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Determination of elemental sulfur by size-exclusion chromatography Optimization and petrochemical applications

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Abstract

Factors affecting the elution of elemental sulfur beyond the total permeation limit of a size-exclusion chromatographic (SEC) column are investigated. The pore diameter of the column packing is found to be the most important parameter, and optimum results are achieved from a single 10^3 Å pore polystyrene–divinylbenzene column with tetrahydrofuran as solvent. It is shown that both the column temperature and solvent flow-rate have little or no influence on the resolution of sulfur from other sample components. The apparent anomalous elution behavior of sulfur is validated by two independent approaches, and is addressed in terms of electronic interactions between sulfur and the phenyl ring of the polystyrene–divinylbenzene packing. The solubilities of sulfur in typical alkylate, naphtha and reformate samples at room temperature have been determined by the SEC method. The amounts of sulfur in typical hydrotreated cracked naphtha and gas oil samples from pilot unit runs have also been measured. These results are discussed in relation to relative solubilities of sulfur in compounds belonging to different hydrocarbon classes. Specifically, the solubility of sulfur is found to decrease with hydrocarbon type in the order, aromatics>naphthenes>olefins>*n*-alkanes>isoalkanes.

Keywords: Naphthas; Gas oils; Alkylates; Reformates; Oils; Sulfur; Hydrocarbons

1. Introduction

Size-exclusion chromatography (SEC) is widely applied to the analysis and separation of macromolecules. In theory, the elution of molecules in SEC is confined within limits representing total exclusion and total permeation through macroporous particles packed into a column. However, elution after the total permeation limit has previously been observed with certain types of compounds including polynuclear aromatic hydrocarbons (PAHs) and molecules with ionic or polar nitrogen and sulfur groups [1–3]. These compounds, in general, were found to provide asymmetric peaks. Elemental sulfur (S_8) was also found to elute beyond the total permeation limit. Unlike PAHs, and sulfur- and nitrogen-compounds, sulfur provided a narrow and symmetric peak [1–6].

The sulfur peak has served as the flow-rate marker in SEC [4–6]. The unique elution behavior of sulfur was the basis of a method for the determination of sulfur in compounded nitrile rubbers [2,6], oil and aqueous media [1]. In an earlier work [1], selective retention of sulfur was achieved on columns with large diameter (15–37 μm) polystyrene–divinylbenzene packings. These columns were 50–100 cm long. Mixed mobile phases composed of methanol and chloroform, and tetrahydrofuran were used. Microparticulate packings (<10 μm in diameter) with different pore sizes on a multiple column set

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were used to resolve the sulfur peak [2,4,5]. A single 50 cm×0.8 cm column (with nominal 8–10 μm particle diameter, 40 Å pore size, and 10^3 polystyrene exclusion limit) was also found to provide similar results [3].

There have been few attempts to investigate factors influencing the resolution of sulfur from other sample components. A systematic study on the effects of column properties, and other experimental variables such as column temperature or solvent flow-rate, should provide insights into the selective interaction of sulfur with the SEC packing matrix (or gel phase). The information should also be useful for optimizing the separation process so that the use of a very long column or multiple column set, and concomitant long analysis times, can be avoided.

In this work, several SEC columns with microparticulate polystyrene–divinylbenzene packings are evaluated using tetrahydrofuran (THF) as solvent. The elution of sulfur beyond the SEC total permeation limit is verified by independent experiments. Experiments are conducted to explore the effects of pore size, column temperature and solvent flow-rate in the separation and resolution of sulfur from petroleum distillates or similar organic compounds. SEC is shown to be advantageous for the determination of sulfur solubilities in typical gasoline range samples as well as in compounds representing different hydrocarbon types. Examples are also provided for the accurate determination of sulfur present in naphthas and gas oils obtained from pilot unit runs.

