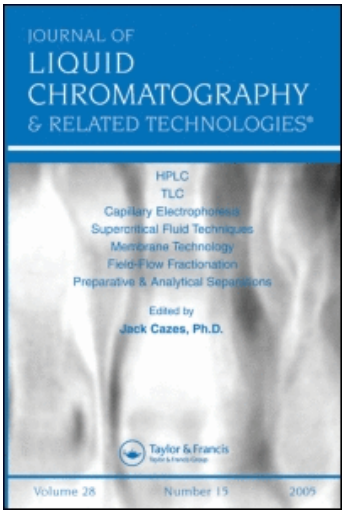

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

The Semi-Quantitative Identification of Hydrophobes in Normal Alcohol Ethoxylates by Hydriodic Acid Cleavage and Reversed-Phase HPLC Analysis with UV Detection

Matthew Benning[a]; H. Locke[a]; R. Ianniello[a]
[a] GAF Chemicals Corporation, Wayne, New Jersey

To cite this Article Benning, Matthew , Locke, H. and Ianniello, R.(1989) 'The Semi-Quantitative Identification of Hydrophobes in Normal Alcohol Ethoxylates by Hydriodic Acid Cleavage and Reversed-Phase HPLC Analysis with UV Detection', Journal of Liquid Chromatography & Related Technologies, 12: 5, 757 — 770
To link to this Article: DOI: 10.1080/01483918908049205
URL: http://dx.doi.org/10.1080/01483918908049205

JOURNAL OF LIQUID CHROMATOGRAPHY, 12(5), 757-770 (1989)

THE SEMI-QUANTITATIVE IDENTIFICATION OF HYDROPHOBES IN NORMAL ALCOHOL ETHOXYLATES BY HYDRIODIC ACID CLEAVAGE AND REVERSED-PHASE HPLC ANALYSIS WITH UV DETECTION

MATTHEW BENNING, H. LOCKE,
AND R. IANNIELLO
GAF Chemicals Corporation
1361 Alps Road
Wayne, New Jersey 07470

ABSTRACT

A method is described for the quantitative reversed-phase HPLC analysis of n-alkyl iodides obtained from HI cleavage of linear alcohol ethoxylated surfactants. The method is an improvement over previous techniques in that the detection is both iodide specific and is demonstrated for carbon chain lengths from 1 to 18.

INTRODUCTION

The four characteristics of a surfactant that need to be specified for unique identification are hydrophile, hydrophobe, functional groups and molecular weight (distribution). As a result of the complex variations that exist in commercial products, no single technique has dominated the analysis of surfactants with analysts making use of complementary techniques

to characterize products. Isolation of a surfactant is typically performed by column chromatography and general classification of the separated components can be made by spectroscopic techniques, primarily NMR, UV/VIS and IR spectroscopies. In ethoxylated surfactants the hydrophobe moiety is often not a single species but a mixture of homologs that cannot be differentiated by NMR. Additionally, an accurate ethylene oxide content cannot be assigned by NMR without an average hydrophobe carbon number (needed as an integration reference).

A wet technique for the determination of ethylene oxide content by cleavage of the polyether with hydriodic acid has been described by Siggia (1,2) and has been in use for many years in surfactant analysis. A polyether surfactant is refluxed in hydriodic acid-water azeotrope to form the normal iodide of the hydrophobe. The hydrophile is cleaved to form the corresponding iodides and if ethylene oxide is present the unstable 1,2 iodides are produced decomposing to liberate iodine and ethane.

$$C_nH_{2n+1}\text{-}(OCH_2CH_2)_x\text{-}OH + (4x+1)\ HI \rightarrow$$

$$C_nH_{2n+1}I + (x+1)\ H_2O + (x)\ I\text{-}CH_2CH_2\text{-}I + (2x)\ HI \rightarrow$$

$$C_nH_{2n+1}I + (x+1)\ H_2O + (x)\ CH_3CH_3 + (2x)\ I_2$$

The reactivity of n-alcohol hydrophobes towards HI was found to be sufficiently complete to merit extraction of the long chain n-alkyl iodides and GC analysis (3). In this modification,

iodides are analyzed by RP-HPLC and compared to GC results obtained by direct injection of alcohols.

