Separation and identification of sulfurized alkylphenols in oil by high-performance liquid chromatography with evaporative light scattering and mass spectrometric detection

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ABSTRACT

Sulfurized alkylphenols, intermediates for the production of detergents, were separated from undesired reaction side products and base oil on a γ-cyclobond II column by high-performance liquid chromatography (HPLC) with evaporative light scattering detection (ELSD), and then identified by direct electron exposure mass spectrometry techniques. This technique was successful in monitoring the quality of the alkylphenols prior to producing the final product. ELSD proved to be superior over other conventional HPLC detection methods in the analysis of sulfurized alkylphenols.

INTRODUCTION

Various types of detergent additives such as alkoxides, sulfonates, phenates and carboxylates have been used in lubricating oils in order to reduce or remove deposits formed by the burning of fuel. In addition, these detergent additives may also function as antioxidants and antiwear agents. The preparation of overbased detergents, in which a large amount of metal base is incorporated, have become important in the petroleum industry [1–4]. During the combustion process, the formation of harmful acidic components has led to the degradation of the lubricating oil and to the corrosion of metal bearings and engine parts. For this reason, overbased detergents have been employed to neutralize these acidic by-products.

Recently, the use of neutralized and overbased phenate detergents has increased since, in addition to acting as detergents, they exhibit increased high-temperature stability properties [5]. This is an important feature since modern automobile engines work harder and generate higher temperatures. The physical characteristics of these detergent additives are highly dependent upon the quality of sulfurized alkylphenols, the reaction intermediates. Specifically, sulfurized dodecylphenols have been used in the production of phenate detergents [6–9].

The analysis of detergent in lubricating oils by high-performance liquid chromatography (HPLC) has been well documented in the literature [10–17]. However,

these analyses need to be extended to the reaction intermediates. The composition of sulfurized alkylphenols has been previously determined by a combination of gas chromatography (GC) and polarography [18] and by mass spectral techniques in conjunction with mathematical processing [19].

The use of evaporative light scattering detection (ELSD), an improved universal detection method for HPLC, has been investigated because of its increased sensitivity, stability from ambient temperature effects and operation with multiple solvent gradients [20–22]. This detector is an excellent candidate for the analysis of sulfurized alkylphenols due to its success in the determination of coal derivatives [23], heavy oil petroleum fractions [24], and surfactant additives [25].

This paper reports the development of an HPLC method that allows for routine determination of sulfurized dodecylphenols in oil. In addition, undesirable reaction side products that can reduce the quality of the detergent additive can be easily monitored.

EXPERIMENTAL

Apparatus

HPLC was performed on a Waters chromatography system (Waters, Milford, MA, USA) equipped with two 590 programmable pumps, a 480 automated gradient controller, a U6K injector and a 490 programmable UV detector. An ELS detector (Varex Corporation, Rockville, MD, USA) was connected in series after the UV detector. The chromatographic data were processed using the PE Nelson 2600 chromatography system (PE Nelson, Cupertino, CA, USA).

Materials

Hexane and unstabilized tetrahydrofuran (THF) (EM Science, Gibbstown, NJ, USA) were of HPLC-reagent grade. The mobile phase was continuously degassed by dry-grade helium (Linde, Danbury, CT, USA).

Chromatographic procedure

The Waters modular HPLC system was set up for gradient elution with the ELS detector connected in series after the UV detector. The solvents were thoroughly degased with helium and the system allowed to equilibriate for at least 20 min. The gradient program used to elute the components is shown in Table I.

The separation was performed on a γ-cyclobond II column (Astec, Whipanny, NJ, USA, 25 cm × 4.6 mm I.D., 5-μm spherical particle size) which can be thermally controlled by a column heater or some insulating wrap. This column was capable of separating sample into oil, sulfurized dodecylphenol, undesirable side products and unreacted material.

Upon equilibration, 10 μl of a 2.0% (w/v) sample in hexane was injected into the HPLC system. All samples were filtered through a 0.45-μm Millex-HV filter (Millipore, Bedford, MA, USA).

Each sample component was collected using 1-ml conical sample vials (Alltech, Deerfield, IL, USA) for further analysis by mass spectrometry (MS).

