Journal of Chromatography, 250 (1982) 43–54
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,210

SEPARATION OF STRUCTURALLY RELATED AROMATIC SULPHONIC ACIDS AND SULPHATES IN SYNTHESIS MIXTURES BY ION-PAIR LIQUID CHROMATOGRAPHY

P.-O. LAGERSTROM
Department of Analytical Chemistry, AB Hässle, S-431 83 Mölndal (Sweden)
(Received July 16th, 1982)

SUMMARY

Separation and determination of products formed by sulphonation of alkylphenols were accomplished by reversed-phase ion-pair liquid chromatography and UV detection. The chromatographic system consisted of aqueous eluents with methanol as organic modifier, tetraethylammonium as ion-pairing agent and LiChrosorb RP-8 as stationary phase. The presence of less than 0.1 % of a compound could be determined with acceptable precision and accuracy.

A comparison was made between various chromatographic systems containing methanol or acetonitrile as organic modifiers and tetraethyl-, tetrapropyl- or tetrabutylammonium as ion-pairing agents. Separation factors were determined between compounds differing in the nature and positions of alkyl and polar substituents.

INTRODUCTION

The mechanism of sulphonation of phenolic compounds has been studied extensively[1–5], but a major problem has been the separation of the different reaction products prior to determination. Spectrophotometry[1], bromodesulphonation[2] and paper chromatography[6] have been used along with gas–liquid chromatography[7–9]. The latter method could not be applied for the determination of more highly sulphonated products, *e.g.*, disulphonic acids, and also comprised a derivatization step thereby introducing the possibility for changes in the proportions between the different compounds in the reaction mixture and thereby jeopardizing the elucidation of the true reaction mechanism. However, during the last five years, high-performance liquid chromatography (HPLC) has been successfully applied for separation of sulphates and sulphonates using ion-exchange[10], ion-pair normal-phase[11–13] and above all reversed-phase ion-pair modes[14–28].

The aim of this study was to develop LC systems for the separation and determination of the components of reaction mixtures resulting from the sulphonation of different alkylphenols, *viz.*, 2-methyl-, 3-methyl-, 2-isopropyl-, 2-cyclohexyl- and 2-*tert.*-butylphenol, in order to elucidate the kinetics and reaction mechanism of the sulphonation[3–5]. The reaction products were mono- and disulphonic acids and phenyl

0021-9673/82/0000–0000/$02.75

hydrogen sulphates, the structures of which could be postulated from their retention behaviour.

EXPERIMENTAL

Chemicals and reagents

Methanol (p.a.; E. Merck, Darmstadt, G.F.R.) and acetonitrile (HPLC grade: Rathburn Chemicals, Walkerburn, Great Britain) were used without further purification. Tetraethylammonium (TEA), tetrapropylammonium (TPrA) and tetrabutylammonium (TBA) hydrogensulphate were obtained from the Department of Organic Chemistry, AB Hässle. Aqueous solutions of the ammonium compounds were neutralized to pH 7–10 with sodium hydroxide before use. All reagent and buffer solutions were prepared from analytical grade chemicals. All reference substances (Table I) were synthesized[3–5] by Dr. Gert Strandlund, AB Hässle, and the purity checked by NMR and LC.

Liquid chromatographic system

The liquid chromatograph consisted of an LDC 711-47 LC-pump, an LDC SpectroMonitor III spectrophotometer and a Rheodyne sampling valve with a sample loop of 20 μl. Chromatographic columns (150 × 4.5 mm) were packed with LiChrosorb RP-8, 5 μm (E. Merck), and operated at 1.0 ml/min. The performance of the columns was maintained over a long period if the top of the columns was exchanged every day. The eluents contained sodium phosphate buffer of pH 6.5. The total ionic strength was 0.20 which included added quaternary ammonium sodium sulphate (Table II). The retention time of an unretained solute, t_0, was determined by injection of dichromate dissolved in the eluent without any alkylammonium present.

Analysis of reaction mixtures

Reaction mixtures from various sulphonations of monoalkylphenols[3–5] were diluted 10–100 times in the mobile phase. The diluted samples (20 μl) were injected onto the chromatographic column. The eluate was monitored by a UV-detector operated at 212 nm. Quantitations were based on peak height measurements and monitored reference samples. The minimum determinable concentration of a compound was less than 0.1 % of the total sulphonate content.

RESULTS AND DISCUSSION

Retention principles

The retention of ionic solutes on a non-polar solid phase can be regulated by the kind and concentration of ionic or neutral modifier and ion-pairing agent (counter ion) present in the aqueous eluent. Ionic and neutral species will compete with the solute for the adsorption capacity of the solid phase. Methanol or acetonitrile was used as neutral modifier and different alkylammonium ions (Q^+) were tested as ion-pairing agents. The anionic solutes (sulphonates and sulphates) were either mono- or divalent anions (X^-, Y^{2-}).

