

CHROM. 9133

DETECTION OF SODIUM ALKANESULPHONATES AND ALKYL-BENZENESULPHONATES BY POLYAMIDE THIN-LAYER CHROMATOGRAPHY

RYUZO TAKESHITA, NARIKO JINNAI and HIROSHI YOSHIDA

Department of Public Health Pharmaceutics, The Institute of Public Health, 6-1, Shirokanedai 4-chome, Minato-ku, Tokyo (Japan)

(Received January 5th, 1976)

SUMMARY

A thin-layer chromatographic method was investigated in which two series of sodium alkanesulphonates (C_4 - C_{18}) and alkylbenzenesulphonates (C_0 - C_{14}) were separated. All of the compounds tested were clearly separated on polyamide layers with aqueous ammonia-pyridine and aqueous ammonia-pyridine-methanol systems and detected with high sensitivity by spraying with a pynacryptol yellow reagent and then observing under UV light (253.6 nm).

INTRODUCTION

Sodium alkylbenzenesulphonates (ABS), sodium alkylsulphates (AS) and sodium alkanesulphonates (PS) are widely used as anionic surfactants. It is well known that they are biologically degraded in the environment and the speed of the oxidative degradation is closely connected with the structure of the surfactants.

Although in general anionic surfactants are easily measured by the colorimetric method using methylene blue¹, the values obtained thereby show only the total amounts of the surfactants. As AS are hydrolyzed to the original alcohols and sulphuric acid by acids, they are separated from ABS and PS, and determined by analyzing the alcohols formed by gas-liquid chromatography. When analyzed by gas-liquid chromatography, however, ABS and PS must be submitted to gas chromatography after conversion into the corresponding hydrocarbons by desulphonation because of their non-volatility.

The main purpose of this study was to establish a method for detecting two series of ABS and PS rapidly without the need to convert them into derivatives.

EXPERIMENTAL

Adsorbent

Polyamide powder B-O for thin-layer chromatography (Wako, Osaka, Japan)

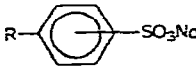
was used as the adsorbent, and cellulose powder for thin-layer chromatograph, (Camag, Muttenz, Switzerland) was used as the binder.

Reagents

The sodium alkanesulphonates and alkylbenzenesulphonates listed in Table I were of guaranteed reagent grade (Tokyo Kasei Kogyo, Tokyo, Japan). The test solutions of sodium alkylbenzenesulphonates were prepared by dissolving 100 mg of each compound in 10 ml of methanol, while those of sodium alkanesulphonates with carbon chains shorter than C₁₁ were dissolved in water to make 1% solutions and the others were dissolved in methanol to make 0.5% solutions. The other reagents were of analytical-reagent grade. A 0.2% ethanolic solution of pinacryptol yellow was used as a spray reagent.

TABLE I

SODIUM ALKANESULPHONATES AND ALKYL BENZENESULPHONATES STUDIED

<i>Sodium alkanesulphonates</i>		<i>Sodium alkylbenzenesulphonates</i>	
<i>R-SO₃Na</i>	<i>R</i>		<i>R</i>
<i>n</i> -Butane-1-sulphonate	C ₄ H ₉	Benzenesulphonate	H
<i>n</i> -Pentane-1-sulphonate	C ₅ H ₁₁	Toluenesulphonate	CH ₃
<i>n</i> -Hexane-1-sulphonate	C ₆ H ₁₃	<i>n</i> -Butylbenzenesulphonate	C ₄ H ₉
<i>n</i> -Heptane-1-sulphonate	C ₇ H ₁₅	<i>n</i> -Hexylbenzenesulphonate	C ₆ H ₁₃
<i>n</i> -Octane-1-sulphonate	C ₈ H ₁₇	<i>n</i> -Octylbenzenesulphonate	C ₈ H ₁₇
<i>n</i> -Nonane-1-sulphonate	C ₉ H ₁₉	<i>n</i> -Decylbenzenesulphonate	C ₁₀ H ₂₁
<i>n</i> -Decane-1-sulphonate	C ₁₀ H ₂₁	<i>n</i> -Dodecylbenzenesulphonate	C ₁₂ H ₂₅
<i>n</i> -Undecane-1-sulphonate	C ₁₁ H ₂₃	<i>n</i> -Tetradecylbenzenesulphonate	C ₁₄ H ₂₉
<i>n</i> -Dodecane-1-sulphonate	C ₁₂ H ₂₅		
<i>n</i> -Tridecane-1-sulphonate	C ₁₃ H ₂₇		
<i>n</i> -Tetradecane-1-sulphonate	C ₁₄ H ₂₉		
<i>n</i> -Hexadecane-1-sulphonate	C ₁₆ H ₃₃		
<i>n</i> -Octadecane-1-sulphonate	C ₁₈ H ₃₇		