TABLE I

GRADIENT ELUTION PROGRAM FOR THE SEPARATION OF SULFURIZED ALKYLPHE-NOLS

Time (min)	Flow (ml/min)	Hexane (%)	Tetra-hydrofuran (%)	Curve[a]
Initial	1	70	30	–
2	1	70	30	7
3	1	50	50	7
4	1	50	50	6
6	1	0	100	6
9	1	0	100	6
12	1	70	30	6

[a] Curves are generated by the automated gradient controller (AGC).

HPLC detection

The sample components were monitored by the UV detector (set at 280 nm), then by ELSD. The operating conditions for ELSD were optimized for sensitivity and baseline stability by adjusting the drift tube temperature and the carrier gas flow. The best detector response was achieved at an exhaust temperature of approximately 55°C and a nitrogen flow of 12 p.s.i. The range was set at 10×.

HPLC RESULTS AND DISCUSSION

Cyclodextrin bonded phases

The use of cyclodextrin stationary phases for HPLC has gained increased attention due to their versatility in normal and reversed-phase modes and their ability to form inclusion complexes to effect a variety of chemical separations [26–28]. Cyclobond columns are packed with silica gel material which is covalently bonded to the cyclodextrin molecules via a stable, non-hydrolytic, non-nitrogen-containing silane linkage [29].

The α-, β- and γ-cyclodextrins are cyclic oligosaccharides that contain 6, 7 or 8 glucopyranose units, respectively, and are arranged in the shape of a hollow truncated cone. The interior cavity is hydrophobic, being primarily comprised of methylene and 1,4-glucoside linkages. The exterior, on the other hand, is hydrophilic due to the primary and secondary hydroxyl groups [30].

The most unique characteristic of cyclodextrins is their ability to selectively form inclusion complexes with a variety of organic and inorganic molecules within their hydrophobic cavity [29]. In addition to the size and shape of the analyte, the mechanism of separation is dependent upon other factors such as dipole–dipole interactions and hydrogen bonding.

ELSD

The principle of operation involves converting the column effluent into a very fine mist after passing through a nebulizer. A stream of carrier gas then directs this

mist into a temperature-controlled drift tube where the mobile phase is vaporized leaving the fine particles of interest in the carrier gas. These sample particles are then passed through the path of a laser light source and the light that is scattered is detected by a photodetector system.

ELSD is an improved universal detection method compared to the widely used refractive index (RI) detection method. It is capable of operating free from ambient temperature effects and with multiple solvent gradients without detectable baseline drift. The detector response is a function of the mass of the solute passing through the detector, unlike most HPLC detectors whose response is based upon the concentration of the solute. These characteristics make ELSD and excellent candidate over RI detection for the analysis of sulfurized alkylphenols.
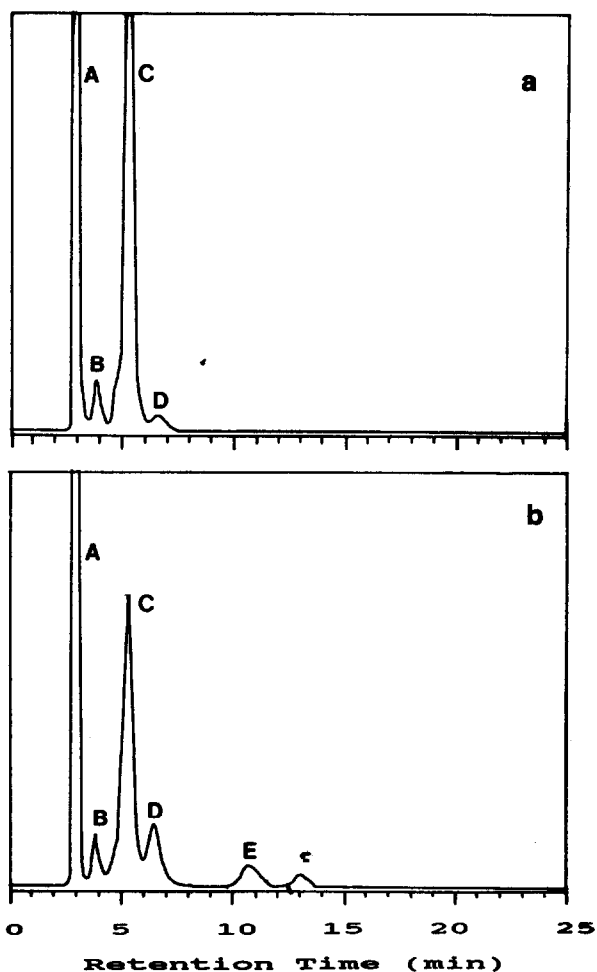

