marized in Table IV. The technical-grade trisodium citrate is comparable in appearance and other physical properties to the high-purity material. The slight amounts of impurities in technical-grade trisodium citrate appear to be unobjectionable for detergent use, and its cost-performance is significantly better than the currently available high-purity trisodium citrate. In summary, an efficient process to produce technical-grade trisodium citrate suitable for detergent use has been demonstrated.

ACKNOWLEDGMENT

The invaluable collaborations of N. E. Stahlheber in developing the technical-grade trisodium citrate process are gratefully acknowledged.

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Determination of Surfactant Mixtures in Shampoos and Detergents by HPLC

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ABSTRACT

A technique for separating 4 nonionic, 7 anionic and 4 amphoteric surfactants with n-dodecyl groups was studied by high performance liquid chromatography (HPLC) and applied to the determination of these surfactants in commercial shampoos and household detergents. Conditions used for the separation were: column packing and size, TSK-LS 410 (5μ) and 6 mm i.d. × 500 mm (2 connected, 250 mm columns); mobile phase, water/methanol (25/75, v/v) containing 0.25 M sodium perchlorate adjusted to pH 2.5 with phosphoric acid; column temp., 50 C; detector, RI. Surfactants in shampoos and detergents were clearly distinguished from each other and determined without column chromatographic pretreatment, e.g., ion-exchange chromatography.

INTRODUCTION

Commercial shampoos and household detergents usually consist of different ionic surfactants, and general properties of these commercial products depend on the combination of surfactants. A combination of fatty acid diethanolamides and sodium alkylsulfates or polyoxyethylene (POE) sodium alkylsulfates has been most widely used. Recently, other surfactants, e.g., alkyldimethylamino acetic acid betaine, sodium N-acyl-N-glutamates, alkyldimethylamine oxide and so forth, have often been used in these products. These surfactants are formulated in the products in small amounts, but strongly affect the properties.

Thin layer chromatography (TLC) (1,2), ion-exchange chromatography (3,4), salting-out chromatography (5) and other column chromatographies (6,7) have been used to separate and determine surfactants in commercial shampoos and household detergents. However, TLC is not suitable for quantitative analysis and column chromatographic techniques often take a long time to analyze.

In recent years, several papers (8-10) have been published on the separation of surfactants by means of high performance liquid chromatography (HPLC). In these papers, however, the emphasis is on the separation of individual surfactant homologs. Parris (11) successfully separated a combination of long-chain fatty acids; weakly anionic surfactant, sulfopropylated-type amphoteric surfactant and long-chain quaternary ammonium chloride; cationic surfactant with a combination of ion-suppression and ion-pair technique by using acetic acid and sodium dodecylbenzenesulfonate. However, strongly anionic surfactants, e.g., sodium alkylsulfate, are not applicable to the technique developed by Parris because they are not suppressed in an acid medium, as described in our previous papers (12,13), and are not ion-paired with an anionic counterion, e.g., sodium dodecylbenzenesulfonate. As sodium alkyl sulfate is the surfactant most widely used in commercial shampoos and household detergents, Parris's technique is not suitable for separating surfactant mixtures in these commercial products.

We have been studying the separation of surfactant homologs by HPLC using reversed-phase packing containing an octadecyl silane group chemically bonded to silica gel (ODS/Silica) (12-14). In our previous paper (14), nonionic, anionic, cationic and amphoteric surfactants were separated into their individual homologs and simultaneously distinguished from each other with a mixture of methanol, water, sodium perchlorate ($NaClO_4$) and phosphoric acid as the mobile phase.

In order to develop a rapid analytical method, the technique described in the previous paper (14) was applied to the determination of individual surfactant in commercial shampoos and household detergents that usually contain nonionic, anionic and amphoteric surfactants. Although the

surfactants in commercial products have the lipophilic group distribution, their main alkyl groups are generally n-dodecyl groups. n-Dodecyl derivatives, therefore, were chosen as the components to be determined in this study. Consequently, 4 nonionic, 7 anionic and 4 amphoteric surfactants with n-dodecyl groups were clearly distinguished from each other and rapidly determined without complicated column chromatographic pretreatment, e.g., ion-exchange chromatography.