MATERIALS

Reagents

Derivatization and extraction was performed using hydriodic acid aqueous azeotrope (Aldrich Chemical), HPLC grade 2-propanol (Aldrich), 20% potassium iodide (Baker Analyzed Reagent Grade) in laboratory distilled water, HPLC grade hexane (Aldrich), reagent grade anhydrous sodium sulfate (Aldrich) and nitrogen (AGL Welding). BioRad AG1-X2 hydroxide form analytical grade ion-exchange resin was used for removal of ionic interferences.

Apparatus

The derivatization was performed in a 50 ml round bottom flask with a stopcocked gas inlet arm connected to a pressure regulated nitrogen tank, a 300 mm water jacketed condenser, a 90° degree elbow, Tygon tubing, a gas scrubbing bottle and a hot plate. Extraction was performed using a Kontes selective take-off funnel, Whatman No. 41 ashless filter paper and a glass funnel. Sample cleanup was aided by the use of Baker Solid Phase Extraction 3 ml Filter Tubes hand packed with Biorad AG 1-X2 200-400 mesh hydroxide form ion-exchange resin in isopropanol and a Solid Phase Extraction Manifold (Supelco #5-7030).

Liquid Chromatograph System

An HPLC system consisting of a Kratos 430 low pressure gradient former, a Kratos 400 pump, a Kratos SF769 UV detector,

and a Rheodyne 7125 injector with a 20 ul sample loop was used for the analysis. The stationary phase consisted of a Waters uBondapak C18 Analytical Column of 30 cm length by 3.9 mm id. and an Alltech Universal 5u C18 Adsobosphere Precolumn Cartridge. Peak areas were used for quantitation and were obtained with a Shimadzu C-R4A Data Processor.

Gas Chromatographic System

A system consisting of a Hewlett Packard Model 5870 GC with a 25 m by 0.32 mm i.d. HP-1 (dimethyl silicone, 0.52 u film) column and FID was used with an injection and detector temperature of 320°C.

METHODS

Cleavage Procedure

Enough surfactant to yield approximately 100 mg of cleaved hydrophobe was weighed to the nearest 0.1 mg into the 50 ml round bottom flask and connected to the apparatus. Nitrogen flow was adjusted so that it could can be seen emanating from the sparge tube at a rate equivalent to 2 bubbles per second. After sparging the apparatus for 15 minutes, the adapter atop the Allihn condenser was removed and 10 ml of refrigerated HI was pipetted in. The system was reassembled, heat was applied, and the reaction mixture was allowed to reflux for 90 minutes then cooled to ambient temperature. After removing the top adapter and turning off the nitrogen, the inside of the condenser was washed down with 20 ml of KI solution then 15 ml

of isopropanol. Undissolved iodine, crystallized in the condenser, was washed into a 400 ml beaker by pouring the reaction mixture back through the condenser and into the beaker. A final rinse of equal amounts of KI solution and IPA cleaned up the condenser.

The alcoholic mixture was titrated to a colorless endpoint with the 2N sodium thiosulfate then neutralized with 0.5N NaOH. The reaction mixture was transferred to a selective take-off funnel and extracted three times with 75 ml hexane, each time the hexane being allowed to clarify by standing, then passed through 15 grams of anhydrous sodium sulfate. The beaker was placed under a steady stream of nitrogen to drive off the hexane and weighed. The residue was dissolved in IPA to approximate 0.2% wt. and analyzed by HPLC. An aliquot (5 ml) of this solution was passed through an activated and IPA equilibrated amine SPE column at such a rate that the eluting drops could be visually distinguished. The treated solution was analyzed by HPLC.

Chromatographic Analysis

HPLC analysis was performed using a starting mobile phase composition of 75/25 % v/v methanol/H_2O under a first order linear gradient to 50/50 % v/v methanol/isopropanol in 30 minutes with a subsequent hold for 5 minutes at a flow rate of 1.5 ml/min. UV detection was used at 252 nm. The column was equilibrated with the initial mobile phase composition for one hour each day before analysis. Additionally, whenever the

initial system back pressure rose from 150 barr to 200 barr, the precolumn cartridge was replaced in order to equilibrate column back pressure and restore the UV baseline.