In a chromatographic system, the distribution process of a solute to an adsorbing surface can be illustrated by

$$Q_m^+ + X_m^- + A_s \rightleftharpoons QXA_s$$

TABLE I

COMPOUNDS STUDIED AND THEIR CAPACITY FACTORS WITH 30% METHANOL IN PHOSPHATE BUFFER pH 6.5, AS THE ELUENT

Compound No.	*Designation (R in R–Ph)*	*k'*
2-Methylphenol series		
1	1-SO_3H-2-OH-3-CH_3	0.50
2	1-SO_3H-3-OH-4-CH_3	−0.01
3	1-SO_3H-3-CH_3-4-OH	−0.43
4	1,3-di-SO_3H-4-OH-5-CH_3	−0.55
5	1-OSO_3H-2-CH_3	0.43
6	1-SO_3H-3-CH_3-4-OSO_3H	−0.94
7	1-OH-2-CH_3	1.05
3-Methylphenol series		
8	1-SO_3H-2-OH-4-CH_3	0.26
9	1-SO_3H-2-OH-6-CH_3	0.36
10	1-SO_3H-2-CH_3-4-OH	−0.57
11	1,3-di-SO_3H-4-OH-6-CH_3	−0.45
12	1-OSO_3H-3-CH_3	0.48
13	1-SO_3H-2-CH_3-4-OSO_3H	< −1
14	1-OH-3-CH_3	1.03
2-Isopropylphenol series		
15	1-OSO_3H-2-$CH(CH_3)_2$	1.14
16	1-SO_3H-2-OH-3-$CH(CH_3)_2$	1.32
17	1-SO_3H-3-$CH(CH_3)_2$-4-OH	0.27
18	1-SO_3H-2-OH-5-$CH(CH_3)_2$	1.02
2-Cyclohexylphenol series		
19	1-OSO_3H-2-cyclohexyl	>2
20	1-SO_3H-2-OH-3-cyclohexyl	>2
21	1-SO_3H-3-cyclohexyl-4-OH	1.12
22	1-SO_3H-3-cyclohexyl-4-OSO_3H	0.30
23	1,3-di-SO_3H-4-OH-5-cyclohexyl	1.01
2-tert.-Butylphenol series		
24	1-OSO_3H-2-$C(CH_3)_3$	1.45
25	1-SO_3H-2-OH-3-$C(CH_3)_3$	1.80
26	1-SO_3H-3-$C(CH_3)_3$-4-OH	0.84
27	1-SO_3H-3-$C(CH_3)_3$-4-OSO_3H	−0.19
28	1,3-di-SO_3H-4-OH-5-$C(CH_3)_3$	0.68
29	1-OSO_3H-2,4-di-$C(CH_3)_3$	>2
30	1-SO_3H-2-OH-3,5-di-$C(CH_3)_3$	>2
31	1-OSO_3H-4-$C(CH_3)_3$	1.55
32	1-SO_3H-2-OH-5-$C(CH_3)_3$	1.26
33	1-SO_3H-2-OSO_3H-5-$C(CH_3)_3$	0.62
34	1-OH-2-$C(CH_3)_3$	1.70
35	1-OH-4-$C(CH_3)_3$	1.90
36	1-OSO_3H	0.08
37	1-SO_3H-2-OH	−0.11
38	1-SO_3H-4-OH	−0.77
39	1,3-SO_3H-4-OH	< −1
40	1-OH	0.66

where the subscripts m and s refer to the eluent and solid phase respectively and A is the number of available adsorption sites in moles per gram of solid phase. The equilibrium constant for the process is given by:

$$[QXA]_s/[Q^+]_m[X^-]_m[A]_s = K_{QX} \quad (1)$$

TABLE II

CHROMATOGRAPHIC SYSTEMS

Stationary phase: LiChrosorb RP-8, 5 μm, 150 × 4.5 mm. Eluents: phosphate buffer solutions pH 6.5 with listed modifiers and ion-pair reagents. The total ionic strength is 0.20 in all cases. Flow-rate: 1 ml min. Detector wavelength: 212 nm.

Eluent No	*Organic solvent*		*Quaternary ammonium ion*	
1	Methanol	10%	–	
2		20%	–	
3		30%	–	
4		35%	–	
5		55%	–	
6		10%	Tetraethylammonium	0.01 mol/l
7		10%		0.03 mol l
8		10%		0.05 mol l
9		35%		0.01 mol l
10		55%		0.01 mol/l
11		10%	Tetrapropylammonium	0 01 mol i
12		30%		0 01 mol l
13		10%	Tetrabutylammonium	0 01 mol l
14	Acetonitrile	10%	–	
15		20%	–	
16		10%	Tetrapropylammonium	0.01 mol l
17		20%		0.01 mol l

Anions from the buffer are similarly distributed to the solid phase as ion pairs which compete with QX for the available adsorption sites. The buffer and solute anions can also be adsorbed as the NaX ion pair (Na^+ is the buffer cation).

The capacity ratio of the sulphonates and sulphates retained as ion pairs is defined as:

$$k'_x = q([QXA]_s + [NaXA]_s)/[X^-]_m \quad (2)$$

This expression is valid provided that $[HX]_m$ can be disregarded, as is the case at pH 6.5. ($q = V_s/V_m$ is the ratio of solid phase to eluent in the column.)

