Technical

Separation and Determination of C_{21} Dicarboxylic Acid and Xylenesulfonate Hydrotropes in Mixtures with Dodecylbenzenesulfonate

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ABSTRACT

Column chromatographic procedures have been developed for separating binary mixtures of commercial sodium dodecylbenzenesulfonate (DDBS) with the hydrotropes sodium *m*-xylenesulfonate (SXS) and 8-[5(6)-carboxy-4-hexyl-cyclohex-2-enyl] octanoic acid (DAC) and ternary mixtures of these three materials. The materials are separated on a specially purified silica gel column. The C_{21} dicarboxylic acid (DAC) is eluted with 2:3 (v/v) chloroform/acetone in the presence of SXS, with 3:2 (v/v) chloroform/acetone in its absence. The DDBS is eluted with 1:9 (v/v) isopropyl alcohol/acetone in the presence of SXS, with methanol in its absence. The SXS is eluted with methanol in the presence of DAC, with 8:2 (v/v) isopropyl alcohol/acetone in its absence. The presence of SXS in mixtures with DDBS in greater than equimolar amounts interferes with the Hyamine 1622, mixed indicator titration for DDBS.

INTRODUCTION

Alkylbenzenesulfonates with short alkyl groups, such as xylene-, cumene- and toluenesulfonates, are frequently used as hydrotropes, i.e., to increase the water solubility of surfactants such as sodium dodecylbenzenesulfonate, in detergent formulations. The accurate determination of the hydrotrope content of such formulations is difficult when both hydrotrope and surfactant adsorb in the same ultraviolet (UV) range. Complete separation of the two materials by chromatographic or extractive (1-3) methods is often complicated by the presence in commercial dodecylbenzenesulfonates of impurities that are not readily separated from the hydrotropes and that adsorb in the same UV range. The introduction (4-6) of a new type of hydrotrope, Westvaco DIACID® 1550, 8-[5(6)-carboxy-4-hexyl-cyclohex-2-enyl] octanoic acid, stimulated our search for a method of determining the concentration of both of these types of hydrotropes in their mixtures with commercial sodium dodecylbenzenesulfonate.

MATERIALS AND METHODS

Sodium *m*-xylenesulfonate (SXS): 2,4-Dimethylbenzenesulfonic acid, a sodium salt from Eastman Kodak, was used as received. UV absorption maximum was at 276 nm (ϵ = 410). Mol wt = 208.2. DIACID® 1550 (DAC), supplied by Westvaco, was used as received. The equivalent weight was 265 as determined by titration with 0.1 N KOH. Sodium linear dodecylbenzenesulfonate (DDBS): Commercial grade (Custofac), supplied by Westvaco, was freed from unsulfonated material and inorganic salts by the following procedure: dissolve 20 g in a mixture of 300 mL of distilled water and 300 mL of 95% ethanol. Extract the solution seven times with 100-mL portions of hexane to remove unsulfonated material. Evaporate the extracted aqueous alcohol solution to dryness on a steam bath. Heat the residue with hot isopropyl alcohol (water, 0.2% max) and filter the mixture to remove inorganic salts. Evaporate the solvent and dry the residue to constant weight in a vacuum desiccator over phosphorus pentoxide. Purity of the product is 99.2%, by two-phase titration with Hyamine 1622 using mixed indicators (7,8) and assuming a mol wt of 348.5 for the DDBS. UV absorption at 276 nm: ϵ = 254. Chloroform: use reagent grade. Remove water and ethanol by drying over anhydrous calcium chloride for several hours and then filtering the mixture. Hyamine 1622 (Rohm and Haas): concentrations of Hyamine solutions were determined by UV absorbance at 269.5 nm, using ϵ = 1266 (9). Acetone: use reagent grade, 0.5% water, max. Isopropyl alcohol: Reagent grade, 0.2% water, max. Methanol: use reagent grade, 0.2% water, max.

Silica Gel Treatment

This was done to remove fines and polyvalent cations. Suspend 300 g of silica gel (Davison grade 922) in 1,200 mL of distilled water and 2 mL of concentrated hydrochloric acid. Stir the suspension gently for 10 min. Allow the suspension to settle for 10 min and then decant the upper suspension containing fines. Add 1,200 mL of distilled water and repeat the stirring and decantation process 10 times. Finally, filter the mixture with suction and wash the silica gel on the filter with distilled water until it is free of Cl^-. Dry the silica gel at 100-120 C and activate it at 120 C for 2 hr before use.