Apparatus

A thin-layer applicator and other accessories were obtained from Yazawa Seisaku Co., Tokyo, Japan. Glass plates were of dimensions 20 × 20 cm. The chromatographic chamber (12 × 22 × 25 cm) was equipped with a suspension unit devised for pre-equilibrating the thin-layer plates with the solvent systems, as previously reported². The UV light source (253.6 nm) was supplied by Manasulu Ultra Violet Kagaku Kogyo Co., Tokyo, Japan.

Preparation of polyamide thin-layer plates

A slurry was prepared by mixing 20 g of the polyamide powder, 0.4 g of the cellulose powder and 80 ml of isopropanol in a homogenizer. The glass plates were coated with the slurry using the applicator to give a thin layer approximately 300 μm thick. After standing for 15 min at room temperature, the layers were dried for 30 min at 70°.

Solvent systems for thin-layer chromatography

The following solvent systems were used: (1) 0–1.0 *N* aqueous ammonia–pyridine (15:1); (2) 0.1 *N* aqueous ammonia–pyridine–methanol (15:1:0–15).

Application of samples and development of chromatographic layers

Volumes of 0.3–1 μl of the test solutions were spotted with a micropipette on the starting line 2 cm from the lower edge of the layer. In the chamber containing the solvent system, the side of which had been partially lined with filter-paper soaked with the solvent system, the layer was equilibrated with the solvent vapour for 20 min before commencing the development. The development was carried out at $20 \pm 1^\circ$ by immersing the layer in the solvent system to a depth of about 0.5 cm without opening the cover of the chamber, and was continued until the solvent front had travelled 10 cm from the starting line. After development, the layer was removed from the chamber and dried immediately with an air drier.

Detection of spots on the chromatographic layers

After spraying with the pinacryptol yellow reagent, the layers were examined under UV light (253.6 nm). The spots showing yellow fluorescence were observed.

RESULTS AND DISCUSSION

In our previous investigation on the separation of 20 water-soluble acid dyes by polyamide thin-layer chromatography³, the addition of a small amount of pyridine to solvent systems consisting of methanol plus aqueous ammonia prevented the spots of the dyes from tailing and gave increased R_F values. For the separation of PS and ABS on polyamide layers, development with a mixture of pyridine and water (1:15) did not give a good pattern and most of the compounds were distributed near the