EXPERIMENTAL PROCEDURES

Materials

Fifteen standard surfactants with n-dodecyl groups were used in this study. Their chemical structures and symbolic names in this study are illustrated in Table I. SDS, SNDG, SDMT, DDAB and SDAP were all the same grade used in the previous studies (12-14). DSS and SD were special-grade reagents (Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan) and were used without further purification. SDOS, DDAO and DADB were obtained from Nikko Chemical Co., Ltd. (Tokyo, Japan), Japan Oil and Fats Co., Ltd. (Tokyo, Japan) and TH. Goldschmidt (Essen, West Germany), respectively, and were used without further purification. UCIB were prepared by extraction with 2-propanol from the one obtained through Toho Chemical Ind. Co. (Tokyo, Japan). DDA, DMA and DPA were prepared and purified from their corresponding commercial coconut fatty acid derivatives by the preparative chromatographic techniques described in Sample Preparation. All solvents were of analytical reagent grade, shampoos and household detergents were the ones commercially available on the market.

TABLE I

Chemical Structures of Surfactants Studied

Surfactant name	Symbolic name	Chemical structure
Nonionic surfactant		
Dodecanoyldiethanolamide	DDA	$C_{11}H_{23}CON(CH_2CH_2OH)_2$
Dodecanoylmonoethanolamide	DMA	$C_{11}H_{23}CONHCH_2CH_2OH$
Dodecanoylmono-2-propanolamide	DPA	$C_{11}H_{23}CONHCH_2CH(CH_3)OH$
Dimethyldodecylamineoxide	DDAO	$C_{12}H_{25}N(CH_3)_2\rightarrow O$
Anionic surfactant		
Sodium 1-dodecanesulfonate	DSS	$C_{12}H_{25}SO_3Na$
Sodium dodecylsulfate	SDS	$C_{12}H_{25}OSO_3Na$
Sodium N-dodecanoyl-N-methyl taurate	SDMT	$C_{11}H_{23}CON(CH_3)CH_2CH_2SO_3Na$
Sodium N-dodecanoylsarcosinate	SNDS	$C_{11}H_{23}CON(CH_3)CH_2COONa$
Sodium N-dodecanoyl-L-glutamate	SNDG	$C_{11}H_{23}NHCH(CH_2CH_2COONa)COOH$
Sodium dodecanoate	SD	$C_{11}H_{23}COONa$
Sodium di-2-ethylhexylsulfosuccinate	SDOS	$NaO_3SCH(CH_2COOC_8H_{17})COOC_8H_{17}$
Amphoteric surfactant		
Dodecyldimethylaminoacetic acid betaine	DDAB	$C_{12}H_{25}-N^+(CH_3)_2-CH_2COO^-$
2-Undecyl-1-hydroxyethyl imidazolinium betaine	UCIB	$C_{11}H_{23}-C=N-CH_2-N^+-CH_2-NaOOC_2HC(CH_2CH_2OH)$
Sodium dodecylaminopropionate	SDAP	$C_{12}H_{25}NHCH_2CH_2COONa$
Dodecanoylamidopropyl-N,N-dimethylaminoacetic acid betaine	DADB	$C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$

Sample Preparation

DDA. Ca. 5 g of commercial coconut fatty acid diethanolamides were dissolved in 20 mL water/methanol (15:85, v/v) and injected into a Model PrepLC System 500 (Waters Assoc., Milford, MA). The conditions are described in Preparatory Separation. As shown in Figure 1a, coconut fatty acid diethanolamides were fractionated into 5 components. Vertical lines indicate the start and end of the fractions collected. Although n-dodecanoyldiethanolamide (DDA) was collected in fraction 2, fraction 2 was contaminated with a little decanoyl- and tetradecanoyldiethanolamide. To remove these components, fraction 2 was refractionated as shown in Figure 1b with the PrepLC System 500; the shadowed part was collected. As shown in Figure 1c, the refractionated materials had purities greater than 99% as dodecanoyldiethanolamide. In this study, refractionated materials were used as the standard material. Other fractions (1, 3, 4 and 5), were purified with the same procedures used with fraction 2. As shown in Figure 1c, their purities were all greater than 99%.