Regulation of retention

Reversed-phase LC using aqueous eluents was preferred since the sample from the reaction mixtures could be injected directly on to the chromatographic column. Various chromatographic systems were used with LiChrosorb RP-8 as the column packing and eluents containing different quaternary ammonium ions such as tetraethyl-, tetrapropyl- and tetrabutylammonium as ion-pairing agents (Table II). Methanol or acetonitrile as organic modifier in sodium phosphate buffer solutions of pH 6.5 constituted the eluent. By varying the type and concentration of the ion-pairing agent (counter ion, Q^+) the retention could be adapted to the separation problem. One example is shown in Fig. 1, where the change in $\log k'$, $\Delta \log k'$, is plotted for mobile phases containing an increasing concentration of TEA, 0.01, 0.03 and 0.05 mol/l, or 0.01 mol/l of TPrA or TBA. Three groups of compounds can be distinguished, phenols (compound 7), monovalent sulphonates or sulphates (1–3,5) and divalent

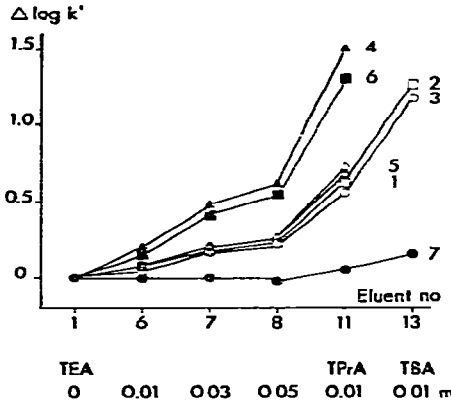


Fig. 1. Influence of quaternary ammonium ions in the eluent on log k' of some substituted 2-methylphenols. Δ log k' = log $k'_{quatern}$ − log $k'_{eluent\ 1}$. Eluents 1, 6, 7, 8, 11 and 13 refer to Table II and compounds 1–7 to Table I.

anions (4,6). The divalent anions are more strongly influenced than the monovalent ones, while the phenol is only slightly affected. The effect of TEA (0.01 mol/l) is limited, resulting in an increase of log k' by about 0.1 (monovalent) and 0.2 log units (divalent anion) as compared with 0.7 and 1.4 for TPrA and 1.2 and 2.1 for TBA (Table III). The increase in log k', calculated per additional methylene group in the counter ion, is as low as 0.13–0.15, going from TEA to TBA. By increasing the content of methanol from 10% to 30%, Δ log k' between TPrA and TEA decreased from 0.69 to 0.22 for monovalent anions and from 1.40 to 0.47 for divalent ones. A decrease of the same magnitude was seen in acetonitrile, where a 10% increase in content lowered Δ log k' from 0.55 to 0.40 (monovalent) and from 1.17 to 0.75 (divalent). Accordingly, a high selectivity is favoured by a low content of organic modifier.

TABLE III

INCREASE IN LOG k' (Δ log k') FOR MONOVALENT AND DIVALENT SULPHONIC ACIDS, OBTAINED WITH ELUENTS CONTAINING A QUATERNARY AMMONIUM ION (0.01 mol/l)

Eluent No.	*Quaternary ammonium ion and organic solvent*	*Δ log k'*	
		Monovalent acids	*Divalent acids*
6 and 1	Tetraethylammonium 10% Methanol	0.08 ± 0.02 (n = 15)	0.20 ± 0.05 (n = 9)
11 and 1	Tetrapropylammonium 10% Methanol	0.69 ± 0.09 (n = 12)	1.40 ± 0.22 (n = 6)
13 and 1	Tetrabutylammonium 10% Methanol	1.22 ± 0.04 (n = 4)	2.06 (n = 1)
16 and 14	Tetrapropylammonium 10% Acetonitrile	0.55 ± 0.07 (n = 12)	1.17 ± 0.02 (n = 5)
12 and 13	Tetrapropylammonium 30% Methanol	0.22 ± 0.04 (n = 21)	0.47 ± 0.06 (n = 8)
17 and 15	Tetrapropylammonium 20% Acetonitrile	0.40 ± 0.06 (n = 20)	0.75 ± 0.05 (n = 6)