Fig. 1. (a) HPLC analysis by ELSD of a sulfurized dodecylphenol which met engine test specifications and (b) one which had failed the engine tests. See text for explanation.

Analysis of sulfurized dodecylphenols

Two sulfurized dodecylphenols were separated from undesirable reaction side products and oil by the normal-phase chromatographic method summarized in Table I. The signals from each separated component were then monitored and compared by both UV and ELS detection.

This multi-detector gradient HPLC system, in conjunction with mass spectral identification of the isolated components, was designed to monitor those intermediates which may or may not meet the standard engine test specifications. The first sample, shown in Fig. 1a, was previously determined to have met engine test specifications, while the second sample, shown in Fig. 1b, had failed the engine tests.

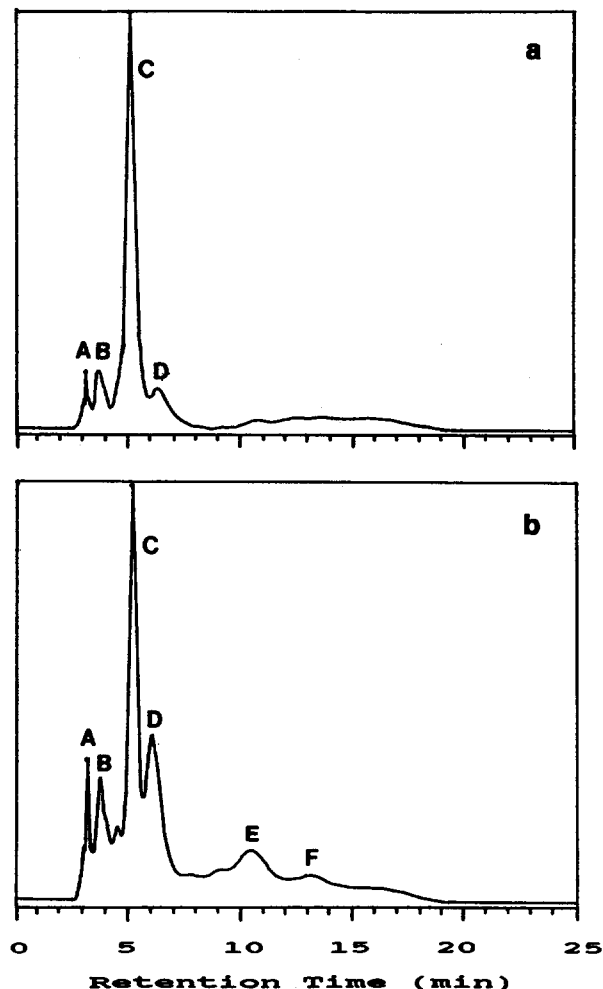It can be seen from the resulting chromatograms that the first sample contained

Fig. 2. (a) HPLC analysis by UV detection of sample in Fig. 1a and (b) of sample in Fig. 1b. See text for explanation.

