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SEPARATION OF SULFONATE AND CARBOXYLATE MIXTURES BY ION-EXCHANGE HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Aromatic sulfonate and carboxylate mixtures are separated by an ion-exchange high-performance liquid chromatography method. The separation is carried out on a strong anion exchanger (quaternary amine) with a gradient of three solvents: tetrahydrofuran (THF) water (50:50), THF–0.1 *M* potassium dihydrogen phosphate (pH 4.5) (50:50) and THF–0.2 *M* potassium dihydrogen phosphate (pH 6.5) (50:50). The change in ionic strength and pH of the mobile phase during elution results in excellent resolution of mixtures by charge and ionic group. Small variations in retention time within each class of ionic group were noted and are due to electronic and steric effects introduced by substituents on the hydrophobic part of the molecule.

When applied to petroleum sulfonates, *i.e.*, complex mixtures of alkylaryl sulfonates, this procedure gives information on the degree of sulfonation as well as the extent of variation in the structure of the alkylaryl part of the anions.

INTRODUCTION

Petroleum sulfonates used as surfactants in enhanced oil recovery (EOR) are prepared by sulfonating various refinery feedstocks. The sulfonated products may encompass a range of molecular weights with diverse aromatic skeletons, which may be mono-, di- and polysulfonated. In addition, carboxylates, which could behave as anionic surfactants, may be present[1,2]. In order to understand better the performance of these complex mixtures when used in EOR processes, it is necessary to have reliable and simple techniques which will help to identify the components of the mixture as well as to characterize the mixture as a whole.

High-performance liquid chromatography (HPLC) provides two basic paths for separating complex mixtures of organic carboxylates and sulfonates: (1) by type and number of anionic groups on a molecule; or (2) by the difference in structure of the species carrying the charge group(s), *i.e.*, by the hydrophilic end, or by the hydrophobic part. Separation according to the hydrophilic end may be achieved by anion-exchange HPLC. The separation of carboxylates in this way is well documented[3–8], as is that of the sulfonates[9,10]. However, conditions thus far reported do not allow the simultaneous separation of carboxylates and sulfonates of like degree of functionality.

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This paper reports the development of an anion-exchange HPLC method that allows high-resolution separation of a wide variety of carboxylates and sulfonates. Taking advantage of the difference in acid strength by operating at a pH where carboxylic acid dissociation is incomplete, provides a unique means for the separation of carboxylates from sulfonates with the same number of anionic charges while an ionic-strength gradient is used to control the rate of elution of the different anions. Control of pH also offers a simple means of controling the nature of the counter-ion species and thus improving selectivity. A typical analysis requires less than 30 min and is applicable to a large number of carboxylate and sulfonate compounds as well as to mixtures found in commercial petroleum sulfonates.

EXPERIMENTAL

Apparatus

A DuPont 8850 high-performance liquid chromatograph with a four-solvent gradient controller, a heated column compartment, and a data system was used. The column compartment contained a sample injection valve (Valco No. 851086-901) with a 20-μl sample loop, a guard column (Whatman pellicular anion exchanger 25 × 4.6 mm I.D.), and an anion-exchange analytical column (DuPont Zorbax SAX 250 × 4.6 mm I.D.). A DuPont variable-wavelength UV spectrophotometric detector set at 254 nm was used for detection.

Chemicals and sample preparation

High-purity water and reagent-grade tetrahydrofuran (THF) without preservative were obtained from Burdick & Jackson Labs. Potassium hydroxide and potassium dihydrogen phosphate were obtained from Mallinckrodt. Model compounds and petroleum sulfonates are listed in Tables I and II. The model compounds were dissolved in water to yield 0.01 *M* solutions. The pH of the samples was adjusted with sodium hydroxide to 4–6. Compounds insoluble in water were dissolved in methanol or THF. Surfactant compounds and petroleum sulfonate samples, listed in Table II, were prepared as 1% solutions in either water or THF and were deoiled prior to analysis. All solutions were filtered through 0.45-μm Millipore filters.