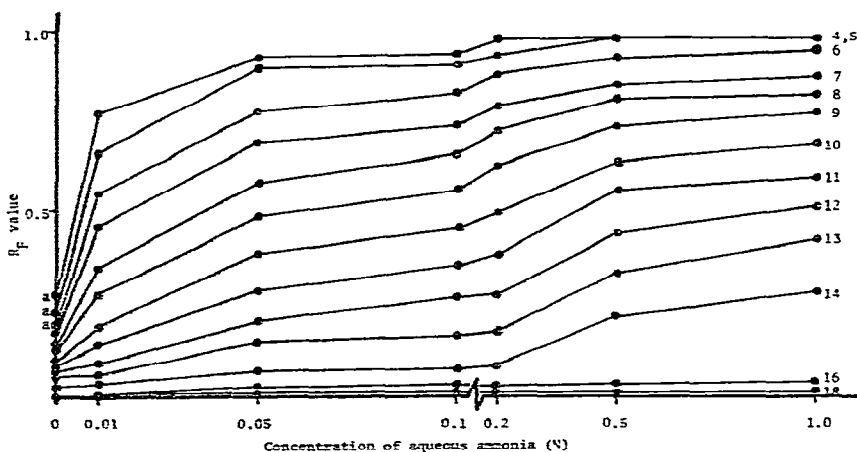


Fig. 1. Relationship between the distribution of alkanesulphonic acids ($R\text{-SO}_3\text{H}$) and concentration of aqueous ammonia in the solvent system. Solvent system: aqueous ammonia–pyridine (15:1). Layer: polyamide. R: 4 = C_4H_9 ; 5 = C_5H_{11} ; 6 = C_6H_{13} ; 7 = C_7H_{15} ; 8 = C_8H_{17} ; 9 = C_9H_{19} ; 10 = $\text{C}_{10}\text{H}_{21}$; 11 = $\text{C}_{11}\text{H}_{23}$; 12 = $\text{C}_{12}\text{H}_{25}$; 13 = $\text{C}_{13}\text{H}_{27}$; 14 = $\text{C}_{14}\text{H}_{29}$; 16 = $\text{C}_{16}\text{H}_{33}$; 18 = $\text{C}_{18}\text{H}_{37}$. Point a, tailing of spot.

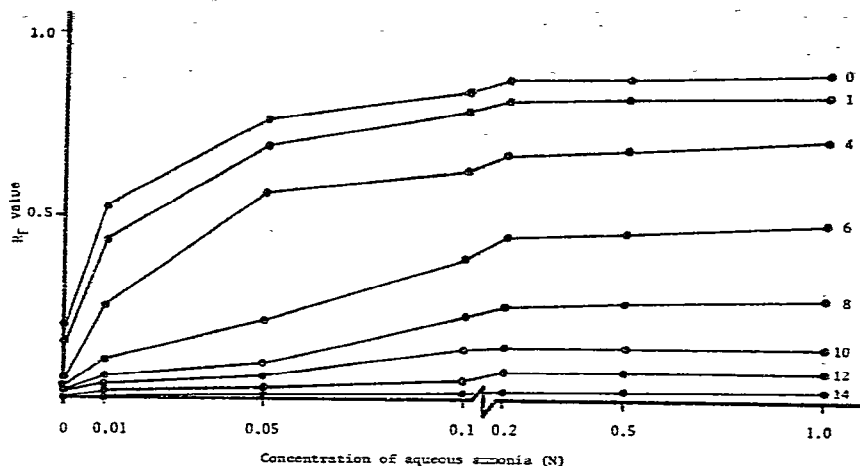


Fig. 2. Relationship between the distribution of alkylbenzenesulphonic acids ($R-\Phi-SO_3H$) and concentration of aqueous ammonia in the solvent system. Solvent system: aqueous ammonia-pyridine (15:1). Layer: polyamide. R: 0 = H; 1 = CH_3 ; 4 = C_4H_9 ; 6 = C_6H_{13} ; 8 = C_8H_{17} ; 10 = $C_{10}H_{21}$; 12 = $C_{12}H_{25}$; 14 = $C_{14}H_{29}$.

starting line. For satisfactory migration of the compounds on polyamide layers, it was necessary for the solvent systems to contain both aqueous ammonia and pyridine.

In order to establish the effect of ammonia in the solvent systems on the separation, the development was carried out with a series of solvent systems consisting of pyridine-aqueous ammonia (1:15) in which the concentration of the latter varied from 0.01 to 1.0 N. The patterns obtained are shown in Figs. 1 and 2. PS and ABS showed a good distribution when developed with the solvent systems in which the concentration of aqueous ammonia was in the range 0.05–0.1 N for the former compounds and 0.1–1.0 N for the latter.

The solvent systems, however, were not always suitable for the separation of PS with carbon chains longer than C_{14} or for the separation of ABS with carbon

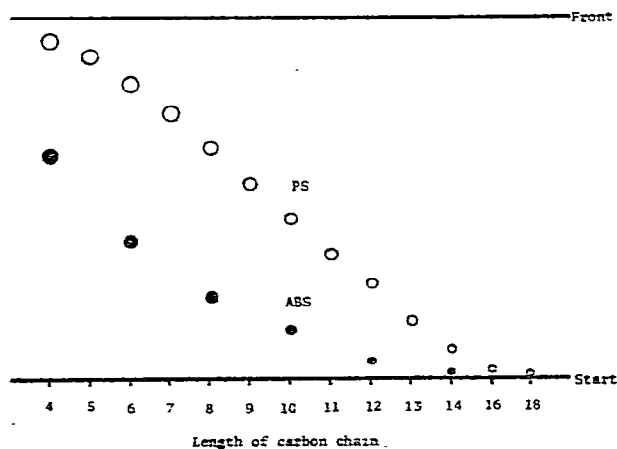


Fig. 3. Chromatogram of alkanesulphonic acids and alkylbenzenesulphonic acids on polyamide layer. Solvent system: 0.1 N aqueous ammonia-pyridine (15:1).

chains longer than C_{10} . The chromatograms of PS and ABS obtained when developed with a mixture of 0.1 *N* aqueous ammonia-pyridine (15:1) are shown in Fig. 3.