a larger amount of the desired product (peak C) compared to the second sample. Also, the second sample contained more prominent undesirable reaction side products and unreacted material (peaks B, D–F). This method was also successful in isolating the base oil (peak A) from the other components. The significant differences between these two chromatograms demonstrated that the HPLC–ELSD system was an excellent technique for effective quality control monitoring of these types of samples.
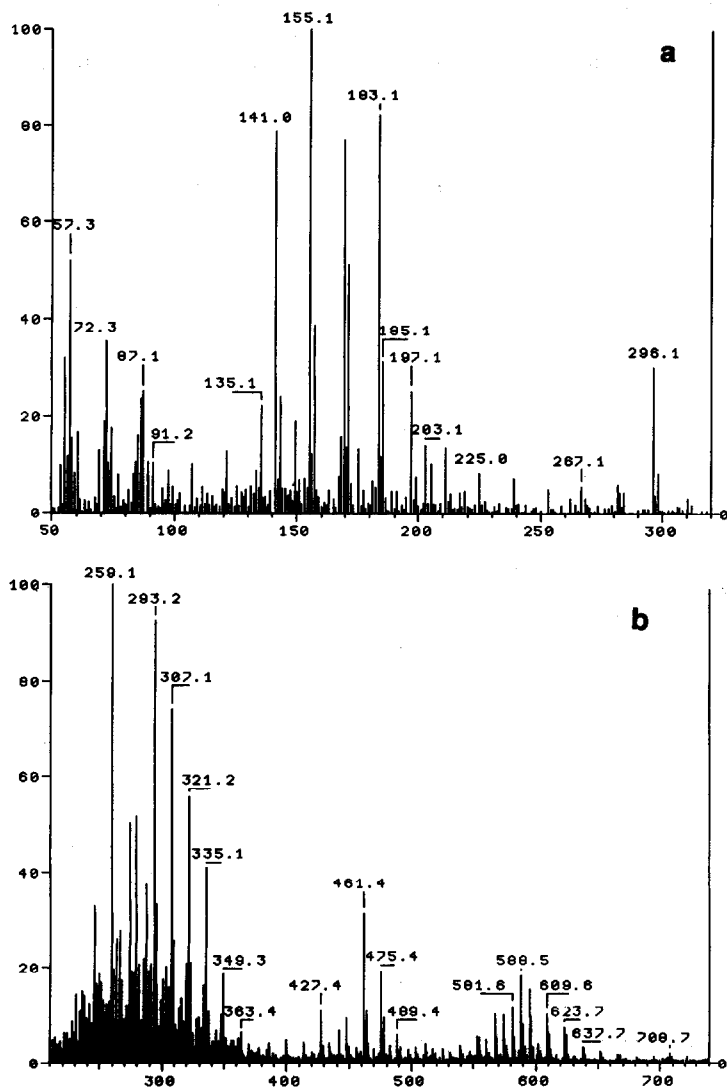

Fig. 3. (a) Mass spectra of dodecylchlorophenol **1** (peak B in Fig. 1b) and (b) dodecylhydroxyphenyl didodecylhydroxyphenyl sulfide **2** and dodecylhydroxyphenyl dodecylchlorohydroxyphenyl sulfide **3** (both also contained in peak B, Fig. 1b).

The mechanism of separation for the sulfurized dodecylphenols was more likely to be partition rather than the formation of inclusion complexes. In this case, the diameter of the solutes was too large to form complexes with the interior cavity of the cyclodextrin molecule. Since both mobile phases, hexane and THF, had strong affinities for the hydrophobic cabity, solute retention was probably due to the adsorption of the component on the outer hydrophilic portion of the cyclodextrin [30]. In addition, hydrogen bonding to the surface hydroxyls and other electrostatic interactions may have played a role in the separation process.

The corresponding UV detector chromatograms of the first and second samples are shown in Fig. 2a and b, respectively. Both chromatograms had poor resolution between peaks and noticeable baseline drift due to the interfering THF mobile phase. In addition, only a small response was observed for the non-UV absorbing base oil peak. In spite of these major disadvantages, the complementary nature of the UV detector was quite useful. Several injections were made in order to obtain repeatable and accurate retention times necessary for the collection of each sample component for mass spectral identification. The repeatability for the desired major product was found to be ± 0.03 min. This could not be accomplished with ELSD because of its destructive design.

This technique was successful in monitoring the quality of sulfurized dodecylphenols prior to producing the final detergent additive. Also, ELSD was capable of operating with multiple solvent gradients without solvent interferences.