2. Experimental

The SEC system consisted of a Model 1090 liquid chromatograph from Hewlett-Packard (Atlanta, GA, USA) equipped with a solvent-delivery system, an auto injector, a diode array detector, and an oven compartment. A Hewlett-Packard HPLC ChemStation (Pascal Series) was used for system automation, data collection and data analysis.

THF from a newly opened bottle was used (with continuous sparging with helium). A number of 30 cm×0.78 cm I.D. Ultrastyragel columns with different pore sizes and with a nominal particle diameter of 7 μm were used. These columns were packed with cross-linked styrene–divinylbenzene copolymer particles and were purchased from Waters (Milford, MA, USA). Unless noted otherwise, the columns were kept at room temperature (24±2°C) and a flow-rate of 1.0 ml/min was used. Sulfur was detected at 270 nm (absorption maximum) using the diode array detector.

For solubility experiments, excess flowers of sulfur (USP grade) were added to each solvent and the mixture was then sonicated for about an hour at about 50°C. The mixture was cooled down to room temperature and the resulting saturated solution was filtered through a 0.45-μm disposable PTFE filter. Whenever necessary, the filtered solution of sulfur was diluted with THF prior to its analysis by SEC.

3. Results and discussion

3.1. Optimization of SEC conditions

The column temperature, solvent flow-rate, and particle diameter and pore size of the packing materials are important variables in SEC. The dependence of solute retention on column temperature has been reported where both steric exclusion (entropic effect) and adsorption of solute molecules to the gel phase (enthalpic effect) were considered [7]. However, in a parallel study, it was concluded that the reduction of analysis time with an increase in temperature is simply due to the reduction of viscosity of the mobile phase at an elevated temperature [8]. The elution volume (elution time multiplied by flow-rate) for SEC was found to be almost invariant with flow-rate for components which elute between the total exclusion and total permeation limits [9,10]. .

The chromatograms in Fig. 1 demonstrate that packing pore size affects the resolution between sulfur and naphtha peaks. A single column was used in each experiment. The column with an average pore size of 10^3 Å was found to provide the highest resolution between the two peaks (Fig. 1c). The 500 Å and 10^4 Å columns provided partial resolution. However, both 100 Å and 10^5 Å columns were ineffective in separating sulfur from naphtha. In subsequent experiments, a single 10^3 Å column was found adequate for rapid separation and resolution of

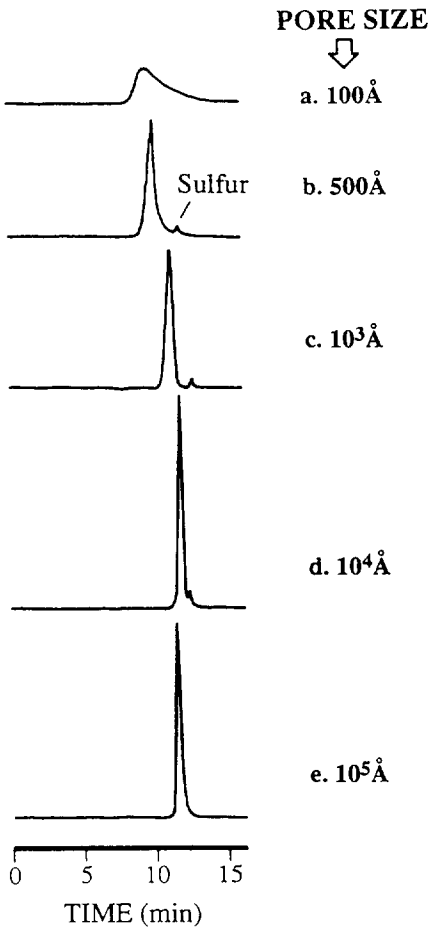

Fig. 1. Effects of pore size on the resolution of sulfur from naphtha.

sulfur from petroleum distillates or similar compounds.

It should be noted that the pore size results (in Fig. 1) are only valid for the packing materials as well as solvent used in this work. The optimum pore size may vary if columns with different particle diameters and other properties are used, or other solvents are tried.