DMA and DPA. DMA and DPA were prepared and purified from their corresponding commercial coconut fatty acid derivatives with the same procedures as described for DDA. Their purities were also greater than 99%.

Preparatory Separation

The PrepLC System 500 was equipped with a Waters Model PerpPAK/C_{18} column (57 mm i.d. × 300 mm) and a Waters Model R401 differential refractometer monitor. The mobile phase was a mixture of water/methanol (15:85, v/v) and the flow rate was set at 300 mL/min. For the analysis of the fractionated materials, the following instrumentation and conditions were used. The HPLC system was composed of a Waters Model 6000A pump, a Waters Model U6K septumless loop injector, a Model SPD-1 variable wavelength detector (Shimazu Corp., Kyoto, Japan). The SPD-1 detector was operated at 210 nm. A chromatographic column (stainless steel, 6 mm i.d. × 250 mm) was packed with TSK Gel LS-410 (5μ, spherically shaped ODS/Silica; Toyo Soda Manufacturing Co., Ltd., Tokyo, Japan) according to the packing technique described in the previous paper (14). The mobile phase was a mixture of water/methanol (15:85, v/v), and the flow rate was set at 1.5 mL/min. The column temperature was maintained at 50 C with warm water circulating through the jacket.

Analytical Separation

The HPLC system was composed of the 6000A pump, the U6K injector and the R401 detector to detect all the surfactants employed in this study. Chromatograms obtained from the R401 detector were recorded with a Waters Model 730 data module. Two chromatographic columns (stainless steel, 6 mm i.d. × 250 mm) were connected with a stainless-steel tube (0.23 mm i.d. × 50 mm). The columns were packed with TSK Gel LS-410. All experiments were done at 50 C under isocratic conditions. The flow rate of the mobile phase was set at 1.5 mL/min. All the standard samples were prepared as 0.2-1.0% methanol solutions, and 30 μL was injected into the HPLC column. Capacity factors (k′) and number of theoretical plates (N) were evaluated from the chromatograms as follows:

$$k' = (t - t_0)/t_0, \quad N = 16\,(t/w)^2,$$

where t is retention time of a peak, t_0 is hold-up time and w is peak width. The mobile phase hold-up times were measured by injecting methanol and the retention time of the peak at the front was taken as t_0.

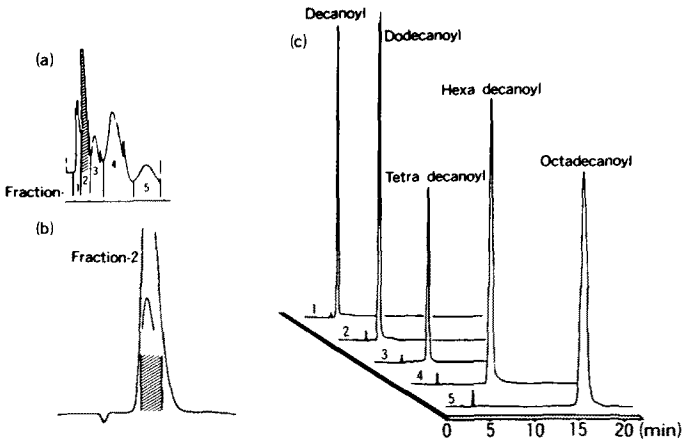

FIG. 1. Purification of DDA from commercial coconut fatty acid diethanolamide; (a) and (b) are preparative liquid chromatograms; (c) is the final chromatogram of purified materials. (LS-410, 6 mm i.d. × 250 mm, water/methanol [15:85], 1.5 mL/min, UV [210 nm]).