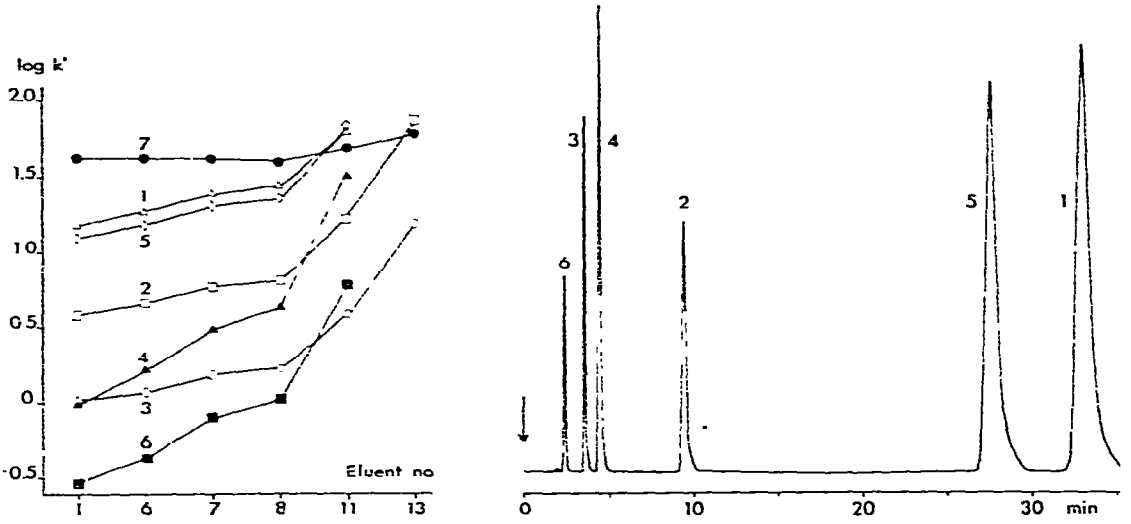


Fig. 2. Separation of some substituted 2-methylphenols using different quaternary ammonium ions in the eluent. Experimental conditions as in Fig. 1.

Fig. 3. Separation of substituted 2-methylphenols. Experimental conditions: eluent 6 (10% methanol + 0.01 mol/l TEA). Compounds 1–6 refer to Table I.

Plotting log k' of compounds 1–7 (Fig. 2) for the same eluents as in Fig. 1 shows that eluent 6 along with eluents 7 and 8 could be chosen for the separation (Fig. 3). Increasing the concentration of TEA (0.05 mol/l) or using TPrA or TBA (0.01 mol/l) would result in lower resolution.

Methanol was chosen as organic modifier in this study, its effect on the retention being compared with that of acetonitrile (Table IV). Log α ($\log k'_2 - \log k'_1$) was determined for compounds 1–7 in four eluents containing 10% of methanol or acetonitrile (eluents 1 and 14), 30% methanol or 20% acetonitrile (eluents 12 and 17, both of which also contained 0.01 mol/l TPrA). Comparing eluents 1 and 14 showed no difference in selectivity (log α) and the chromatographic performance was similar. Turning to eluents 12 and 17 (including TPrA) some pairs of compounds seemed to be better separated using methanol (*e.g.*, compounds 1 and 5, 2 and 4, 3 and 6).

Substituent effects

Owing to the large number of eluents and compounds studied it was possible to elucidate the effect of different substituents. Table V shows the difference in log k' (log α) between unsubstituted phenols and substituted ones. The sulphonate group made the phenol more hydrophilic, the effect being more pronounced the larger the distance between the groups. In *ortho*-position (1,2), hydrogen-bonding has a strong influence, in *para*-position (1,4) the polar groups are completely separated, while in *meta*-position (1,3) a weak hydrogen-bonding seemed to occur. Phenols with two sulphonate groups (*ortho* and *para*) do not differ in log α compared with the monosulphonate (*para*), the extra *ortho*-sulphonate thus not contributing to the polar character.

Table VI shows the separation factor (log α) for substituted 2-alkylphenols only differing in the size of the alkyl substituent. Four different eluents were ex-

TABLE IV

SEPARATION FACTORS (log α) OBTAINED IN THE SEPARATION OF SUBSTITUTED 2-METHYLPHENOLS USING EITHER METHANOL OR ACETONITRILE AS THE ORGANIC MODIFIER

Compound No.	*Eluent No.*							
	1 (10% CH_3OH)		*14 (10% CH_3CN)*		*12 (30% CH_3OH)**		*17 (20% CH_3CN)**	
	log k'	*log α*	*log k'*	*log α*	*log k'*	*log α*	*log k'*	*log α*
7	1.62		1.49		1.04		1.06	
		0.44		0.56		0.31		0.35
1	1.18		0.93		0.73		0.71	
		0.08		0.04		0.07		0.01
5	1.10		0.89		0.66		0.70	
		0.52		0.60		0.50		0.60
2	0.58		0.29		0.16		0.10	
		0.57		0.52		0.26		0.00
4	0.00**		−0.23		−0.10		0.10	
		0.01		0.00		0.19		0.11
3	0.01**		−0.23		−0.29		−0.21	
		0.53		0.53		0.25		0.02
6	−0.53		−0.76		−0.54		−0.23	

* 0.01 mol/l TPrA as counter ion.

** Retention order is reversed.

amined, 1 and 3 with 10 and 30% methanol, 15 with 20% acetonitrile and 17 the corresponding eluent with 0.01 mol/l TPrA. Three different groups of compounds were studied, one with the sulphonate group *ortho* to the phenol, one with the sulphonate *para* to the phenol and one with a sulphate ester group replacing the phenol. The results were similar for the last two groups, *i.e.*, the increase in log k' calculated per carbon atom in the alkyl substituent (= log α per carbon) was about 0.25–0.45, the larger figure being obtained with the eluent with a low content of organic modifier. The first group, with the sulphonate group *ortho* to the phenol, gave values of

TABLE V

SUBSTITUENT EFFECT: SEPARATION FACTORS (log α) BETWEEN NON-SULPHONATED AND SULPHONATED ALKYLPHENOLS

$\log \alpha = \log k'_{\text{alkylphenol}} - \log k'_{\text{substituted}}$. Eluents 1 and 3, 10 and 30% methanol. Eluents 14 and 15: 10 and 20% acetonitrile.