For the purpose of the separation of PS with carbon chains longer than C_{14} and ABS with carbon chains longer than C_{10} , the development was carried out with a series of solvent systems prepared by adding methanol to the system 0.1 *N* aqueous ammonia-pyridine (15:1) in volume ratios of 5, 10 and 15. Figs. 4 and 5 show that

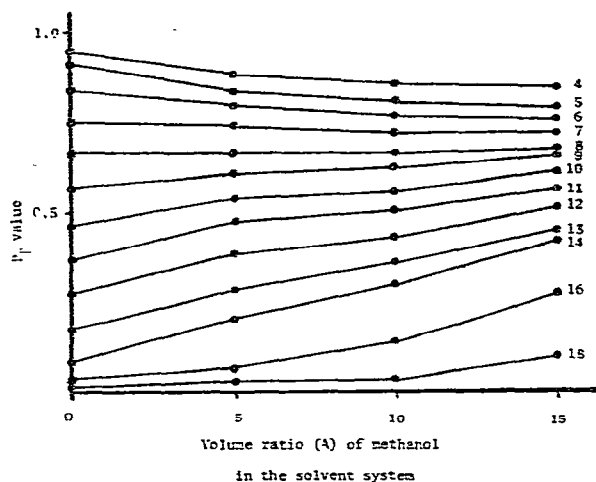


Fig. 4. Relationship of the distribution of alkanesulphonic acids ($R-SO_3H$) and volume ratios of methanol (*A*) in the solvent system. Solvent system: methanol-0.1 *N* aqueous ammonia-pyridine (*A*: 15:1). Layer: polyamide. *R*: 4 = C_4H_9 ; 5 = C_5H_{11} ; 6 = C_6H_{13} ; 7 = C_7H_{15} ; 8 = C_8H_{17} ; 9 = C_9H_{19} , 10 = $C_{10}H_{21}$; 11 = $C_{11}H_{23}$; 12 = $C_{12}H_{25}$; 13 = $C_{13}H_{27}$; 14 = $C_{14}H_{29}$; 16 = $C_{16}H_{33}$; 18 = $C_{18}H_{37}$.

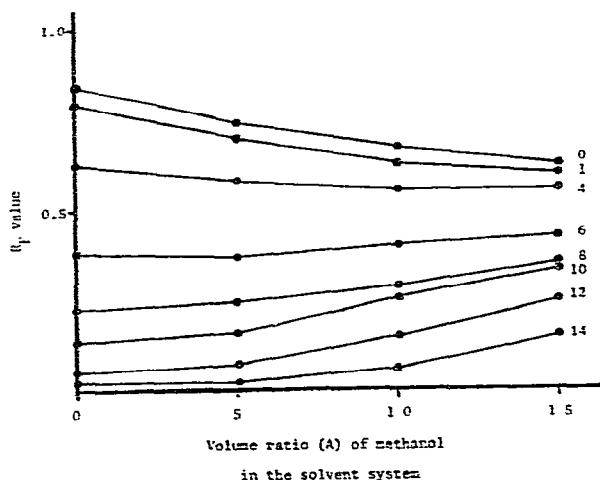


Fig. 5. Relationship of distribution of alkylbenzenesulphonic acids ($R-\phi-SO_3H$) and volume ratios of methanol (*A*) in the solvent system. Solvent system: methanol-0.1 *N* aqueous ammonia-pyridine (*A*: 15:1). Layer: polyamide. *R*: 0 = H; 1 = CH_3 ; 4 = C_4H_9 ; 6 = C_6H_{13} ; 8 = C_8H_{17} ; 10 = $C_{10}H_{21}$; 12 = $C_{12}H_{25}$; 14 = $C_{14}H_{29}$.

increasing contents of methanol in the systems lead to slightly higher R_F values for PS with carbon chains longer than C_9 and for ABS with carbon chains longer than C_8 , and to slightly lower R_F values for PS with carbon chains shorter than C_4 . Therefore, the development with 0.1 *N* aqueous ammonia-pyridine-methanol (15:1:15) was efficient for the separation of PS and ABS with long carbon chains that were not separated by development with 0.1 *N* aqueous ammonia-pyridine (15:1). The long migration distance of PS and ABS with the long carbon chains in the former solvent system and the short migration distance in the latter can be explained in terms of their solubilities in the systems.