Sample solutions of commercial shampoos and household detergents were prepared as follows: ca. 4 g of the commercial products was accurately weighed into a 100 mL beaker and heated in a steam bath for 2 hr to remove water. The residues were dispersed to 10 mL water/methanol (25:75, v/v), and transferred to a 10 mL centrifugal tube. Then, the sample solution was centrifuged for 10 min. The supernatant liquid was decanted to a 25 mL measuring flask. With the other 10 mL of water/methanol (25:75, v/v), the procedure was repeated. The supernatant liquid was accurately diluted to 25 mL with methanol. Thirty μL of this solution was injected into the HPLC column, and a chromatogram was obtained under the following mobile phase conditions: water/methanol (25:75, v/v) containing 0.25 M $NaClO_4$, pH adjusted to 2.5 with phosphoric acid.

RESULTS AND DISCUSSION

Separation of 15 Surfactants with n-Dodecyl Groups

Our previous study (14) revealed that $NaClO_4$ concentrations, mobile phase pH and the water content in the mobile phase affected the separation of surfactant homologs. In this study, the results indicate that column length also greatly affects the separation. These factors make optimal conditions necessary.

The separation of 2 components is generally represented as follows:

$$R_S = (1/4)(\alpha - 1)\, N^{1/2}\, [k_2'/(k_2' + 1)],$$

where α stands for the relative retention, N is the number of theoretical plates and subscript 2 represents the second component. N generally increased with increasing column length in the same mobile phase condition and column packings. Table II shows the effect of the column length on k′ and N values of several surfactants. Doubling the column length, the N values of the respective surfactants increased to 2-3 times, whereas the k′ values did not vary. From the above equation, the increase of N values resulted in improved separation. As shown in Figure 2, 4 amphoteric surfactants were separated in a 500 mm column but not separated in a 250 mm column. A 3-column connection produced high pressure over 4500 psi. As operation at high pressure generally shortened the column life, column length

TABLE II

Effect of Column Length on K' and N

Surfactant	250 mm[b]		500 mm[a,b]	
	K'	N	K'	N
DMA	4.05	4316	4.12	13966
DDA	3.05	5529	3.60	11774
SDS	5.16	3882	5.32	12519
DSS	4.48	5893	4.62	17580
DDAB	2.23	3463	2.27	13438
SDAP	2.89	5011	2.93	13580

[a]Connected 2 250 mm columns.
[b]Hold-up time(t_0)—3.0 min and 6.0 min for 250 mm and 500 mm column, respectively.

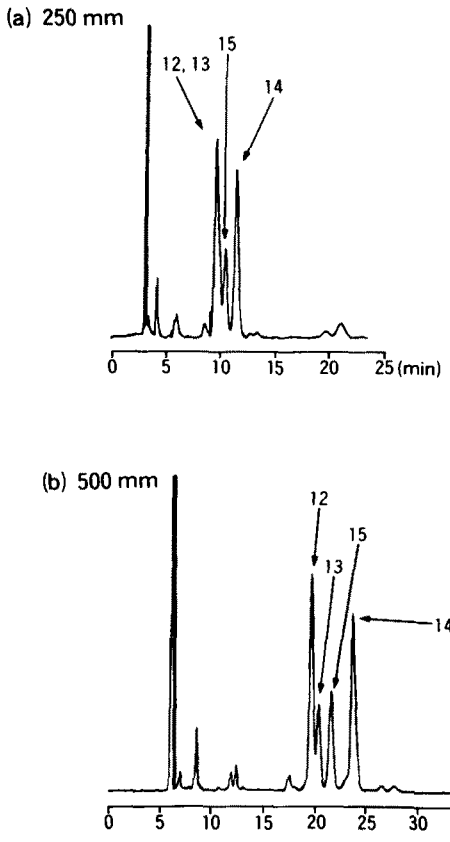

FIG. 2. Effect of column length on separation of 4 amphoteric surfactants. Numbers on peaks correspond to those in Table I (water/methanol [25:75] containing 1.0 M $NaClO_4$ and adjusted to pH 2.5 with phosphoric acid, 1.5 mL/min).