Substituent	*log α*				*n*
	1	*3*	*14*	*15*	
1-SO_3-2-OH	0.60	0.61	0.78	0.82	5
1-SO_3H-3-OH	1.04	1.06	1.20	1.34	1
1-SO_3H-4-OH	1.60	1.45	1.65	1.70	4
1-OSO_3H	0.52	0.55	0.50	0.76	4
1-SO_3H-4-OSO_3H	2.01	2.04	2.06	2.43	2
1,3-di-SO_3H-4-OH	1.51	1.48	1.61	1.83	3

TABLE VI

SEPARATION FACTORS (log α) PER CARBON IN THE SUBSTITUENT FOR SUBSTITUTED ALKYL PHENOLS

Eluents 1 (10% CH_3OH); 3 (30% CH_3OH); 15 (20% CH_3CN) and 17 (20% CH_3CN, 0.01 mol l TPrA).

Compound No.	*R*	*log α per carbon in eluent*			
		1	*3*	*15*	*17*
Substituents: 1-SO_3H-2-OH-3-R					
37	H				
1	CH_3	0.80	0.61	0.49	0.48
16	$CH(CH_3)_2$	–	0.48	0.42	0.58
25	$C(CH_3)_3$	–	0.48	0.43	0.55
20	Cyclohexyl	–	–	0.34	–
Substituents: 1-SO_3H-3-R-4-OH					
38	H				
3	CH_3	0.48	0.34	–	0.21
17	$CH(CH_3)_2$	0.46	0.35	0.28	0.25
26	$C(CH_3)_3$	0.51	0.40	0.33	0.31
21	Cyclohexyl	0.41	0.32	0.27	0.25
Substituents: 1-OSO_3H-2-R					
36	H				
5	CH_3	0.44	0.35	0.35	0.23
15	$CH(CH_3)_2$	–	0.35	0.33	0.29
24	$C(CH_3)_3$	–	0.34	0.32	0.29
19	Cyclohexyl	–	–	0.31	–

TABLE VII

THE INFLUENCE ON log k' FROM ALKYL SUBSTITUTION IN DIFFERENT POSITIONS

Experimental conditions: see Table II. $\log \alpha = \log k'_1 - \log k'_2$.

Substance No.	*Substituents*	*log α in eluent*	
		1	*14*
7	1-OH-2-CH_3	0.01	0.03
14	1-OH-3-CH_3		
1	1-SO_3H-2-OH-3-CH_3	0.14	0.14
9	1-SO_3H-2-OH-6-CH_3		
3	1-SO_3H-3-CH_3-4-OH	0.21	0.07
10	1-SO_3H-2-CH_3-4-OH		
		log α in eluent	
		10	*15*
34	1-OH-2-$C(CH_3)_3$	0.19	0.19
35	1-OH-4-$C(CH_3)_3$		
25	1-SO_3H-2-OH-3-$C(CH_3)_3$	0.31	0.51
32	1-SO_3H-2-OH-5-$C(CH_3)_3$		
24	1-OSO_3H-2-$C(CH_3)_3$	−0.06	−0.18
31	1-OSO_3H-4-$C(CH_3)_3$		

log α per carbon of around 0.4–0.6. An explanation for this might be that the phenol function is directed away from the alkyl substituent towards the hydrogen-bonding sulphonate. Going vertically down the groups it can be concluded that the cyclohexyl substituent gives somewhat lower values of log α per carbon than the other substituents. The addition of a counter ion, TPrA, to the mobile phase had no effect on the separation factor.

Table VII shows the difference in separation factor (log α) for the compounds containing alkyl substituents in different positions with respect to the phenol group, *viz. ortho*, *meta* and *para*. No difference in log k' was obtained for the 2- and 3-methylphenols. A sulphonate group *ortho* or *meta* to the methyl group made a significant difference since the compounds with the methyl group *meta* to the sulphonate were more lipophilic than the *ortho*-methyl sulphonate. The methyl group is so small that the larger sulphonate group shields it from the interaction with the stationary phase. A corresponding behaviour was seen with the last three pairs of compounds in Table VII, where in two cases a bulky *tert.*-butyl group shields the smaller phenol group, thus giving the *ortho-tert.*-butyl compounds a more lipophilic character than the *para* analogues. The situation was slightly more complicated with a *tert.*-butyl and a sulphate ester *ortho* and *para* to each other (nos. 24 and 31).