GC analysis was performed by direct injection of 1 ul volumes using a 6:1 helium carrier split at an initial temperature of 100°C with a thermal gradient of 10°C/minute to 250°C on hold for 5 min.

RESULTS AND DISCUSSION

Since HPLC is a technique finding increased use in the analysis of pure and formulated surfactant products, it seemed logical to adapt the ASTM GC method (3) for hydrophobe analysis to HPLC. Limited literature references show that LC has been used for alkyl iodide analysis (4) but not for the higher carbon chain lengths typical of surfactant hydrophobes, e.g. Ziegler alcohols sold by Vista (Conoco).

The published methods used isopropanol to purge the cleavage apparatus of any iodide products and the solubility of n-alkyl iodides is such that carbon chain lengths under 20 will be eluted. A UV scan of a 0.1 weight % n-iododecane in IPA (Figure 1) shows a single maximum at 252 nm defining the detection wavelength. This wavelength corresponds to the n to σ^* transition (5).

A standard solution containing 0.1 wt. % each of 14 n-alkyl iodides was analyzed 12 times with the described LC conditions (Figure 2).

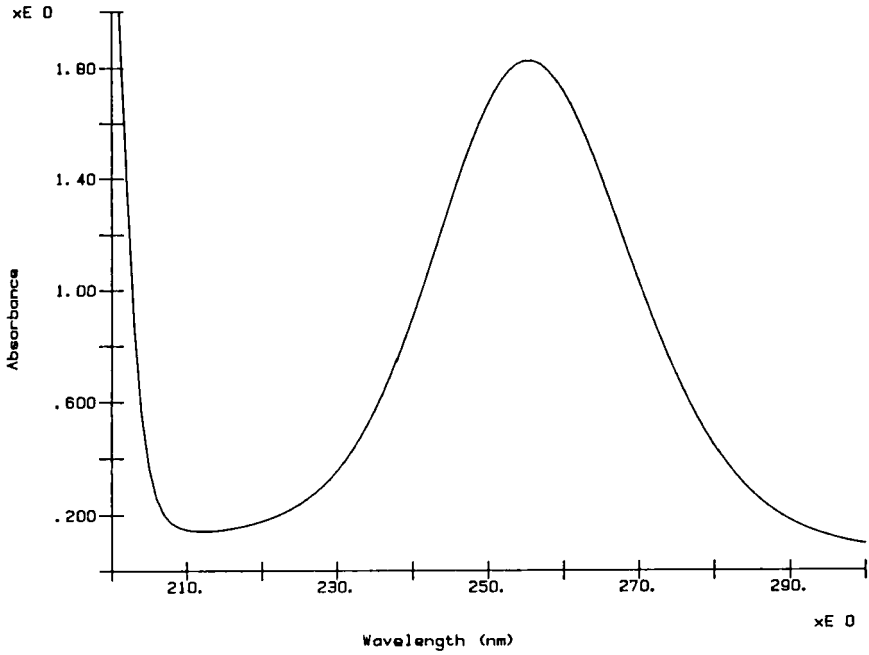

FIGURE 1 UV spectrum of 0.1 weight % n-iodododecane in isoporpanol versus isopropanol reference.

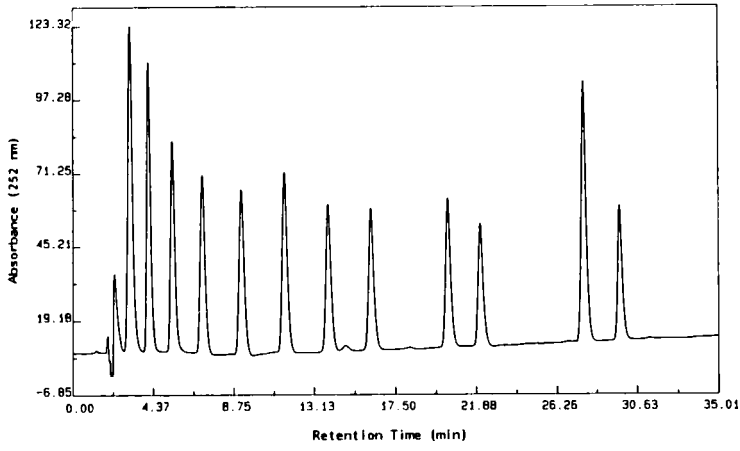

FIGURE 2 Standard solution of 0.1 weight % each of Aldrich n-alkyl iodides in isopropanol.