The retention behavior of naphtha and sulfur at three different column temperatures is shown in Fig. 2. Here, only a slight decrease in the retention times of both sulfur and naphtha peaks is observed as the temperature is increased. It appears that the resolution between naphtha and sulfur peaks remains unchanged in the temperature range 25 to 50°C. This

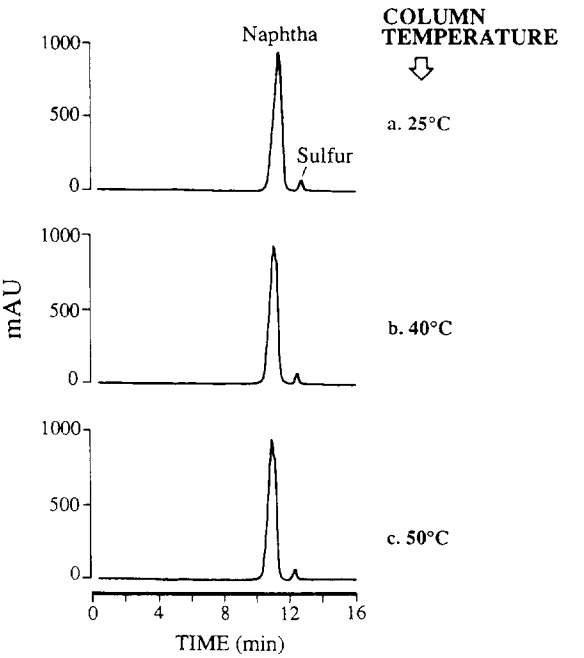

Fig. 2. Separation and resolution of naphtha and sulfur at different column temperatures.

is consistent with a separation mechanism dominated by entropic effects as in conventional SEC.

Experimental flow-rates were varied between 0.5 and 2.0 ml/min to examine the effects flow-rate on the separation of sulfur from toluene. In Fig. 3, a proportional decrease in the retention time with an increase in the flow-rate is observed. It is observed that flow-rate does not affect the resolution between the sulfur and toluene peaks. Only minor changes in peak heights are observed, which could be due to band broadening effects. As peak area is a function of time and absorbance, the peak area of each component should decrease when a higher flow-rate is used. Interestingly, the ratio of peak areas was found to be independent of flow-rate. Specifically, the ratio of toluene peak area to sulfur peak area at all three flow-rates was 44:56; sulfur peak areas (in arbitrary units) were 10 750, 5450 and 2725 at the flow-rates of 0.5, 1.0 and 2.0 ml/min, respectively.

Since peak areas are affected significantly with the change in flow-rate, flow-rate was checked regularly when SEC was applied to the determination of sulfur using an external calibration (see later).

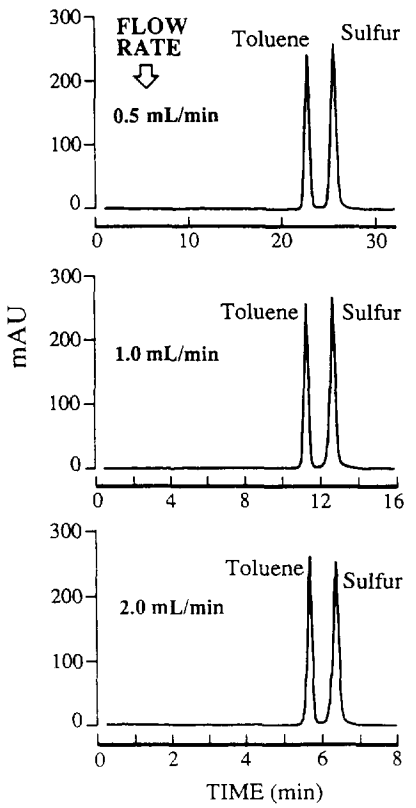

Fig. 3. Chromatograms showing the separation and resolution of toluene and sulfur at different flow-rates.