Applications

The sulphonation of phenols can result in rather complex reactions as illus-

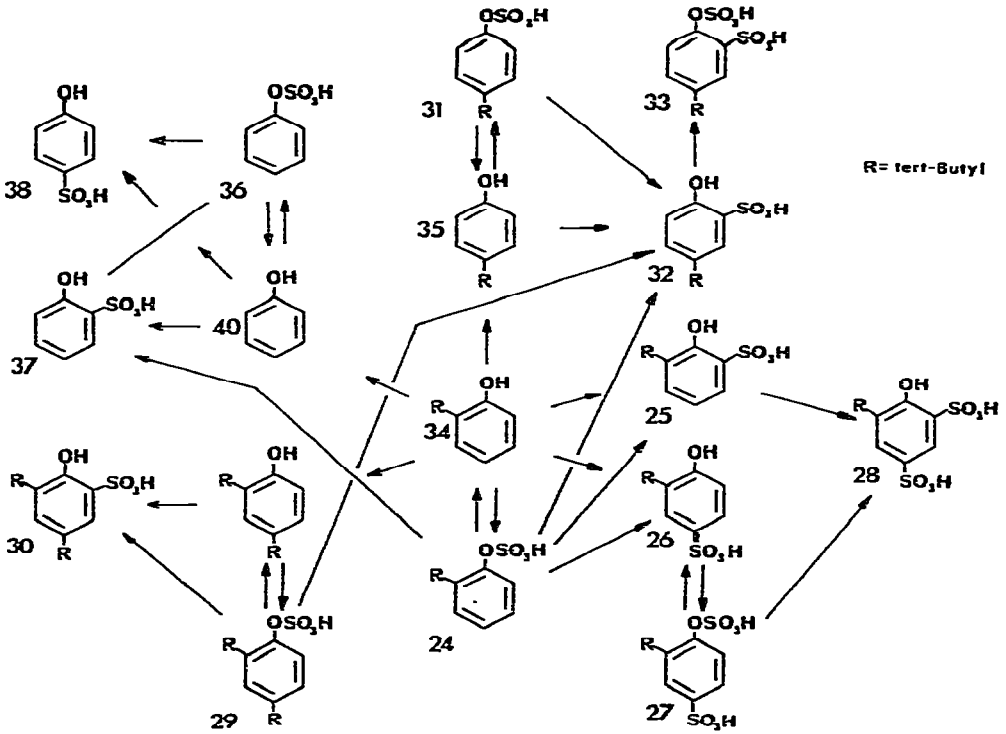


Fig. 4. Proposed reaction scheme for sulphonation of 2-*tert.*-butylphenol with chlorosulphonic acid (taken from ref. 5).

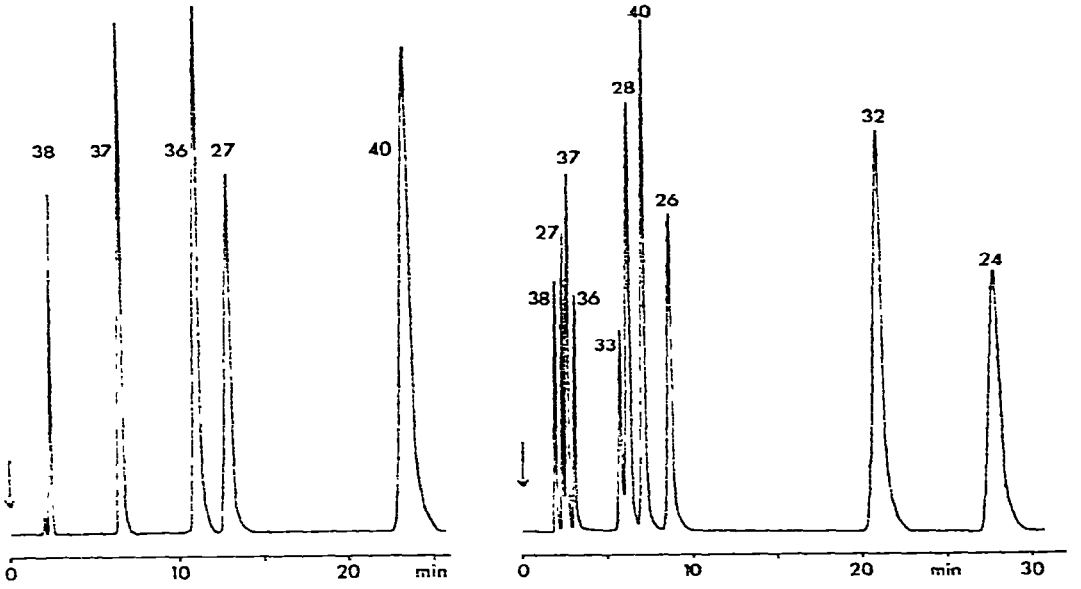


Fig. 5. Separation of substituted phenols and 2-*tert.*-butylphenols. Experimental conditions: eluent 6. Compounds as in Table I.

Fig. 6. Separation of substituted phenols and 2-*tert.*-butylphenols. Experimental conditions: eluent 9 (35% methanol – 0.01 mol l TEA). Compounds as in Table I.