MASS SPECTRAL EXPERIMENTAL AND IDENTIFICATIONS

Approximately 1 ml of each major HPLC fraction was collected in a conical 1-ml vial, and then concentrated by evaporation to about 0.1 ml using a gentle nitrogen stream just prior to mass spectrometric analysis. The fraction was then deposited onto the rhenium wire filament of a direct insertion probe and allowed to dry. The probe was inserted into the source of a Finnigan-MAT TSQ 70 quadrupole mass spectrometer in close proximity to the transverse electron beam. The sample was rapidly volatilized into the source by linearly heating the probe filament from 20 to 1150°C over a 1-min time period. The source temperature was held at 150°C. Its ion current was 200 μA at 70 eV. The first quadrupole was scanned from 50 to 900 u at 1 scan per 0.75 s.

The HPLC chromatogram of the first sample, which had previously met engine test specifications, resulted in four well-defined peaks (Fig. 1a). All of these peaks were identifiable by their mass spectra. The first chromatographic peak (designated A in Fig. 1a) represented the base oil in which the sulfurized alkylphenol was dissolved during the manufacturing process. The second peak (B) contained several components, mainly dodecylchlorophenol 1 along with some dodecylhydroxylphenyl didodecylhydroxylphenyl sulfide 2 and dodecylhydroxyphenyl dodecylchlorohydroxyphenyl sulfide 3, all of which were apparently minor side products. The third peak (C) was identified solely as the desired major product, di(dodecylhydroxyphenyl) sulfide 4. Finally, the last peak (D) was determined to be di(dodecylhydroxyphenyl) disulfide 5.
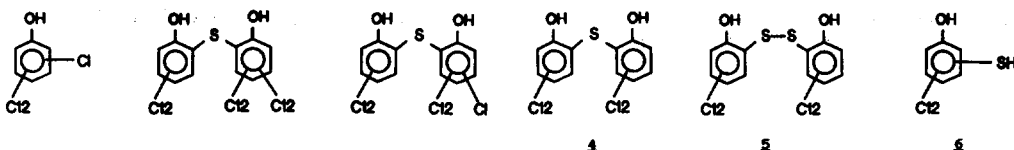
The mass spectra of these compounds are shown in Fig. 3 and 4. The dodecyl-chlorophenol **1** and its isomers volatilized more readily from the other components in the HPLC fraction representing peak B, and therefore produced a relatively clean mass spectrum, as shown in Fig. 3a. The molecular ion, m/z 296, and the major fragment ions, m/z 141, 155, 169 and 183, resulting from the losses on the dodecyl chain, were the major ions observed. The corresponding chlorine isotope peaks were also observed at the expected intensities. Since compounds **2** and **3** simultaneously
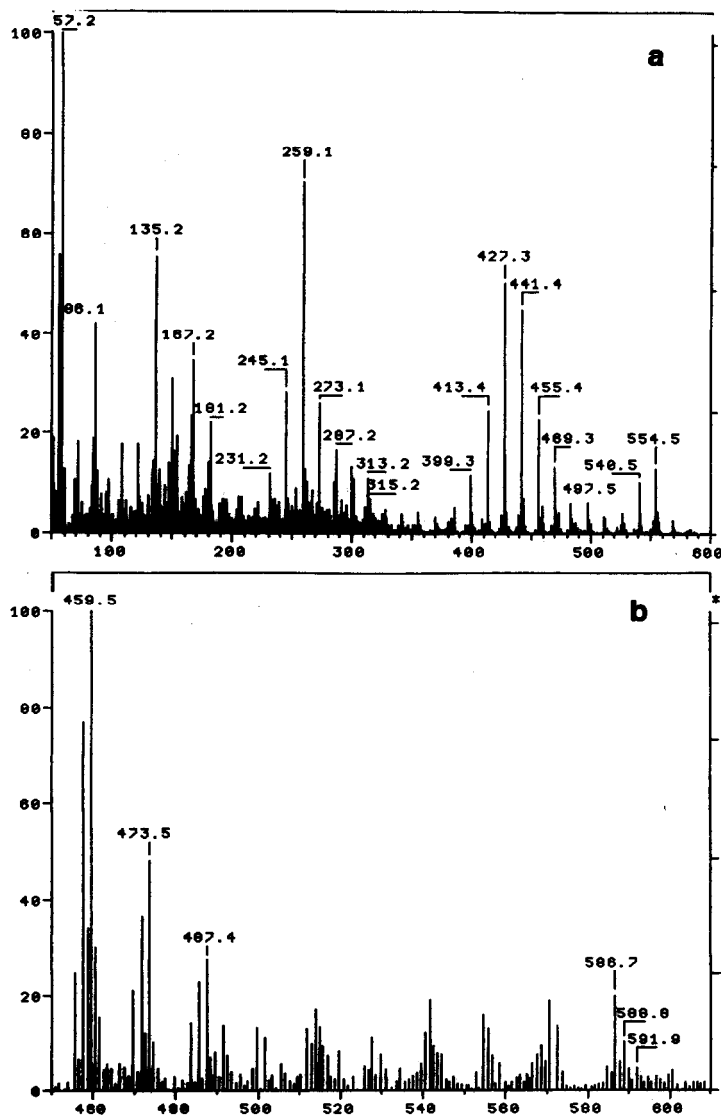