Replication of both retention times and integrated areas was excellent (Table I).

Factors converting integrated areas to iodide concentrations were defined by dividing the weight % iodide standard by the average integrated area. A plot of chain length versus integration factor (Figure 3) resulted in a first order linear equation with a correlation coefficient of 0.996. Elimination of the C18 factor (Aldrich C18 iodide had a technical grade purity of < 98 %) improved the value to 0.999. This equation gave refined integration factors for the standards as well as those iodides not commercially available. The iodide distribution is finally converted to a normalized alcohol distribution.

The applicability of this method is demonstrated for fatty alcohols and cross-referenced to GC analysis by direction

Table I

Chain Length	R.T. Avg	Std. Dev.	Coeff. Var. %	Int. Area	Std. Dev.	Coeff. Var. %
1	2.79	0.06	2.45	326533	37894	11.6
2	3.23	0.04	1.51	2141740	37497	1.7
3	3.80	0.06	1.61	2984550	57275	1.9
4	4.67	0.06	1.45	2816111	80102	2.8
5	7.79	0.12	1.65	2624348	29998	1.1
6	10.0	0.17	1.71	2800968	20300	0.7
7	12.4	0.19	1.56	1807945	24927	1.3
8	14.9	0.21	1.43	2038109	67274	3.3
9	17.2	0.22	1.27	1929256	22365	1.1
10	19.5	0.21	1.11	2136071	27935	1.3
11	21.5	0.21	0.99	1878702	41748	2.2
12	23.3	0.22	0.96	1887978	40571	2.1
16	28.9	0.19	0.68	2520121	47044	1.8
18	30.9	0.17	0.57	1325839	34704	2.6

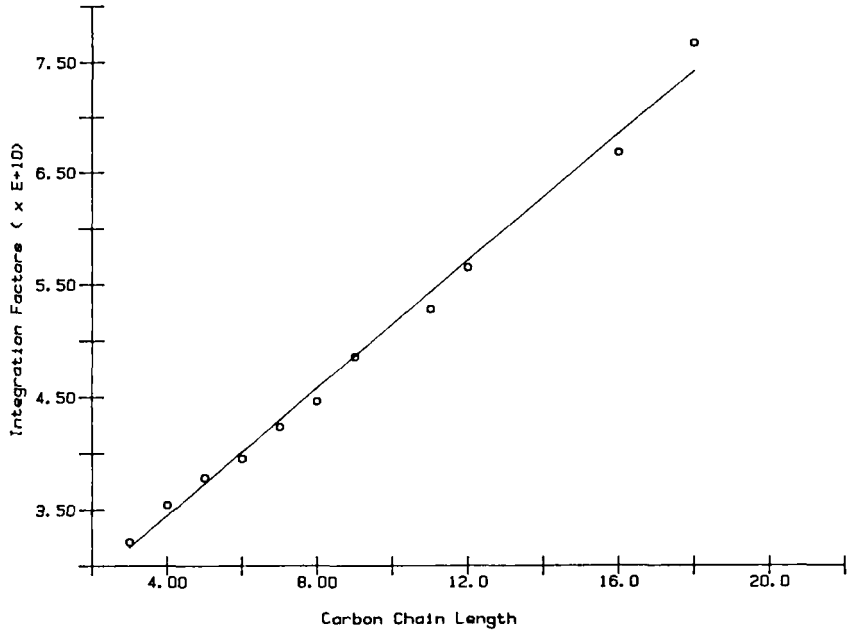

FIGURE 3 Linear regression plot defining integration factors for n-alkyl iodides (o = experimental factors).

injection. The results from analyses of three commercial hydrophobes are compared in Table II and show good agreement.

When the HPLC procedure was applied to formulated products, unexpected peaks having reproducible retention times but inconsistent intensities (varying with separate cleavages) were noticed. Analysis of a PEG 1000 (J.T. Baker) showed these same peaks were present in the cleavage extract. A simple ion-exchange procedure removed iodine and these spurious peaks (Figure 4).