Chromatographic procedure

Three solvents were used for the separation: (solvent A) THF–water (50:50); (solvent B) THF–0.1 *M* KH_2PO_4 (pH 4.5) (50:50); and (solvent C) THF–0.2 *M* KH_2PO_4 (pH 6.5) (50:50). The pH of KH_2PO_4 solutions was adjusted with KOH. The solvent flow-rate was 2.00 ml/min. The column compartment was held at 35°C throughout the analysis. The column was prepared for the analysis by passing through solvent C (100%), followed by solvent B (100%), and then solvent A–solvent B (80:20), each for 15 min. At this point, the column was equilibrated and ready for sample injection. A 30-min gradient system was used for the analysis and is diagrammed in Fig. 1. The gradient begins with solvent A–solvent B (80:20). During the first 5 min (segment 1) the concentration of solvent A is decreased exponentially from 80% to 0% while the concentration of solvent B is increased exponentially to 100%. Segment 2 starts with 100% solvent B for 5 min, then solvent C is introduced and increased exponentially to 100% in 5 min for a total segment time of 10 min. Segment

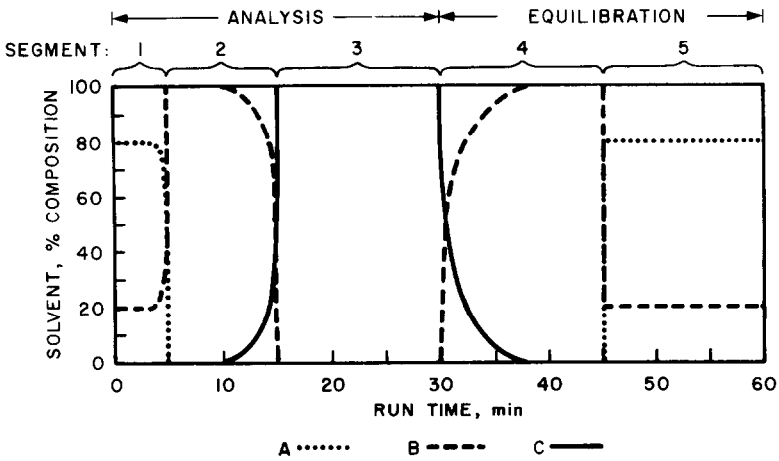


Fig. 1. Mobile-phase gradient program. Solvent A = THF–water (50:50); solvent B = THF–0.1 *M* KH_2PO_4 (pH 4.5) (50:50), solvent C = THF–0.2 *M* KH_2PO_4 (pH 6.5) (50:50).

3, consists of 100% solvent C for 15 min. At the end of segment 3 the analysis is completed, whereupon the column is reequilibrated with 100% solvent B for 10 min, then with the initial conditions of solvent A–solvent B (80:20) for 15 min.

Column efficiency

The performance of the analytical column used throughout this study was found to be satisfactory. No variation in capacity factor was observed with column aging. Peak shape and resolution were reproducible. However, during early work on optimization of the solvent system, the column efficiency deteriorated rather quickly. At that time, the buffer concentration of the strongest solvent (C), was only 0.05 *M*. A background peak appeared near the trisulfonate region and continued to grow as the column aged. After a few injections, resolution and reproducibility were lost. All indications were that some ionic impurity was held strongly on the column and the solvent strength was not sufficient for complete elution. The problem was overcome by increasing the phosphate buffer concentration of solvent C to 0.1 *M*. Reproducibility of the separation was also influenced by equilibration time. As in all cases of ion-exchange analysis, equilibration time with all solvents had to be established and maintained constant throughout the study.

RESULTS AND DISCUSSION

Mobile-phase composition effect

For the separation of a mixture containing both carboxylates and sulfonates two variables must be considered: (1) the number of acidic substituents on the molecule, and (2) the degree of acid dissociation. At high pH, where both carboxylic and sulfonic acids are highly dissociated, separation between anions of different charge can be controlled by the ionic strength of the mobile phase. An ionic-strength gradient provides good separation according to the total charge on the anion but does not allow separation between carboxylates and sulfonates of the same charge. This