Fig. 4. (a) Mass spectra of di(dodecylhydroxyphenyl) sulfide **4** (peak C in fig. 1b) and di(dodecylhydroxyphenyl) disulfide **5** (peak D in fig. 1b).
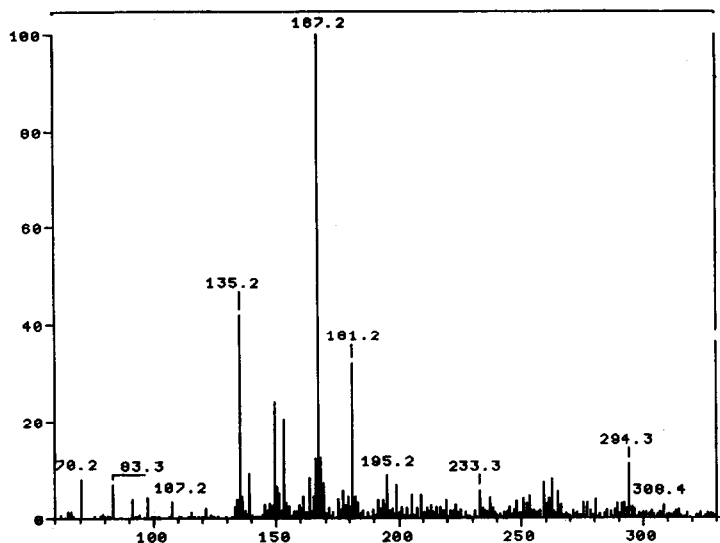
Fig. 5. Mass spectrum of dodecylmercaptophenol 6 (peak E in Fig. 1b).

volatilized, they produced a common mass spectrum shown in Fig. 3b. Furthermore, both compounds consisted of a homologous series with a range of approximately four carbons. Homologs of compound 2 had weak molecular peaks at m/z 680, 694, 708 and 722. Major fragmentation peaks at m/z 581, 595, 609 and 623 resulted from the losses from the alkyl chain. Homologs of compound 3 had molecular ion peaks at m/z 574, 588 and 602 with corresponding chlorine isotope peaks. These molecules had major fragmentation ions at m/z 279, 293, 307, 321, 461, 475 and 489. The mass spectrum in Fig. 4a represents di(dodecylhydroxyphenyl) sulfide 4. It had homologous molecular ions at m/z 526, 540, 554 and 568. Fragmentation produced major ions at m/z 245, 259, 273, 413, 427 and 441. The corresponding disulfide 5 had a molecular ion at m/z 586 and fragment ions at m/z 459, 473 and 487, as shown in Fig. 4b.

The second sample, which had failed the engine test, contained six well-defined HPLC chromatographic peaks (see Fig. 1b). The first four peaks had the same retention times and mass spectra as the first sample, differing only in intensities. The fifth HPLC fraction, representing peak E in Fig. 5, was identified by its mass spectrum to be dodecylmercaptophenol 6. It had a molecular ion peak at m/z 294 and corresponding fragment peaks at m/z 153, 167, 181 and 195 from losses along the alkyl chain. The last peak (F) was not identified.