Table II

Alcohol Name	HPLC Distribution	GC Distribution
Alfol 8-10	17.8 % C_8	20.3
	82.2 % C_{10}	79.7
Alfol 1214	67.3 % C_{12}	69.9
	32.7 % C_{14}	30.1
Alfol 1618	62.4 % C_{16}	62.5
	37.6 % C_{18}	37.5

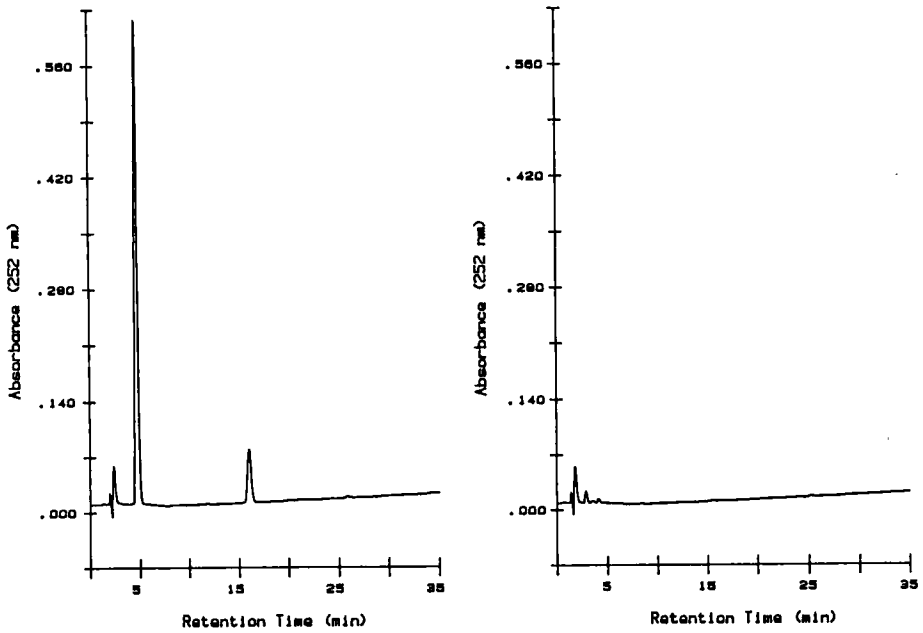

FIGURE 4 Chromatograms of PEG (MWt 1000) cleavage extracts.
Left: Before ion-exchange.
Right: After ion-exchange.

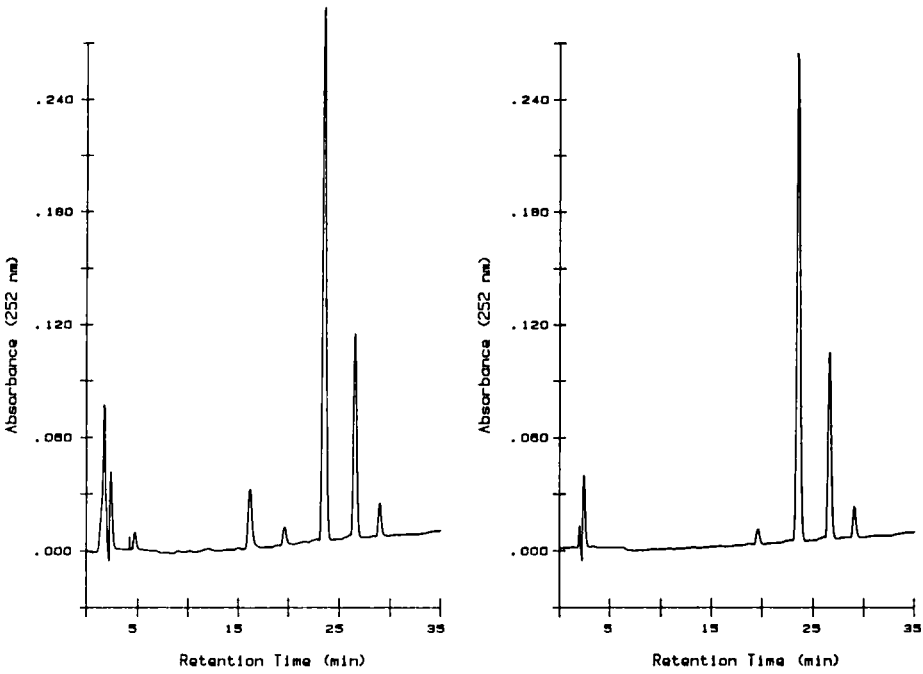

FIGURE 5 Chromatograms of sulfated ethoxylated alcohol cleavage extracts.
Left: Before ion-exchange.
Right: After ion-exchange.