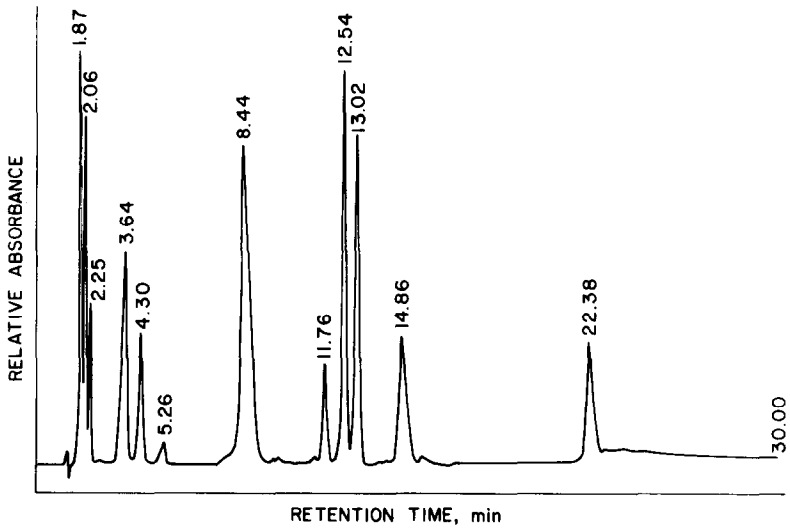


Fig. 2. Separation of model carboxylate and sulfonate compounds. Stationary phase: Dupont Zorbax SAX. Mobile phase: gradient of THF–water (50:50), THF–0.1 *M* KH_2PO_4 (pH 4.5) (50:50) and THF–0.2 *M* KH_2PO_4 (pH 6.5) (50:50). Solutes: 2-naphthalenecarboxylate (1.87 min), 1-naphthalenecarboxylate (2.06 min), benzoate (2.25 min), 2-naphthalenesulfonate (3.64 min), 1-naphthalenesulfonate (4.30 min), benzenesulfonate (5.26 min), 2,6-naphthalenedicarboxylate and terephthalate (8.44 min), isophthalate (11.76 min), 2,6- and 2,7-naphthalenedisulfonate (12.54 min), 1,5-naphthalenedisulfonate (13.02 min), 1,3-benzenedisulfonate (14.86 min) and 1,3,6-naphthalenetrisulfonate (22.38 min).

separation is achieved by operating in a pH range where carboxylic acid dissociation is incomplete while sulfonic acid dissociation is unaffected. A typical chromatogram obtained for the separation of a mixture of model carboxylates and sulfonates is shown in Fig. 2. The mobile phase during the first segment of the analysis program is maintained at a pH of 4.5 to suppress ionization of the carboxylates with the ionic strength at 0.01 *M* (as described in the Experimental section and shown in Fig. 1). With this solvent, the monocarboxylates are eluted at *ca.* 2 min and the monosulfonates within 3–5 min. After the elution of monobasic anions, the ionic strength is further increased to 0.05 *M* while the pH is maintained at 4.5. Under these conditions, the dicarboxylates are eluted at *ca.* 8 min and the disulfonates in the 12–16 min range. When the disulfonates begin to be eluted both the ionic strength and the pH are increased to 0.1 *M* and 6.5, respectively. The increase in pH alters the nature of the counter ion as the divalent ion, HPO_4^{2-}, becomes predominant. This dibasic HPO_4^{2-} is more effective in displacing the strongly bound trisulfonates from the resin than is the monovalent $H_2PO_4^-$ species. The trisulfonates are eluted sharply at *ca.* 22 min. Fig. 3 illustrates the range of retention times obtained from the set of model anions used in this study.

Molecular structure effects

The separation of carboxylated and sulfonated molecules both by the type of anionic group and by the number of anionic groups is shown in Table I and by Fig. 3. From the results with model compounds, it is evident that molecular structure