ANALYSIS OF SXS-DDBS MIXTURES

Preparation of the Silica Gel Column

Mix 80 mL of 1:9 (v/v) isopropyl alcohol/acetone with 4.3 g of activated silica gel, purified by the above procedure. Pour the mixture into a glass chromatography tube, 40 cm x 2 cm id, with a cotton plug at the bottom. Rinse any silica gel remaining in the container onto the column with additional solvent mixture and wash the column with the same solvent mixture until evaporation of a drop of the eluate on a clean watch glass leaves no trace of a residue. The height of the silica gel column is about 26 cm.

Separation and Determination of the Components

For this separation, it is necessary that the SXS constitute no more than 1/6 by wt of the mixture. Weigh about 0.6 g of the dry mixture into a 50-mL beaker, dissolve or suspend it in 20 mL of 1:9 (v/v) isopropyl alcohol/acetone and transfer it to the column. Rinse the beaker several times with the same solvent mixture to ensure complete transfer, since SXS has only limited solubility in the solvent mixture. Elute most of the DDBS from the column with the same

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solvent mixture until about 350 mL of eluate has been collected. Elute the remaining DDBS and the SXS from the column with 8:2 (v/v) isopropyl alcohol/acetone (180-200 mL).

Evaporate both eluates to dryness on the steam bath. Heat the residue from the second eluate for 40-min periods to constant wt (W_RII) in an oven at 95-100 C.

Dissolve the residue from the first eluate in distilled water and dilute it exactly to 1,000 mL (soln I). Use 10-mL aliquots of this solution to determine its DDBS molar concentration (M_{DDBS} I) by titration with Hyamine 1622, using mixed indicators (7,8). Dissolve the residue from the second eluate in distilled water and dilute it exactly to 500 mL (soln II). Use 10-mL aliquots of soln II to determine its DDBS molar concentration (M_{DDBS}II) in similar fashion, by titration with Hyamine 1622. Determine the UV absorbance at 276 nm of soln II (A_{276}II).

Calculation of Results

The weight of DDBS (g) in soln I = M_{DDBS}I × 348.5 × 100.

The weight of DDBS (g) in soln II = M_{DDBS}II × 348.5 × 50. The total DDBS content of the sample of the original mixture is the sum of the weights of DDBS in solns I and II.

The weight of SXS in the original sample can be obtained in two ways—(a) by UV absorbance and Hyamine titration:

$$\text{weight (g) of SXS in original sample} = \frac{(A_{276}\text{II}) - (254 \times M_{DDBS}\text{II})}{410} \times \frac{208.2}{2} = [(A_{276}\text{II}) - (254 \times M_{DDBS}\text{II})] \times 0.254;$$

(b) by weight and Hyamine titration:

$$\text{weight (g) of SXS in original sample} = \frac{W_R\text{II} - M_{DDBS}\text{II} \times 348.5}{2}$$

Results are listed in Table I.

TABLE I

Percentage Recovery of DDBS and SXS from Their Mixtures

Run	Recovery of DDBS	Recovery of SXS: by wt and titration	Recovery of SXS: by UV absorption and titration
1	98.6	98.4	97.8
2	98.9	96.7	98.0
3	98.7	98.6	96.2

ANALYSIS OF DAC-DDBS MIXTURES

Preparation of the Silica Gel Column

Prepare the column as discussed above, except that 3:2 (v/v) $CHCl_3$/acetone is used to transfer the silica gel to the chromatography tube and to wash any fines from the column (the $CHCl_3$ was freed of water and ethanol, as already described.)

Separation and Determination of the Components

Weigh about 0.6 g of the dry mixture into a 50-mL beaker and dissolve or suspend it in 5 mL of 3:2 $CHCl_3$/acetone ($CHCl_3$ was freed of water and ethanol, as described above). Transfer the solution to the chromatographic column and rinse the test beaker four times with 5-mL portions of the same solvent mixture. Elute the DAC with a total of about 140 mL of the solvent mixture.

Determine the amount of DAC either by weighing the residue after evaporating the solvent (and drying to constant weight in a vacuum desiccator) or by titrating the residue with 0.1 N KOH solution (if unsulfonated material is suspected of being present in the DDBS).

Elute the DDBS from the column with about 120 mL of methanol. Determine its quantity either by weighing the residue after evaporating the solvent (and drying to constant weight in a vacuum dessiccator) or by two-phase titration with Hyamine 1622, using mixed indicators.

ANALYSIS OF DAC-SXS-DDBS MIXTURES

Preparation of the Silica Gel Column

Prepare the column as for DAC-DDBS mixtures, above.