A cleaved sulfated ethoxylated alcohol was analysed before and after the ion-exchange procedure (Figure 5). Peak intensities of the artifacts dropped significantly. The expected iodide peaks showed a slight drop after ion-exchange, either due to dilution from the alcohol displacing water in the resin or the conversion of iodide back to alcohol by the resin. However, normalized alcohol distributions showed little change.

To demonstrate the integrity of the hydrophobe distributions derived from nonionic and anionic surfactants with

identical hydrophobes, products from different stages of a synthesis sequence were cleaved and analysed. The hydrophobe distributions were identical (Table III).

Reproducibility was evaluated by analyzing Alfol 1412-60, an ethoxylated alcohol nonionic containing an Alfol 1412 hydrophobe (Table IV). Eight separate samples were cleaved, subjected to ion-exchange, and analyzed by HPLC. Comparison of data to the hydrophobe specifications is shown in Table IV.

The larger deviation noticed in the n-decyl and n-hexadecyl alcohols is due to the relative smallness of the peaks which had correspondingly smaller signal/noise ratios. Still, the variations noted for the cleavage procedure fall well within the production variations quoted by the manufacturer.

Table III

Surfactant Species	% C10	% C12	% C14	% C16
Alfol 1216 CO	0.52	69.01	24.85	5.62
Alfol 1216 + 50 moles EO	0.52	68.24	25.40	5.84
Alfol 1216 + 50 moles EO + $SO_4^{(-1)}/NH_4^{(+1)}$	0.42	68.19	25.95	5.43
GC of Alfol 1216 CO	0.50	69.33	24.67	5.50

Table IV

Alcohol	Mean %	Std Dev	RSD %	Manufacturer Specs %
$n\text{-}C_{10}$	1.81	0.24	13.24	2.0 max
$n\text{-}C_{12}$	37.16	1.03	2.77	38.0 ± 4
$n\text{-}C_{14}$	59.12	1.13	1.91	59.0 ± 4
$n\text{-}C_{16}$	1.91	0.37	19.44	5.0 max

The HPLC conditions were cursorily evaluated for branched alcohol hydrophobe types. Peak widths and retention times for branched hydrophobes were unique with respect to one another, however these peaks can overlap those of the normal alcohols, making simultaneous detection dependent on the species present.

In addition, the cleavage and HPLC conditions were applied to alkylphenol ethoxylates. The resulting UV absorbing alkyl iodides, aromatic iodides and aromatic species were not resolved from one another. Thus the procedure cannot be applied for these compounds without substantial modification.

CONCLUSIONS

The HPLC analysis of cleaved alcohol ethoxylates has shown to give comparable results to GC using the iodide specificity of UV detection. The specificity of the HPLC method for alkyl iodides is particularly advantageous, compared to GC/FID, due to the non-selective detection of unknown fragments occasionally observed by GC. The stability of the external standard method used for HPLC is a decided advantage over the internal standards required by GC (4). Accuracy and precision are of sufficient quality to make this procedure suitable for both quality control of alcohol ethoxylates as well as identification of unknown related nonionic and anionic types.

REFERENCES

1. Siggia, S., Starke, A., Garis, J. and Stahl, C., Determination of Oxyalkene Groups in Glycols and Glycol and Polyglycol Ethers and Esters, Analytical Chemistry, 30, 115, 1958.

2. Siggia, S., Quantitative Analysis via Functional Groups, 3rd Edition; John Wiley, New York, 1963.

3. ASTM D12.12.38, Task Group Communique from K.F. Guin dated July 13, 1979.

4. Dumont, E., HPLC for Selective Alkoxyl Group Determination, Fresenius Z. Anal. Chem. 295, 21, 1979.

5. Gordon, A., Ford, R., The Chemists Companion: A Handbook of Practical Data, Techniques, and References, John Wiley, New York 1972.