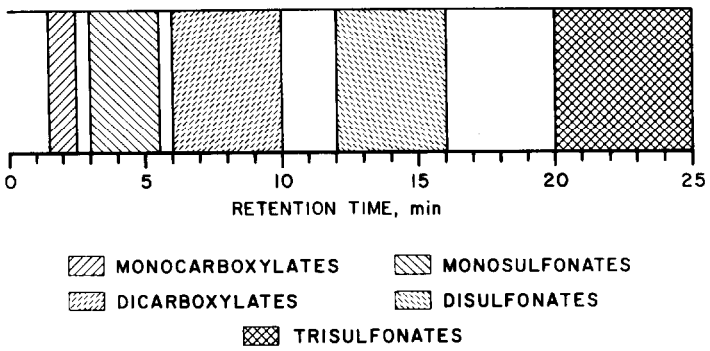


Fig. 3. Elution regions of carboxylate and sulfonate anions. Stationary phase and mobile phase as in Fig. 2.

influences the elution order within each elution group. Changes in molecular structure which affect the concentration of negative charge on the anionic functional group or sterically hinder the anion in its binding to the resin will be reflected in retention times.

If total dissociation of the acids and the absence of steric effects is assumed, then the retention time of the anion should be correlated with the pK_a of the corresponding acid. In other words, the more basic anion would have the longer retention time. However, in the pH range used in this study the carboxylic acids are only partially ionized and are thus always eluted before the corresponding sulfonates, which are completely dissociated strong acids. Any inductive or resonance effect due to changing the nature or location of substituents on the aromatic ring may alter the pK_a of the carboxylic acid, increasing or decreasing its retention time. Substituents which decrease the pK_a of the carboxylic acid should increase the retention time, while those which increase the pK_a should decrease the retention time. In the case of the totally ionized sulfonates, inductive and resonance effects of the substituents influence the concentration of negative charge on the sulfonate group, causing changes in sulfonate retention times.

The comparison of naphthalene monocarboxylates and monosulfonates with the corresponding benzene derivatives illustrate the influence of both steric and electronic effects on retention. The larger naphthalene derivatives are always eluted before the corresponding benzene analogues. The 1-naphthalenecarboxylate and -sulfonate are more acidic, due to greater resonance stabilization of the anion, than are the 2-analogues. Thus, the 1-naphthyl derivatives have longer retention times than do the 2-naphthyl derivatives. Likewise, 1,5-naphthalenedisulfonate has a longer retention time than do the 2,6- and 2,7-isomers, for similar reasons. Resonance effects are pronounced for the dicarboxylate isomers: phthalate (pK_a values: 2.98, 5.28), isophthalate (pK_a values: 3.46, 4.46), and terephthalate (pK_a values: 3.51, 4.82) where large differences in retention times are observed. The *meta* substituted isophthalate has no possible resonance interactions between the carboxyls and dissociation of the second carboxyl is less difficult. In fact, isophthalate is so strong an acid that it is eluted close to the region of disulfonates. Dissociation of the second carboxyl in both the *ortho-* and the *para*-dicarboxylates (phthalate and terephthalate) is reduced by efficient resonance interactions giving higher second pK_a values and, consequently,

shorter retention times. The second ionization of phthalic acid is further retarded by the proximity of the two negative charges, resulting in very early elution. Strong electron-withdrawing substituents, such as the nitro group may decrease the pK_a sufficiently to cause elution with the next group, *e.g.*, *p*-nitrobenzoic acid.

Of special interest are compounds containing both carboxylate and sulfonate groups. As shown in Table I, the retention of *o*-sulfobenzoate and 4-sulfophthalate

TABLE I

MODEL COMPOUNDS

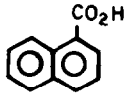
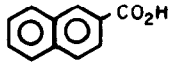
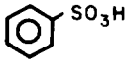
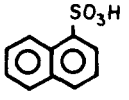
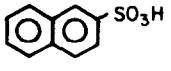
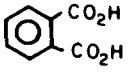
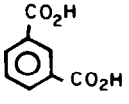
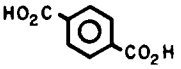
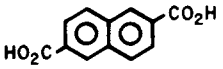
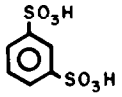
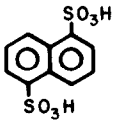
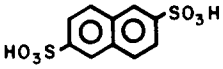
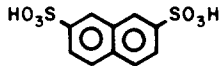
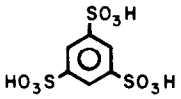
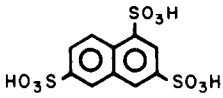
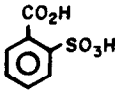
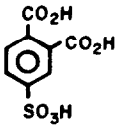
Compound	*Structure*	*Retention time (min)*
Benzoic acid		2.25
1-Naphthalene carboxylic acid		2.06
2-Naphthalene carboxylic acid		1.87
Benzene sulfonic acid		5.26
1-Naphthalene sulfonic acid		4.30
2-Naphthalene sulfonic acid		3.64
Phthalic acid		5.32
Isophthalic acid		11.76