3.2. Validation of sulfur peak

The sulfur peak obtained with the 10^3 Å column was subject to validation. The total permeation limit of this column was assumed to be the same as the elution time of toluene (as in Fig. 3) which was 11.4 min at a flow-rate of 1.0 ml/min. Sulfur eluted at 12.8 min under identical conditions. The identity of the sulfur peak was verified by collecting fractions from a chromatogram similar to the middle chromatogram in Fig. 3, and subsequently analyzing these fractions by thin-layer chromatography (TLC) using a silica gel plate and hexane as the developing solvent. A characteristic blue spot displaced just behind the solvent front was observed on the TLC plate under short wavelength UV light (Ultraviolet Products, St. Gabriel, CA, USA) for a fraction from the sulfur peak. The retention of this spot matched a spot obtained from a sulfur solution used as a reference. Additional support was obtained by derivatizing sulfur with triphenylphosphine (TPP) to yield triphenylphosphine sulfide [11,12]

$$8(C_6H_5)_3P + S_8 \rightarrow 8(C_6H_5)_3P{=}S$$

The derivatization was carried out at room temperature with three hours of sonication [12]. Evidence for the elimination of sulfur from its solutions in THF and naphtha due to the above reaction are shown in Fig. 4 and Fig. 5 respectively. The chromatograms in both figures were obtained by injecting 8 μl of the sample solution. The concentration of sulfur in the THF solution (Fig. 4a) was 523 μg/ml and that in the naphtha solution (Fig. 5a) was 675 μg/ml. About 0.7 and 1.9 times the stoichiometric amounts of TPP were added in samples used for Fig. 4b and Fig. 4c, respectively. Residual sulfur is observed in Fig. 4b as the amount of TPP was insufficient for a quantitative reaction. In both Fig. 4c and Fig. 5b, the product triphenylphosphine sulfide and unreacted TPP elute within the total permeation limit, as expected of a normal SEC elution mechanism.

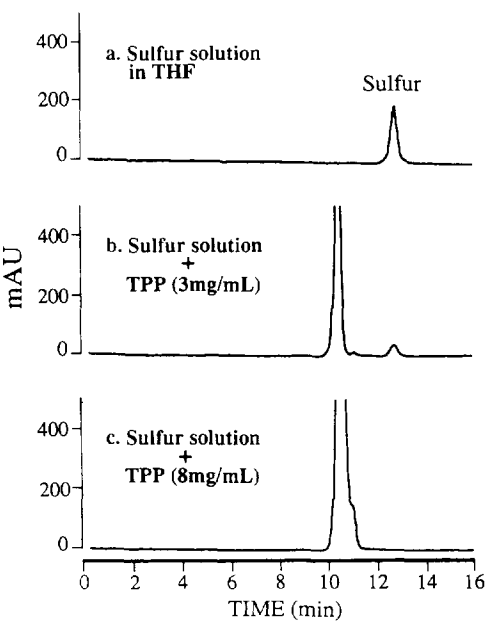

Fig. 4. Chromatograms supporting reaction of sulfur in THF with triphenylphosphine.

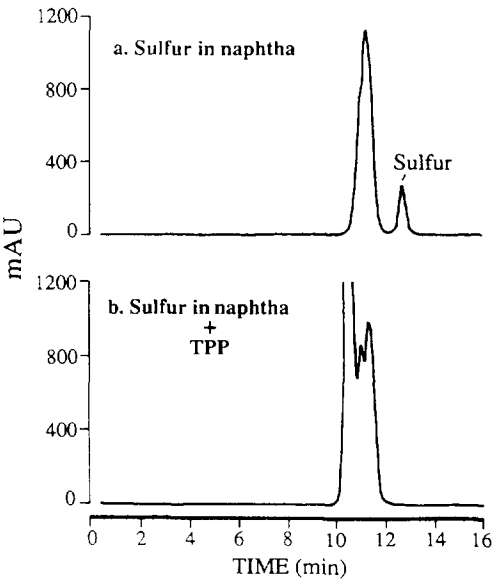

Fig. 5. Reaction of sulfur in naphtha with triphenylphosphine.