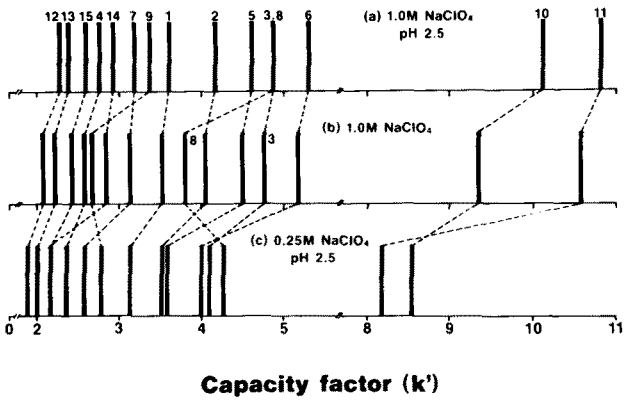

FIG. 3. Capacity factors of 15 surfactants at 3 conditions. Numbers correspond to those in Table I.

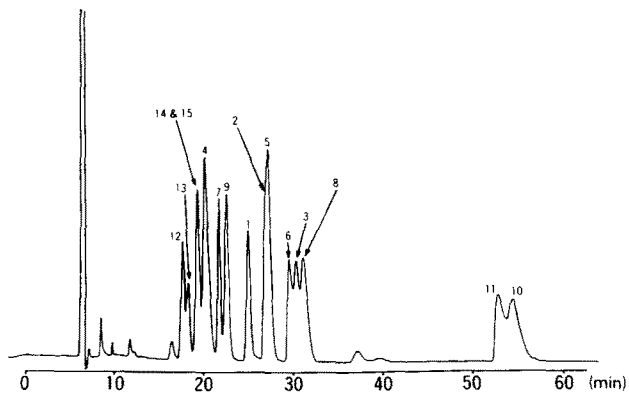

FIG. 4. Separation of 15 surfactants with n-dodecyl groups. Numbers on peaks correspond to those in Table I (6 mm i.d. × 500 mm, water/methanol [25:75] containing 0.25 M $NaClO_4$ and adjusted to pH 2.5 with phosphoric acid, 1.5 mL/min.

was set at 500 mm (2 connected 250 mm columns) in this study (operating pressure—2500 psi).

The relative retention, α, is varied by changing the combination of the mobile phase and the stationary phase. Drastic change of α would not be expected, because use of ODS/Silica as the stationary phase was an earlier premise in this study. The effect of α was not discussed in detail.

Values for k' are varied by changing solvent strength, that is, $NaClO_4$ concentrations, mobile phase pH and water content in the mobile phase. As reported in the previous paper (14), $NaClO_4$ concentrations and mobile phase pH greatly affected the k' values of ionic surfactants. In this study, therefore, 3 combinations of $NaClO_4$ concentrations and the mobile phase pH were examined. A volume ratio of water to methanol was set at 25:75 as a first step in establishing the analytical times of the combinations. The 3 combinations were: (a) 1.0 M/L $NaClO_4$, pH 2.5 (adjusted with phosphoric acid); (b) 1.0 M/L $NaClO_4$; (c) 0.25 M/L $NaClO_4$, pH 2.5 (adjusted with phosphoric acid). The k' values of 15 standard surfactants are summarized in Figure 3. In the case of *a*, almost all the surfactants were distinguished from each other. However, DPA and SNDS had the same k' values and were not separated. In the case of *b*, 15 surfactants were clearly chromatographed. However, SD and SDOS had k' values that were too large and the analytical time was over 100 min, as in the case of *a*. In *c*, SDAP and DADB had the same k' values, whereas other surfactants were clearly separated and analytical time was within 60 min. As described later, SDAP and DADB were not found in 50 commercial products and condition *c* was finally used as the mobile phase because of the shorter analytical time. A chromatogram of surfactant mixtures under condition *c* is shown in Figure 4.

Table III shows reproducibility of retention times under condition *c*. Good reproducibility was obtained, and the percentage of Cv was found to be ca. 0.3-0.4%, except for the 1.16% obtained from SDMT.