TABLE I (*continued*)

Compound	*Structure*	*Retention time (min)*
Terephthalic acid		8.44
2,6-Naphthalene dicarboxylic acid		8.44
1,3-Benzene disulfonic acid		14.86
1,5-Naphthalene disulfonic acid		13.02
2,6-Naphthalene disulfonic acid		12.54
2,7-Naphthalene disulfonic acid		12.54
1,3,5-Benzene trisulfonic acid		22.38
1,3,6-Naphthalene trisulfonic acid		22.38
2-Sulfobenzoic acid		16.08
4-Sulfophthalic acid		21.10

(Continued on p. 72)

TABLE I (*continued*)

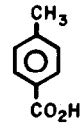
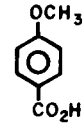
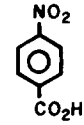
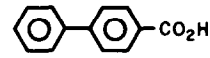
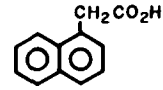
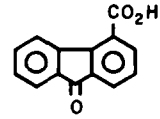
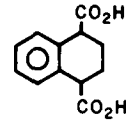
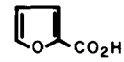
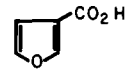
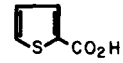
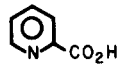
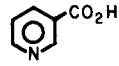
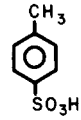
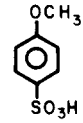
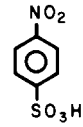
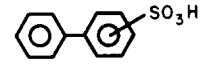
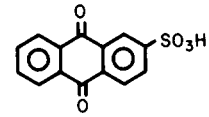
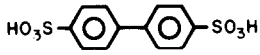
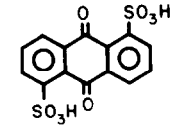
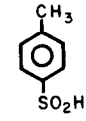
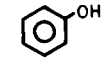
Compound	*Structure*	*Retention time (min)*
Toluic acid		2.07
p-Methoxybenzoic acid		1.87
p-Nitrobenzoic acid		3.71
4-Biphenyl carboxylic acid		1.87
1-Naphthalene acetic acid		2.12 2.22
9-Fluorenone-4-carboxylic acid		2.91
Dihydronaphthalene-1,4-carboxylic acid		11.33
2-Furoic acid		5.28
3-Furoic acid		3.33
2-Thiophene carboxylic acid		4.06

TABLE I (*continued*)

Compound	*Structure*	*Retention time (min)*
Picolinic acid		6.16
Nicotinic acid		5.08
Isonicotinic acid		5.28
p-Toluene sulfonic acid		4.76
p-Methoxybenzene sulfonic acid		5.27
p-Nitrobenzene sulfonic acid		3.88
Biphenyl sulfonic acid		3.01
2-Anthraquinone sulfonic acid		2.73
4,4′-Biphenyl disulfonic acid		11.08
1,5-Anthraquinone disulfonic acid		13.01
p-Toluene sulfinic acid		5.54
Phenol		1.37

is nearly equivalent to the retention of the disulfonates and trisulfonates, respectively. This is due to the initial stability of the anion through the ionized sulfonate group. As the analysis progresses, the pH of the mobile phase rises and the carboxylate groups become completely dissociated. The separation is then based only on charge, regardless of group type. As a result and under the conditions used here, compounds containing both groups are eluted in the same region as compounds containing only sulfonate groups of corresponding charge.

Heterocyclic carboxylic acids, listed in Table I, were studied to determine the effect of the hetero atoms: O, N and S on the retention of carboxylates. The separation obtained for picolinic, nicotinic and isonicotinic acids agrees well with the predicted effect of the electronegative nitrogen atom on the pK_a of the acids. These highly ionized acids were eluted in the monosulfonate region in the order: *meta, para, ortho*. As shown in Table I, the same effect is observed for the other hetero aromatic systems, furan and thiophene.