3.3. Quantitation of sulfur

A number of chromatograms (as in Fig. 4a) were obtained with solutions differing in the concentration of sulfur in THF. For each experiment, injection volume was 20 μl. Sulfur peak area in each chromatogram was measured. The resulting sulfur concentration versus peak area plot is shown in Fig. 6. This calibration plot is linear for 5–700 μg/ml of sulfur. The regression parameters (with standard deviations in parentheses) are as follows: intercept = 0.45 (0.95), slope = $5.600 \cdot 10^{-2}$ ($0.007 \cdot 10^{-2}$) and correlation coefficient (r^2) = 0.99998.

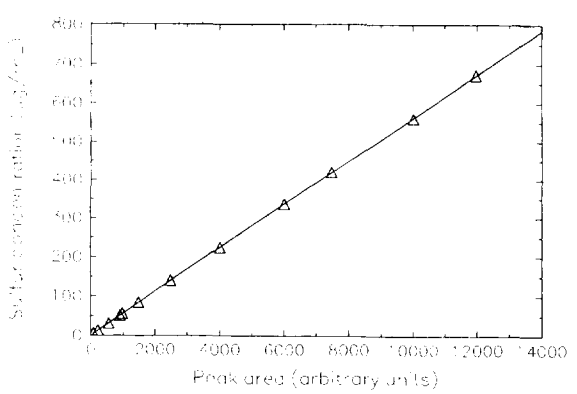

Fig. 6. Calibration plot showing the sulfur concentration versus peak area measured at 270 nm wavelength.

3.4. Solubility of sulfur in light distillates

Sulfur solubilities in typical gasoline range samples such as alkylate, naphtha and reformate, were determined by saturating each with flowers of sulfur as described in the Experimental section. The SEC chromatograms shown in Fig. 7 were for solutions obtained by diluting each saturated mixture 1:11 (v/v) with THF. For SEC analysis, 5 μl each of the diluted sample were injected. Using the calibration plot shown in Fig. 6, and sulfur peak areas from the three chromatograms in Fig. 7, the solubilities of sulfur in the alkylate, naphtha and reformate were found to be 1.86, 12.75 and 12.79 g/l, respectively.

The alkylate sample contained 0.2% (v/v) aromatics, 0.5% (v/v) *n*-alkanes and 99.3% (v/v) isoalkanes measured by multidimensional gas chromatography (or PIONA analyzer) [13]. The amounts of aromatics, naphthenes, olefins and alkanes (*n*-

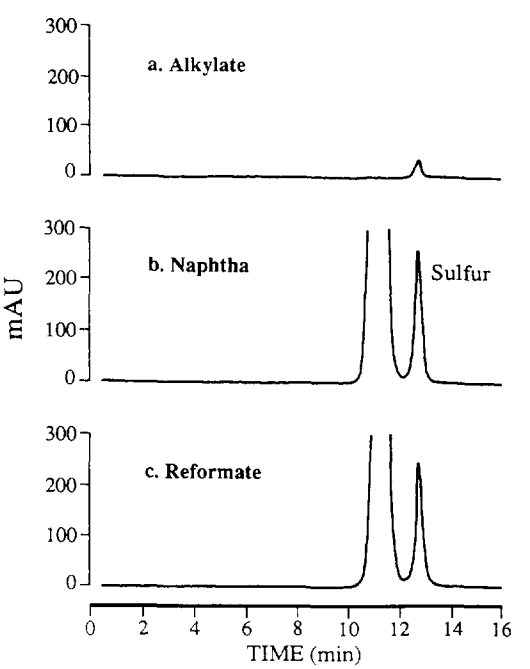

Fig. 7. Chromatograms for the saturated solutions of sulfur in typical alkylate, naphtha and reformate samples.

alkanes plus isoalkanes) in the naphtha sample were 65.0, 5.8, 4.3 and 24.9% (v/v) respectively. The corresponding amounts in the reformate sample were 74.7, 0.7, 0.6 and 24.0% (v/v). We note that as the hydrocarbons in the alkylate sample do not have significant absorbance at 270 nm, the alkylate peak is not detected in the chromatogram a of Fig. 7.