CONCLUSIONS

The coupling of HPLC procedures with both ELSD and MS provided excellent results in the analysis of sulfurized dodecylphenols in oil. ELSD provided highly resolved peaks and was capable of operating with multiple solvent gradients and free from ambient temperature effects unlike other conventional HPLC detection meth-

ods. Complementary mass spectral identification demonstrated its effectiveness in characterization of the sample components. This HPLC–ELSD method was rapid and successful in monitoring the quality of sulfurized alkylphenols prior to producing the final detergent product.

REFERENCES

1 A. R. Sabol, E. W. Blaba and C. G. Brannen, *US Pat.*, 3 609 076 (1971).
2 R. W. Watson, E. E. Richardson and A. R. Sabol, *US Pat.*, 3 492 230 (1970),
3 J. M. King and N. Bakker, *US Pat.*, 3 932 289 (1976).
4 J. J. Valcho, F. J. Slama, J. S. Strukl and C. M. Park, *US Pat.*, 4 614 602 (1986).
5 N. Benfaremo and C. S. Liu, *Lubrication*, 76 (1990) 1.
6 A. D. Abbott and N. L. Allphin, *US Pat.*, 3 367 867 (1968).
7 L. C. Rogers and M. W. Hunt, *US Pat.*, 3 718 589 (1973).
8 R. L. Sung, H. Chafetz, B. H. Zoeleski and W. D. Foucher, *US Pat.*, 3 969 235 (1976).
9 V. C. E. Burnop, *US Pat.*, 4 104 180 (1978).
10 M. Kudoh, H. Ozawa, S. Fudano and K. Tsuji, *J. Chromatogr.*, 287 (1984) 337.
11 H. R. Menez and C. L. Perez, *J. High Resol. Chromatogr.*, 12 (1989) 562.
12 G. R. Bear, C. W. Lawley and R. M. Riddle, *J. Chromatogr.*, 302 (1984) 65.
13 G. R. Bear, *J. Chromatogr.*, 371 (1986) 387.
14 R. J. Hwang and M. Stauffer, *J. Liq. Chromatogr.*, 10(4) (1987) 601.
15 D. R. Zornes, G. P. Willhite and M. J. Michnick, *Soc. Pet. Eng. J.*, 18(3) (1978) 207.
16 P. L. Desbene, B. Desmazieres, J. J. Basselier and L. Minssieux, *Chromatographia*, 24 (1987) 588.
17 B. F. Nilsson and O. Samuelson, *J. Chromatogr.*, 198 (1980) 267.
18 S. V. Monin, A. Y. Levin, L. O. Kogan and A. R. Lipshteyn, *Khim. Tekhnol. Topl. Masel*, 5 (1986) 30.
19 A. A. Polyakova, L. O. Kogan, G. V. Vasilenko, L. G. Nekhamkina, G. B. Belan, Y. D. Muchinskiy, M. S. Khots and R. N. Semanyuk, *Tr.-Mezhdunar. Kongr. Poverkhn.-Akt. Veshchestvam, 7th Meeting*, 1 (1977) 450.
20 A. Stolywo, H. Colin and G. Guiochon, *J. Chromatogr.*, 265 (1983) 1.
21 A. Stolywo, H. Colin and G. Guiochon, *J. Chromatogr.*, 57 (1985) 1342.
22 T. H. Mourey, *J. Chromatogr.*, 357 (1986) 101.
23 K. D. Bartle, M. J. Mulligan, N. Taylor, T. G. Martin and C. E. Snape, *Fuel*, 63 (1984) 1556.
24 S. Coulombe, *J. Chromatogr. Sci.*, 26 (1988) 1.
25 G. R. Bear, *J. Chromatogr.*, 459 (1988) 91.
26 E. Smolkova-Keulemansova, *J. Chromatogr.*, 251 (1982) 17.
27 H. J. Issaq, *J. Liq. Chromatogr.*, 11 (1988) 2131.
28 E. Smolkova-Keulemansova, *J. Chromatogr.*, 184 (1980) 347.
29 D. W. Armstrong, *US Pat.*, 4 539 399 (1985).
30 *Cyclobond Handbook —A Guide to Using Cyclodextrin Bonded Phases*, Astec Inc., Whippany, NJ, 1987.