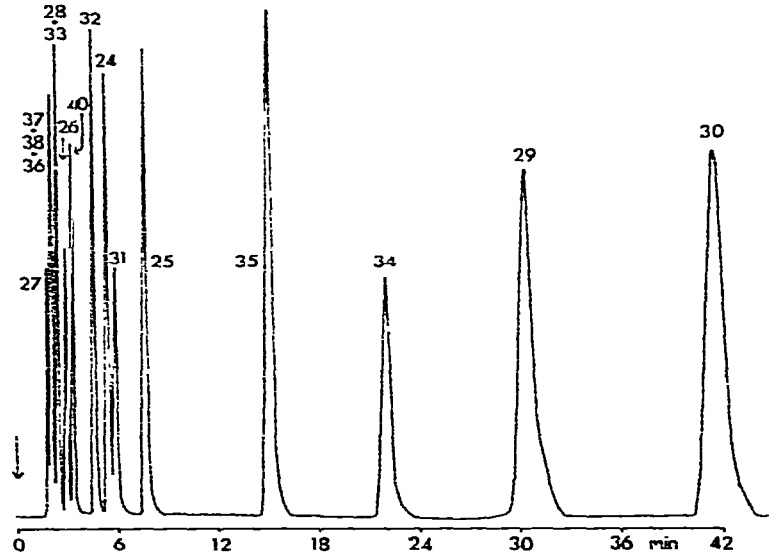
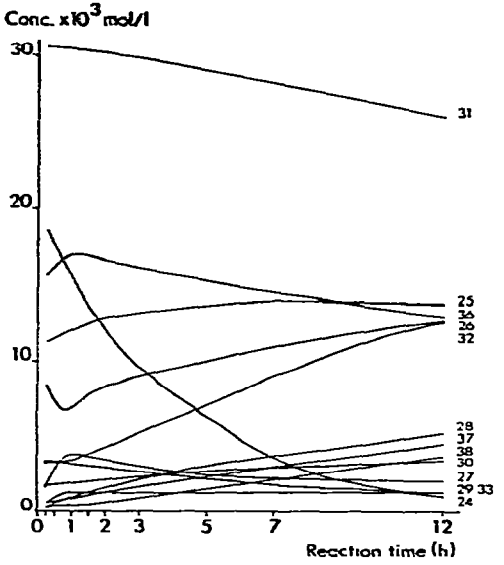


Fig. 7. Separation of substituted phenols and 2-*tert.*-butylphenols. Experimental conditions: eluent 10 (55% methanol + 0.01 mol/l TEA). Compounds as in Table I.



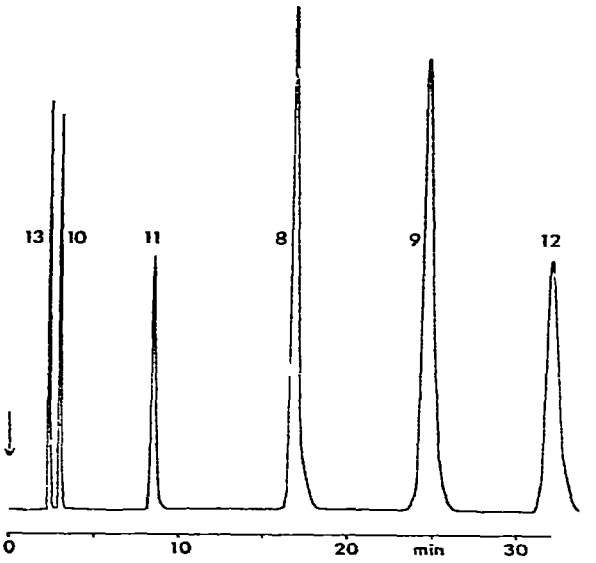
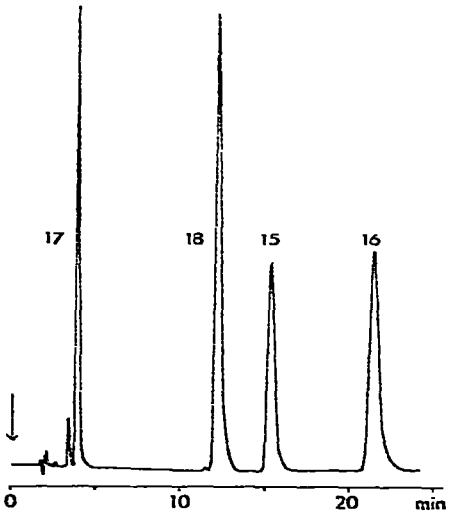


Fig. 8. Sulphonation of 2-*tert.*-butylphenol with chlorosulphonic acid, monitored by liquid chromatography using eluents 6, 9 and 10. Data taken from ref. 5.

Fig. 9. Separation of substituted 3-methylphenols. Experimental conditions: eluent 6. Compounds as in Table I.

trated in Fig. 4 for a proposed reaction scheme for the sulphonation of *tert.*-butylphenol with chlorosulphonic acid. At least thirteen different sulphonic acids or sulphates were obtained. By applying ion-pair liquid chromatography it was possible to separate all of these compounds. Since the capacity factors of the different products varied by almost three orders of magnitude and no gradient elution was



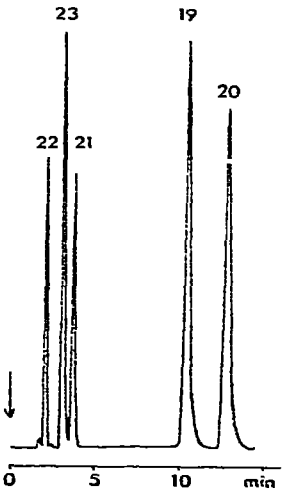


Fig. 10. Separation of substituted 2-isopropylphenols. Experimental conditions: eluent 9. Compounds as in Table I.