The low solubility of sulfur in the alkylate sample and about seven-fold higher solubility in both naphtha and reformate samples compared to that in the alkylate sample are discussed below in relation to the solubility of sulfur in different hydrocarbon types.

3.5. Solubility of sulfur in different hydrocarbons

Gasoline range compounds can be categorized in five different types: *n*-alkanes, isoalkanes, aromatics, naphthenes and olefins. Solubilities of sulfur in some representative compounds belonging to each hydrocarbon type are provided in Table 1. It is observed that the solubility of sulfur is the highest in toluene, followed by methylcyclohexane, 1-heptene, *n*-heptane and isooctane. Table 1 shows that even the poorest solvent (isooctane) is capable of dissolving a substantial amount of sulfur (1.30 g/l) at room temperature.

Sulfur solubility data in different hydrocarbons are scarce [14]. The sulfur solubilities in *n*-heptane and toluene obtained by the SEC method are in excellent agreement with the literature values [14] listed in Table 1. Thus the procedure described in this work, may be considered as a simple and convenient means of determining solubility of sulfur in hydrocarbons or other solvents.

Sulfur solubilities in solvents of a particular hydrocarbon type are found to be very similar [14]. For example, at 25°C, solubilities of sulfur in benzene, toluene and *m*-xylene are within 7% of each other. A similar pattern is observed for sulfur solubilities in *n*-hexane and *n*-heptane. Assuming this generalization applies to all hydrocarbon types, the solubility data for representative compounds listed in Table 1 can be used to predict the solubility of sulfur in each gasoline range distillate by applying additivity rules. The predicted solubilities, calculated in this manner, are 1.3, 12.4 and 13.2 g/l in the alkylate, naphtha and reformate, respectively. These values are in close agreement with the corresponding observed values listed in Table 1.

3.6. Sulfur in pilot unit naphtha and heavy gas oil samples

Fig. 8b and Fig. 8c show typical chromatograms of a hydrotreated full range cracked naphtha and a hydrotreated gas oil. Each is found to contain significant amounts of sulfur. Fig. 8a is a reference chromatogram for a solution of sulfur in THF. Here, naphtha and gas oil samples were injected without dilution and the injection volume was 5 μl. These samples were obtained from pilot units operated

Table 1
Room temperature (24±1°C) solubility of elemental sulfur in different solvents and gasoline distillates

Solvent/Distillate	Solubility by SEC (g/l)	Literature solubility (g/l)[a]
Solvents		
n-Heptane	2.55	2.5 (25°C)
1-Heptene	3.20	
Methylcyclohexane	6.32	
Isooctane	1.30	
Toluene	16.77	17.6 (25°C)
Distillates		
Alkylate	1.86	
Naphtha	12.75	
Reformate	12.79	

[a] Data are from Ref. [14]. The original solubility values in % (w/w) were converted to those in g/l using densities of sulfur, *n*-heptane and toluene as 2.000, 0.680 and 0.862 g/ml respectively.