We concluded that all the surfactants except SDAP and DADB were qualitatively identified with condition *c*. As

TABLE III

Reproducibility of Retention Time

Surfactant	X (min)	Cv(%)[a]	n[b]
DDA	24.35	0.27	9
DMA	26.16	0.28	6
DPA	29.81	0.28	5
DDAO	19.64	0.30	4
SDS	28.64	0.66	6
DSS	26.61	0.16	4
SDMT	20.92	1.16	6
SNDS	30.45	0.23	4
SNDG	21.97	0.37	5
SD	53.22	0.16	4
SDOS	51.47	0.33	4
DDAB	17.14	0.44	9
UCIB	17.71	0.44	6
SDAP	18.64	0.37	5
DADB	18.65	0.40	5

[a]Coefficient of variation.
[b]Number of measurement.

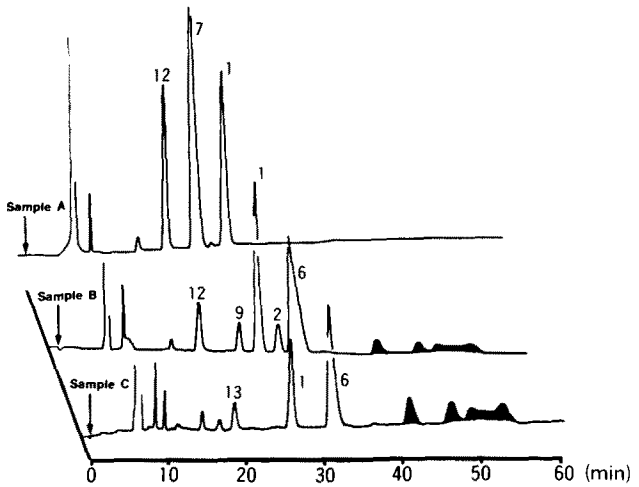

FIG. 5. Typical chromatograms of commercial shampoos and household detergents. Numbers on peaks correspond to those in Table I. Mobile phase condition is the same as in Figure 3.

described above, condition *b* was useful in separating SDAP and DADB although the analytical time was over 100 min.

Analysis of Surfactants in Commercial Products

Fifty commercial shampoos and household detergents were analyzed using the developed method. Surfactants contained in the samples were identified by comparing the retention times detected from the samples with those of the standard surfactants shown in Table III. The retention times of most peaks agreed with those of standard surfactants with a few exceptions. From the analytical results on 50 commercial products, the following observations were obtained: (a) DDM, SDS and POE-SDS were used in most samples; (b) DDAB, UCIB, SNDG, SDMT, DMA and DDAO were used as the additional surfactants; (c) SDAP and DADB were not found in the 50 commercial products tested. Three typical chromatograms are shown in Figure 5. Unresolved peaks shadowed in Figure 5 were attributed to POE-SDS. This was confirmed by comparing the elution patterns detected from the samples with those of standard POE-SDS. The unresolved peaks would be attributed to the ethyleneoxide distributions of POE-SDS. These peaks did not interfere with the identification of other surfactants employed in this study.

Calibration curves were made for 8 surfactants (DDA, DMA, DDAO, SDS, SNDG, SDMT, DDAB and UCIB) that are often used in commercial products. Injection volumes were set at 30 μL, as with the commercial products. Their peak heights were directly proportional to the concentration in the range 0-10 mg/mL.

Table IV shows the analytical results on recovery rates of 5 surfactants from shampoos. Each standard surfactant (ca. 100 mg) was accurately added to commercial shampoos (ca. 4 g), which did not contain a corresponding surfactant. They were extracted and analyzed using the procedures described above. By using peak height and the corresponding calibration curve, their recovery rate was calculated with the following equation:

$$\text{Recovery rate (\%)} = [(A \times 25)/B] \times 100,$$

where A is the concentration (mg/mL) obtained from the corresponding calibration curve, 25 is the volume (mL) of solution and B is the added weight (mg). As indicated in Table IV, their recovery rates were more than 95% and the