Pinacryptol yellow has been used previously as a convenient reagent for the detection of cyclohexanesulphamic acid (cyclamic acid) in polyamide thin-layer chromatography⁴. The application of the reagent to the detection of the sulphonates was investigated in the present method. When observed under UV light (253.6 nm) after spraying with this reagent, all of the compounds studied appeared as yellow fluorescent spots against a bright background. The detection limits are given in Table II. The lower sensitivities of PS and ABS with shorter carbon chains might be dependent upon dispersion resulting from their long migration distances on the layers.

TABLE II

DETECTION LIMITS OF SODIUM ALKANESULPHONATES AND ALKYL BENZENESULPHONATES ON POLYAMIDE LAYERS

Solvent systems: (1) 0.1 *N* aqueous ammonia-pyridine (15:1); (2) methanol-0.1 *N* aqueous ammonia-pyridine (10:15:1).

Sodium alkanesulphonate	Detection limit (μg)		Sodium alkylbenzenesulphonate	Detection limit (μg)	
	Solvent 1	Solvent 2		Solvent 1	Solvent 2
<i>n</i> -Butane-1-sulphonate	2	1	Benzenesulphonate	2	1
<i>n</i> -Pentane-1-sulphonate	2	1	Toluenesulphonate	1	0.5
<i>n</i> -Hexane-1-sulphonate	1	1	<i>n</i> -Butylbenzenesulphonate	0.5	0.5
<i>n</i> -Heptane-1-sulphonate	1	0.5	<i>n</i> -Hexylbenzenesulphonate	0.5	0.5
<i>n</i> -Octane-1-sulphonate	0.5	0.5	<i>n</i> -Octylbenzenesulphonate	0.2	0.2
<i>n</i> -Nonane-1-sulphonate	0.2	0.2	<i>n</i> -Decylbenzenesulphonate	0.1	0.2
<i>n</i> -Decane-1-sulphonate	0.2	0.2	<i>n</i> -Dodecylbenzenesulphonate	0.1	0.2
<i>n</i> -Undecane-1-sulphonate	0.1	0.2	<i>n</i> -Tetradecylbenzenesulphonate	0.1	0.1
<i>n</i> -Dodecane-1-sulphonate	0.1	0.1			
<i>n</i> -Tridecane-1-sulphonate	0.1	0.1			
<i>n</i> -Tetradecane-1-sulphonate	0.1	0.1			
<i>n</i> -Hexadecane-1-sulphonate	0.05	0.1			
<i>n</i> -Octadecane-1-sulphonate	0.05	0.05			

CONCLUSION

When PS with C_4 - C_{18} carbon chains and ABS with C_0 - C_{14} carbon chains were developed with a mixture of 0.1-1.0 *N* aqueous ammonia-pyridine (15:1) on polyamide layers, most of the compounds were clearly separated as circular spots. Compounds with a shorter carbon chain showed higher R_F values than corresponding

compounds with longer carbon chains owing to the difference in their solubilities in the solvent systems. The addition of methanol to the system 1.0 *N* aqueous ammonia-pyridine (15:1) increased the R_F values of compounds with long carbon chains and gave a better distribution. The compounds were detected with high sensitivity by pinacryptol yellow reagent under UV light, appearing as yellow fluorescent spots.

REFERENCES

- 1 *Standard Methods for the Examination of Water and Waste Water*, American Public Health Association, New York, 13th ed., 1971.
- 2 R. Takeshita, *Chem. Pharm. Bull.*, 19 (1971) 80.
- 3 R. Takeshita, T. Yamashita and N. Itoh, *J. Chromatogr.*, 73 (1972) 173.
- 4 R. Takeshita, *J. Chromatogr.*, 66 (1972) 283.