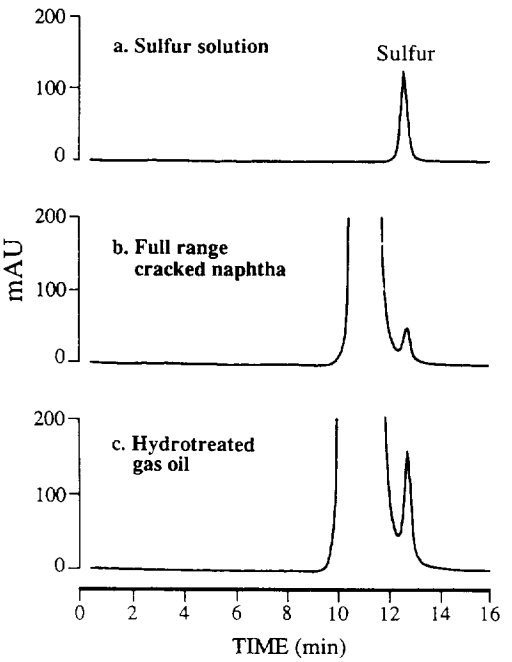

Fig. 8. Evidence for the presence of elemental sulfur in hydrotreated cracked naphtha and gas oil obtained from pilot unit runs.

without provision for the removal of hydrogen sulfide produced as a major byproduct of hydrodesulfurization [15]. It was suspected that unstripped hydrogen sulfide was being oxidized to sulfur.

The concentrations of sulfur in the naphtha and gas oil, as measured by SEC, were 85 and 290 μg/ml, respectively. The amounts of aromatics, naphthenes, olefins and alkanes in the naphtha sample were 48.7, 8.9, 14.1 and 28.3% (v/v), respectively. The gas oil sample contained 37.9% (w/w) aromatics, 4.9% (w/w) polar aromatics and 57.2% (w/w) saturates, as determined by TLC with flame-ionization detection [16]. A few more naphtha samples obtained from different pilot unit runs were also analyzed. Sulfur concentrations in these samples varied between 0 and 550 μg/ml.

The amounts of sulfur in the naphtha and gas oil samples were much lower than the estimated maximum sulfur concentrations on the basis of sample composition. Since elemental sulfur was absent in the feeds, it appears that the observed concentration in each sample represents elemental sulfur that was produced due to the oxidation of hydrogen sulfide.

3.7. Elution of sulfur beyond the total permeation limit

The dramatic effects of pore size on the resolution of sulfur, as observed in Fig. 1, are worth considering. A maximum resolution of sulfur on an intermediate pore size (10^3 Å) column suggests that there are specific interactions between sulfur and pore structure, and that the average distance between sulfur and the specific binding sites in the gel phase is important to cause a delayed elution of sulfur beyond the total permeation limit.

Sorption studies of ZR- or RZR′-type liquids with polystyrene–divinylbenzene particles [17] have relevance to the selective interaction of sulfur (as well as PAHs, sulfur- and nitrogen-compounds) with the SEC column packing. Here, Z is a phenyl, chloro, bromo, iodo, sulfide or ether functional group, and R and R′ are alkyl moieties. Selective interactions between non-bonded pairs of electrons of substituent Z (or π-electrons of the phenyl group representing Z) and π-electrons of the phenyl group in the polymer matrix were proposed [17].

Sulfur in solution at room temperature exists as S_8 molecules. There, sulfur atoms form eight-membered puckered rings, each atom is bonded to two neighbors by single electron-pair bonds, and each has two non-bonded pairs of electrons. During partitioning of sulfur molecule (S_8) between the mobile phase and gel phase, S_8 must approach a phenyl ring of the styrene–divinylbenzene packing for the electronic interactions to take place. However, for a maximum interaction between S_8 and phenyl ring, the sulfur molecule must sample the entire pore, and must stay at an optimum distance from as many binding sites as possible. These interactions will be reduced if S_8 does not have access to the entire population of binding sites when pore sizes are small. With larger pore particles, selectivity will be lost since the average distance between S_8 and phenyl ring will be too long for an effective interaction.

4. Conclusions

The SEC method described here should be useful for the determination of elemental sulfur in many petrochemical samples including additives. Sulfur

and other components in these samples are expected to elute after and before the SEC total permeation limit, respectively. As demonstrated in this work, optimization requires simply an evaluation of pore sizes of the column packing; using optimized conditions, an analysis can be completed in less than 15 min.

Acknowledgments

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