TABLE IV

Recovery Rate of Typical Surfactants

Surfactant	Added (mg)	Recovery rate[a] (%)	Cv(%)[b]
SDS	100.0	99.0	2.1
SDMT	100.7	99.2	2.8
UCIB	100.2	96.2	1.6
DDA	102.5	98.5	2.4
DDAB	100.4	95.6	2.7

[a]Taken as the average of 5 replicate analyses.
[b]Coefficient of variation.

percentage of Cv was ca. 2.5. From these analytical results, we concluded that surfactants with n-dodecyl groups in commercial shampoos and household detergents could be determined with a combination of an easy extraction procedure and HPLC analysis.

Using the peak height of each surfactant and the corresponding calibration curve, surfactants with n-dodecyl groups were determined. The following equation was used:

$$\text{Surfactant (\%)} = [(A \times 25)/(B \times 1000)] \times 100,$$

where A is the concentration (mg/mL) in the sample solution, 25 is the volume (mL) of solution, B is the sample weight (g) and 1000 is the constant. Several analytical results are indicated in Table V. Although many combination of nonionic, anionic and amphoteric surfactants were used in commercial shampoos and household detergents, they were rapidly identified and accurately determined using the method described in this paper.

The determination results on surfactants with n-dodecyl groups would not represent the total surfactant because surfactants used in commercial products generally had the distribution of lipophilic groups. This disadvantage of the developed method will be solved in the near future.

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TABLE V

Analytical Results of Surfactants in Commercial Shampoos and Household Detergents

Sample	DMA (%)	DDA (%)	DDAO (%)	SDS (%)	SDMT (%)	SNDG (%)	DDAB (%)	UCIB (%)
1	–	0.98	–	15.1	–	–	1.78	–
2	–	0.99	–	14.9	–	–	1.16	–
3	–	2.05	13.3	–	–	–	–	–
4	–	2.81	1.2	–	–	–	–	–
5	–	4.23	–	–	–	–	1.37	–
6	–	5.81	–	–	29.0	–	8.90	–
7	0.95	4.80	–	9.51	–	0.90	1.35	–
8	–	2.51	–	8.65	–	–	–	1.65

Taken as the average of 2 replicate analyses.

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Letter to the Editor

Sirs:

The use of ethanol in gasoline as an octane enhancer is becoming widespread and well established. However, anhydrous ethanol (200 proof) is required for the range of storage and operating conditions normally encountered. The search for methods or materials for eliminating water separation when using moist ethanol continues unabated.

In the course of studying a variety of potential uses for a methyl glucoside-based emulsifier/surfactant, we found that it is capable of producing clear mixtures of unleaded gasoline and 95% ethanol. Typical synthesis of this emulsifier follows. The reaction is carried out in a 1 L, 3 neck round-bottom flask equipped with N_2 sparge tube, mechanical stirrer (glass blade), thermometer, H_2O-cooled condenser and Dean-Stark trap. To the flask is added 500 g (0.568 mol) neutralized, bleached soy oil and 0.25 g Li_2CO_3. After heating to 286 C, three 33.3 g portions of α-methyl glucoside (total: 0.515 mol) are added at 10 min intervals and heated at 286-296 C until 1 volume of the reaction mixture is soluble in 3 volumes of methanol (1.0 hr). The product has a Gardner color of 11 and a Gardner-Holt viscosity of N.

No exhaustive study was made of either this product or varied gasoline-alcohol combinations. However, this alcoholysis product gave a clear solution or microemulsion when combined with 90 mL unleaded gasoline and 10 mL 190 proof ethanol as indicated.

Description	Results at 23 C
5.0 g Product added	slightly cloudy
After 15 min	clear (no water droplets visible)
After 1.0 hr	clear (no water droplets visible)
After 24 hr	clear (no water droplets visible)
After reshaking	clear (no water droplets visible)

A glycerol/soy oil alcoholysis product, made according to a similar procedure using 0.5 mol oil/1.16 mol glycerol, gave only a cloudy solution plus water droplets with the identical alcohol/gasoline blend.

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