The distribution of charge density on the functional group will also influence retention times. For anions with the same equivalent charge, the smaller anion will have the larger charge to size ratio. This larger charge density will increase the distribution coefficient between the anion and the anion-exchange resin, increasing retention. Thus, for totally ionized anions, carboxylates will have longer retentions than will the equally charged sulfonates. This effect is illustrated by the later elution of benzoate when benzoate and benzenesulfonate are separated under isocratic conditions with solvent A–solvent B (80:20) at pH 6.5. The difference in charge–size ratio explains the longer retention of *p*-toluenesulfinic acid (5.54 min) as compared to the retention of *p*-toluenesulfonic acid (4.76 min).

Other effects, such as anion sorption by the anion-exchange resin and salting out[8] have no significant effect on the separation. This was concluded when no change in retention was observed with a change in the anion concentration or the pH of the compounds analyzed.

To summarize, the relationship between chemical structure and observed changes in retention time of substituted aromatic carboxylates and sulfonates can be accounted for by changes in pK_a due to molecular electronic effects of substituents and by the steric properties of the molecule. Other effects, such as anion-group charge density and chromatographic conditions also influence retention times.

Application to petroleum sulfonates

The effect of molecular structure on the retention of the anions present in petroleum sulfonates is significant. Petroleum sulfonates are complex mixtures of aromatic compounds with varying alkyl substituents. Each anion present will experience slightly different steric and electronic effects, depending on the nature and location of its substituents. This leads to a wide distribution in retention times for the compounds within each anion elution group. Figs. 4 and 5 illustrate the separations obtained for the model surfactant compounds sodium dodecylbenzenesulfonate and benzylnaphthalenesulfonate, respectively. As shown, sodium dodecylbenzenesulfonate is primarily a mixture of monosulfonates separated by molecular structure components. The chromatogram of benzylnaphthalenesulfonate shows the presence of mostly mono- and disulfonates with a small amount of trisulfonate. The differently charged anions as well as the components within each anionic group are

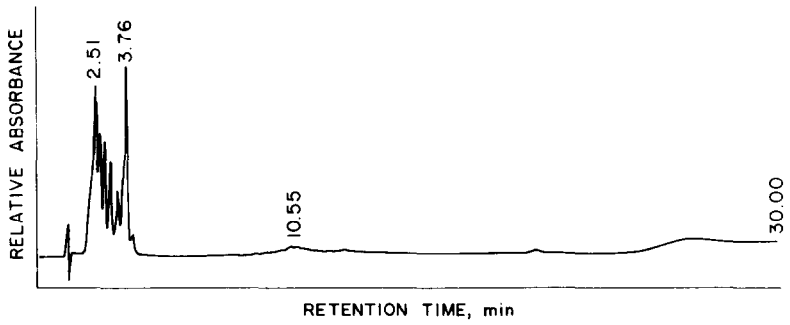


Fig. 4. Separation of sodium dodecylbenzenesulfonate components. Stationary phase and mobile phase as in Fig. 2.

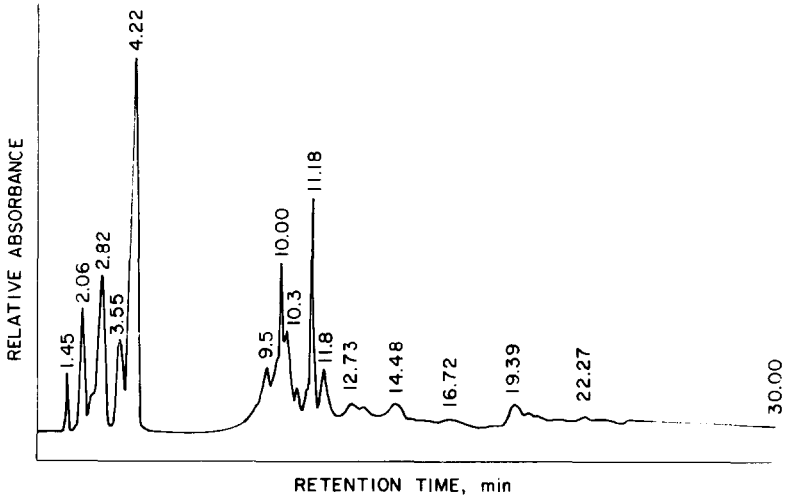


Fig. 5. Separation of sodium benzylnaphthalenesulfonate components. Stationary phase and mobile phase as in Fig. 2.