Separation and Determination of Compounds

For this separation, it is necessary that the SXS constitute no more than 1/7 by wt of the mixture. Weight about 0.7 g of the dry mixture into a small Erlenmeyer flask and dissolve or suspend it in 20 mL of 2:3 (v/v) $CHCl_3$/acetone (with $CHCl_3$ freed of water and ethanol). Generally, only the DAC dissolves completely. Transfer the supernatant liquid onto the silica gel column. Transfer any remaining material in the flask onto the column with four 10-mL portions of the same solvent mixture. Stir the mixture above the silica gel column gently with a small glass stirring rod, to distribute any solid material evenly over the top surface and to increase the elution speed. Elute the DAC with the same solvent mixture until 120 mL of eluate has been collected. Determine the amount of DAC as described above for DAC-DDBS mixtures.

Elute most of the DDBS with 1:9 (v/v) isopropyl alcohol/acetone until 300 mL of eluate has been collected (fraction I). Continue eluting with the same mixed solvent until an additional 50 mL of eluate has been collected (fraction II). Reserve this fraction for combining with the SXS fraction (fraction III, below).

Elute the SXS (and some remaining DDBS) with methanol until about 100-120 mL of eluate has been obtained (fraction III). Combine this with fraction II, reserved above.

Evaporate fraction I and the combined fractions II and III to dryness on the steam bath. Heat the residue from combined fractions II and III for 40-min periods to constant wt (W_RII) in an oven at 95-100 C.

Dissolve the residue from fraction I in distilled water and dilute it exactly to 1,000 mL (soln I). Use 10-mL aliquots of this solution to determine its DDBS molar concentration (M_{DDBS}I) by titration with Hyamine 1622, using mixed indicator. Dissolve the residue from combined fractions II and III in distilled water and dilute it exactly to 500 mL (soln II). Use 10-mL aliquots of soln II to determine its DDBS molar concentration (M_{DDBS}II) in similar fashion, by titration with Hyamine 1622.

Determine the weights of DDBS and SXS in the original sample as described under Calculation of Results of DDBS-SXS mixtures, above. Results are listed in Table II.

TABLE II

Percentage Recovery of DAC, DDBS and SXS from Their Mixtures

Recovery of:	DAC		DDBS	SXS	
Method	Wt	Titration	Titration	Titration and UV	Titration and wt
Run 1	98.4	98.5	99.2	98.4	99.0
Run 2	98.5	98.6	99.6	97.6	98.1

DISCUSSION

The procedures described are only suitable when the ratio of SXS to DDBS is 1:6 or less. The reason for this is that it has not been possible to obtain a complete separation of SXS from all of the components of commercial DDBS. Moreover, it is impossible to determine the exact amount of these DDBS components in the SXS fraction since the presence of SXS in greater than equimolar amounts in mixtures with DDBS interferes with the Hyamine titration of DDBS. Data are given in Table III. Therefore, in the described procedures, sufficient DDBS (at least equimolar with the SXS content) is left in the SXS fraction to permit determination of the DDBS content by Hyamine titration.

A problem inherent in separating ternary mixtures of DAC, DDBS and SXS by column chromatography is the difficulty of finding a solvent that will dissolve all three materials and still be suitable as a first eluting solvent. The procedure described illustrates one method of handling this problem.

TABLE III

Influence of SXS on the Hyamine Titration for DDBS

Original		M_{DDBS} Found	Recovery (%)
M_{DDBS}	M_{SXS}		
$1.00_2 \times 10^{-3}$	–	$9.9_5 \times 10^{-4}$	99.3
$1.00_2 \times 10^{-3}$	$1.25_0 \times 10^{-4}$	$9.9_6 \times 10^{-4}$	99.4
$1.00_2 \times 10^{-3}$	$2.50_1 \times 10^{-4}$	$9.9_6 \times 10^{-4}$	99.4
$1.00_2 \times 10^{-3}$	5.00×10^{-4}	$9.9_6 \times 10^{-4}$	99.4
$1.00_2 \times 10^{-3}$	7.50×10^{-4}	$9.9_8 \times 10^{-4}$	99.6
$1.00_2 \times 10^{-3}$	$1.00_4 \times 10^{-3}$	$9.9_9 \times 10^{-4}$	99.7
$1.00_2 \times 10^{-3}$	$1.25_1 \times 10^{-3}$	$1.00_7 \times 10^{-3}$	100.5
$1.00_2 \times 10^{-3}$	$1.75_1 \times 10^{-3}$	$1.01_2 \times 10^{-3}$	100.9
$1.00_2 \times 10^{-3}$	$2.50_1 \times 10^{-3}$	$1.02_7 \times 10^{-3}$	102.4
$1.00_2 \times 10^{-3}$	$5.00_2 \times 10^{-3}$	$1.07_4 \times 10^{-3}$	107.3
$1.00_2 \times 10^{-3}$	7.50×10^{-3}	$1.12_5 \times 10^{-3}$	112.3

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