0.93
	LS-Na	3.8	25.3	4.1	27.2	4.1	27.3	3.9	26.2	4.0	26.9	+1.6	0.50	1.86
	SAS	4.0	26.7	4.4	29.1	4.2	28.0	4.4	29.5	4.3	28.9	-2.2	0.64	2.21
12	LAS	5.6	28.1	4.9	24.1	5.0	26.0	4.8	24.9	4.9	25.0	-3.1	0.78	3.12
	LS-Na	9.5	47.7	10.3	50.7	9.3	48.0	10.0	51.8	9.9	50.3	+2.6	1.42	2.28
	SAS	4.8	24.2	5.1	25.1	4.9	25.5	4.5	23.3	4.8	24.7	+0.5	0.96	3.89
13	LAS	5.2	26.8	5.7	29.1	5.6	28.6	5.3	27.2	5.5	28.2	-1.4	0.18	2.87
	LS-Na	5.0	25.8	5.1	26.0	5.5	28.0	5.7	29.2	5.4	27.8	+2.0	1.32	4.75
	SAS	9.2	47.4	8.8	44.9	8.5	43.4	8.5	43.6	8.6	44.0	-3.4	0.67	1.52

under the optimal conditions described in Table III. Spot shapes were nearly round and showed no tailing.

Calibration Curves for LS-Na, LAS and SAS

Sample solutions containing known amounts of LAS, LS-Na and SAS were applied with a microsyringe using the optimal separating conditions. A calibration curve for LS-Na, LAS and SAS is shown in Figure 7. The relationship between peak area and the amounts of each of the 3 components was linear from 4 µg to 15 µg. Therefore, quantitations could be made.

Determination of Mixtures

To determine the reproducibility of the method, standard mixtures of either 2 or 3 components were prepared and analyzed. TLC analyses of these mixtures are shown in Table IV. Mean errors for the 2-component systems, LS-Na and LAS, LAS and SAS, SAS and LS-Na, were 0-4.3%, 0.5-4.4%, 0.3-2.0%, respectively. Variation coefficients (CV) were 0.67-3.09%, 1.26-3.94% and 1.20-1.41%, respectively. In the 3-component mixtures, mean errors were 0.2-3.8%, CV were 0.93-4.75%. Analytical results agreed well with known compositions. Mean errors and CV were both within ca. 4%. This is within the limit of experimental error. TLC can therefore be applied to the quantitative determination of anionic surfactants such as LAS, LS-Na and SAS.

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