well separated. There is a substantial decrease in the retention time of the surfactant anions, as compared to the corresponding model anions listed in Table I. The correlation between a decrease in retention time and the size of the hydrophobe is illustrated by the retention data in Table II.

The separation of the petroleum sulfonate Witco TRS-40, a mixture of alkylaryl sulfonates, is shown in Fig. 6. The mixture is separated into broad mono- and disulfonate groups. The lack of fine structure within each group as compared to that obtained for sodium dodecylbenzenesulfonate and benzylnaphthalenesulfonate suggests a narrow molecular structure distribution of components in the mixture which may or may not be very complex. The component eluted at 1.44 min is observed in the separation of the majority of the synthetic and petroleum sulfonates studied and is most likely unsulfonated material. The early elution of these components could interfere with the detection of monocarboxylates, if present. No dicarboxylates are detected in the chromatogram of the TRS-40 mixture and, therefore, the presence of

TABLE II

SURFACTANTS

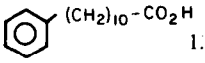
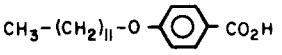
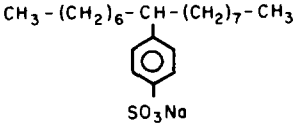
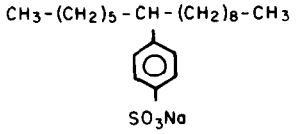
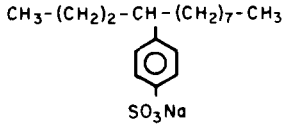
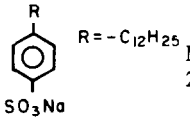
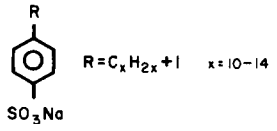
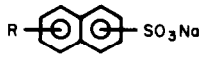
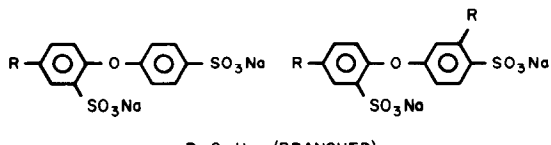
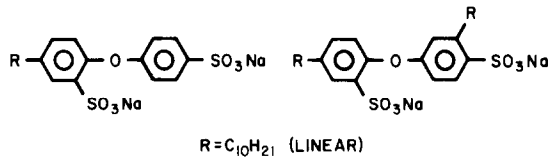
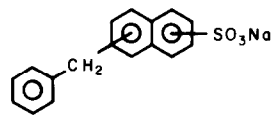
Surfactant	*Structure*	*Retention time (min)*
Phenylundecanoic acid		1.35
p-Dodecyloxybenzoic acid		1.34 1.45
Sodium *p*-(8-hexadecyl)-benzene sulfonate (Texas No. 1)		2.24
Sodium *p*-(7-hexadecyl)-benzene sulfonate		2.21
Sodium *p*-(4-dodecyl)-benzene sulfonate		2.44
Sodium dodecyl benzene sulfonate (Pfaltz & Bauer)		Multiple peaks 2.03–4.03
Conoco		Multiple peaks 1.47–4.12
Sodium alkylnaphthalene sulfonate		1.49, 3.57

TABLE II (*continued*)

Surfactant	*Structure*	*Retention time (min)*
Dowfax 2A1	MIXTURE OF  $R=C_{12}H_{25}$ (BRANCHED)	9.74
Dowfax 3B2	MIXTURE OF  $R=C_{10}H_{21}$ (LINEAR)	8.79, 9.77
Witco TRS-18	COMPLEX MIXTURE OF ALKYLARYL SULFONATES	Multiple peaks 1.9–2.8, 8.3–10.8, 19.4
Witco TRS-40	COMPLEX MIXTURE OF ALKYLARYL SULFONATES	Multiple peaks 1.44, 1.9–3.2, 8.3–12
Sodium benzylnaphthalene sulfonate		Multiple peaks 1.45–4.22, 9.5–16.72, 19.39–22.27

carboxylates is unlikely. Nevertheless, carboxyl groups could still be present on compounds containing sulfonate groups or on heterocyclic aromatic compounds. As demonstrated by several model compounds, these mixed carboxylate–sulfonate compounds are eluted in the same region as the equally charged sulfonates.