Fig. 11. Separation of substituted 2-cyclohexylphenols. Experimental conditions: eluent 10. Compounds as in Table I.

available, it was necessary to use three different mobile phases, all containing 0.01 mol/l TEA. For the more polar compounds (27, 36–38), 10% methanol was used (eluent 6, Fig. 5), for the medium polar compounds (26, 28, 33, 40), 35% methanol (eluent 9, Fig. 6) and for the most lipophilic products (24, 25, 29–32, 34, 35), 55% methanol (eluent 10, Fig. 7). The results (*cf.*, ref. 5) from the liquid chromatographic measurements are shown in Fig. 8. It can be seen that sulphates are formed as intermediates since their concentrations decreased with time (compounds 24, 27, 31 and 36).

Examples are also given on the separation of 3-methylphenols (Fig. 9; *cf.*, ref. 3), 2-isopropylphenols (Fig. 10; *cf.*, ref. 4) and 2-cyclohexylphenols (Fig. 11; *cf.*, ref. 4). In all cases methanol was used as the organic modifier (10, 35 and 55% respectively) and TEA as the counter ion (0.01 mol/l). As is seen in the figures, excellent separations were obtained in all cases.

ACKNOWLEDGEMENTS

I thank Dr. Gert Strandlund for supplying all the reference substances and Dr. Bengt-Arne Persson for discussion of the manuscript.

REFERENCES

1 A. A. Spryskov and B. G. Gnedin, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 7 (1964) 61.
2 B. J. Karavaev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 5 (1962) 766.
3 G. Strandlund and P.-O. Lagerström, *Acta Chem. Scand., Ser. B*, 33 (1979) 261.
4 A. Ericsson, G. Strandlund and P.-O. Lagerström, *Acta Chem. Scand., Ser. B*, 33 (1979) 567.
5 A. Ericsson, G. Strandlund and P.-O. Lagerström, *Acta Chem. Scand., Ser. B*, 34 (1980) 467.
6 F. Langmeier, E. Mück and D. Kokes, *Collect. Czech. Chem. Commun.*, 24 (1959) 2066.
7 D. Klockow, W. Bayer and W. Faigle, *Z. Anal. Chem.*, 292 (1978) 385.
8 K. M. Baker and G. E. Boyce, *J. Chromatogr.*, 117 (1976) 471.
9 J. S. Parsons, *J. Gas Chromatogr.*, 5 (1967) 254.
10 R. J. Pasarell and E. S. Jakobs, *J. Chromatogr. Sci.*, 13 (1975) 153.
11 U. Streule and A. v. Wattenwyl, *Chromatographia*, 12 (1979) 25.
12 J. H. Knox and G. R. Laird, *J. Chromatogr.*, 122 (1976) 17.
13 W. J. T. Brugman and J. C. Kraak, *J. Chromatogr.*, 205 (1981) 170.
14 C. T. Hung and R. B. Taylor, *J. Chromatogr.*, 202 (1980) 333.
15 C. T. Hung and R. B. Taylor, *J. Chromatogr.*, 209 (1981) 175.
16 C. P. Terweij-Groen, S. Heemstra and J. C. Kraak, *J. Chromatogr.*, 161 (1978) 69.
17 A. Tilly Melin, Y. Askemark, K.-G. Wahlund and G. Schill, *Anal. Chem.*, 51 (1979) 976.
18 A. Tilly Melin, M. Ljungcrantz and G. Schill, *J. Chromatogr.*, 185 (1979) 225.
19 B. Fransson, K.-G. Wahlund, I. M. Johansson and G. Schill, *J. Chromatogr.*, 125 (1976) 327.
20 H.-U. Emcke, H. Kelker, K.-H. König and H. Ullner, *Z. Anal. Chem.*, 294 (1979) 251.
21 K.-G. Wahlund, *J. Chromatogr.*, 115 (1975) 411.
22 P. Jandera and J. Churacek, *J. Chromatogr.*, 197 (1980) 181.
23 P. Jandera, J. Churacek and J. Bartosova, *Chromatographia*, 13 (1980) 485.
24 C. Prandi and T. Venturini, *J. Chromatogr. Sci.*, 19 (1981) 308.
25 D. Westerlund and A. Theodorsen, *J. Chromatogr.*, 144 (1977) 27.
26 C. P. Terweij-Groen and J. C. Kraak, *J. Chromatogr.*, 138 (1977) 245.
27 K.-G. Wahlund and I. Beijersten, *J. Chromatogr.*, 149 (1978) 313.
28 D. P. Wittmer, N. O. Nuessle and W. G. Haney, Jr., *Anal. Chem.*, 47 (1975) 1422.