A similar separation is obtained for petroleum sulfonate Witco TRS-18. As shown in Table II, the mixture is separated into mono, di- and trisulfonates. The major monosulfonate and disulfonate components are eluted more quickly for TRS-18 than for TRS-40. This is consistent with their relative hydrophobicity and molecular size. The average equivalent weight of TRS-18 is 520 g/equiv. compared to 340 g/equiv. for TRS-40.

CONCLUSION

Mixtures of mono-, di- and polycarboxylates and sulfonates are separated by anion-exchange chromatography. A gradient of pH and ionic strength is used to

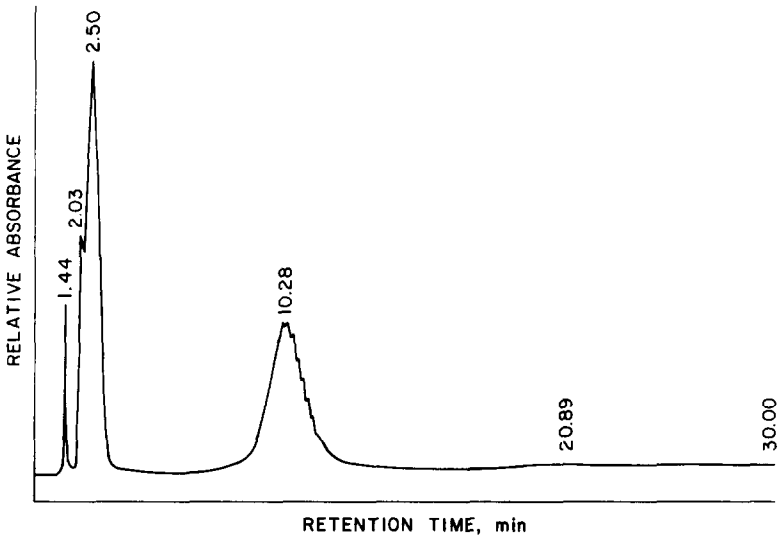


Fig. 6. Separation of petroleum sulfonate Witco TRS-40 components. Stationary phase and mobile phase as in Fig. 2.

control the elution of the anions. Separation by number and type of anionic group is readily obtained. The method is particularly suitable for the analysis of pretroleum sulfonate mixtures. The degree of sulfonation as well as the extent of variation in the structure of the alkylaryl part of the anions can be observed.

REFERENCES

1 E. E. Gilbert, *Sulfonation and Related Reactions*, Wiley, New York, 1965, p. 32.
2 V. I. Antonishin and B. S. Grinenko, *Izv. Vyssh. Uchebn. Zaved., Neft Gaz.*, 8 (5) (1965) 47; *C.A.*, 63 (1965) 6831e.
3 C. D. Scott, J. E. Attrill and N. G. Anderson, *Proc. Soc. Exp. Biol. Med.*, 125 (1967) 181.
4 C. D. Scott, *Clin. Chem.*, 14 (1968) 521.
5 S. Katz and C. A. Burtis, *J. Chromatogr.*, 40 (1969) 270.
6 P. Jandera and J. Churáček, *J. Chromatogr.*, 86 (1973) 351.
7 B. F. Nilsson and O. Samuelson, *J. Chromatogr.*, 198 (1980) 267.
8 L. M. Jahangir and O. Samuelson, *J. Chromatogr.*, 237 (1982) 371.
9 R. H. Stehl, *Anal. Chem.*, 42 (1970) 1802.
10 D. R. Zornes, G. P. Willhite and M. J. Michnick, *Soc. Pet. Eng. J.*, June (1978) 207.