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SEPARATION OF ISOMERIC MONO-, DI- AND TRIBUTYLPHENOLS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY ON OCTADECYLSILICA WITH METHANOL–WATER USING ALKYL NITRILE AND ALKYLAMINE AS SURFACE MODIFIERS

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SUMMARY

High-performance liquid chromatography with octadecylsilica columns has been used to separate a model mixture of isomeric mono-, di- and tributylphenols. The optimum mobile phase composition was evaluated using the criterion of minimum theoretical plate number necessary for a given resolution of the test components. A dynamic modification of the alkylsilica surface was performed by the adsorption of hexyl nitrile and hexylamine, respectively, added in small concentrations to the eluent. This surface modification results in significant changes in the selectivity of the phase system, and an improved separation of the test compounds can be obtained.

INTRODUCTION

Alkyl-substituted phenols are a group of chemicals of great industrial interest. They are often used as antioxidants, raw materials in the production of phenol–formaldehyde resins and plant protection agents. Their analysis is of great importance for environmental protection[1–3] and industrial product control[4–6].

The reaction usually applied for the preparation of these compounds is the alkylation of phenol. The composition of the alkylation products depends on the reaction conditions and the nature of the alkylation agent. In the alkylation of phenol with alkenes a mixture of mono-, di- and trialkylphenols substituted preferentially in *ortho-* and *para-*positions is formed[7,8]. In the case of butenes, phenols with *tert.*-butyl substitutents prevail. *sec.*-Butyl-substituted phenols occur in lower yields. Because of dimerization of the alkylation agent, phenols with longer alkyl chains can also be formed[9].

Much attention has been paid to the separation of butylphenols by high-performance liquid chromatography (HPLC)[10–16]. Callmer *et al.*[16] investigated the elu-

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tion behaviour of alkylphenols in various phase systems and established the effects of the mobile phase composition on the chromatographic separation of these phenols. Popl et al.[17] investigated the influence of chain-branching, evaluating the different contributions of secondary and tertiary carbon atoms in the alkyl chains to the retention indices on polymeric reversed-phase Separon SE systems.

In our study we have evaluated the optimum conditions for the separation of butylphenols by isocratic HPLC using octadecylsilica as the adsorbent and methanol–water mixtures as the eluents. The potential of solvent-induced surface activation by small concentrations of additives in the mobile phase was investigated using hexylamine or hexyl nitrile as additives.

EXPERIMENTAL

Apparatus

Chromatographic experiments were carried out using a high-performance liquid chromatograph (Model S100; Siemens, Karlsruhe, F.R.G.), in combination with a syringe-valve-injector (Model 7125; Rheodyne, Cotati, CA, U.S.A.) and an UV detector (Model LC3-UV; Pye Unicam, Cambridge, U.K.). A prepacked analytical column (250 mm × 4 mm I.D.) (Hibar®; E. Merck, Darmstadt, F.R.G.) packed with 5-μm LiChrosorb RP-18 was used.

Reagents and samples

The solvent components methanol, hexyl nitrile and hexylamine (E. Merck) were of analytical grade. Water used for the eluent preparation was distilled twice. Alkylphenols of 97–99% purity were obtained from different manufacturers.

Procedure

The eluent mixtures were prepared from weighed amounts of the solvent components in order to achieve high precision and accuracy. The weight ratios equivalent to the desired volume ratios were calculated by means of the densities at 25°C. When applying dynamic surface activation, eluents containing low concentrations of hexyl nitrile or hexylamine were prepared. The equilibration of the column with the modifier was achieved by pumping an eluent volume corresponding to about twenty times the column void volume. Establishment of this equilibrium was verified by the constancy of the retention data. At equilibrium, the relative standard deviation of the measurement of the capacity factors was 1%. All experiments were carried out in an isocratic mode at 25°C. The column void volume was estimated from the retention volume of formamide.

UV detection was performed at 254 nm.

RESULTS AND DISCUSSION

Effect of the eluent composition

The chromatographic capacity factors, κ_i, of the most important alkyl-substituted phenols measured for reversed-phase liquid–solid systems consisting of octadecylsilica and binary mixtures of water and methanol are listed in Table I. The data demonstrate the influence of the total number of carbon atoms, the structure and the

TABLE I

VALUES OF THE CAPACITY FACTOR, κ_i, OF VARIOUS BUTYLPHENOLS ON AN OCTADE-
CYLSILICA PACKING WITH METHANOL–WATER ELUENTS

φ is the volume fraction of methanol.

Code	Compound	κ_i				
		$\varphi = 0.55$	$\varphi = 0.60$	$\varphi = 0.70$	$\varphi = 0.80$	$\varphi = 0.90$
1	Phenol	0.79	0.58	0.36	0.19	0.10
2	3-*tert.*-Butylphenol	7.46	4.58	1.86	0.75	0.31
3	4-*tert.*-Butylphenol	7.71	4.83	1.90	0.79	0.32
4	4-*sec.*-Butylphenol	9.88	6.01	2.24	0.79	–
5	2-*sec.*-Butylphenol	10.01	6.10	2.42	0.92	0.37
6	2-*tert.*-Butylphenol	11.67	7.17	2.83	1.03	0.40
7	3,5-Di-*tert.*-butylphenol			6.91	1.88	0.65
8	4-(1,1,3,3-Tetramethylbutyl)-phenol			9.69	2.69	0.84
9	2,4-Di-*tert.*-butylphenol			11.38	2.98	0.83
10	2,4-Di-*sec.*-butylphenol			12.28	3.10	0.90
11	2,6-Di-*tert.*-butylphenol			14.08	3.59	1.19
12	2,4,6-Tri-*tert.*-butylphenol			44.32	9.45	2.03

position of the alkyl groups on the retention order of phenols. The total number of aliphatic carbon atoms in the alkyl groups of the phenol is decisive for the capacity factors and for the slope in a semilogarithmic diagram, where ln κ_i is plotted *versus* the volume fraction of the organic solvent component (see eqn. 1). Such a dependence was previously found by Callmer *let al.*[16] and Schabron *et al.*[10]. Besides the length of the alkyl chain, also the alkyl position in the aromatic ring as well as the branching of the chains influence the elution. The data in Table I show that in these octade-cylsilica systems the effect of alkyl chain branching on retention differs for *ortho*- and non-*ortho*-substituted phenols: 2-*tert.*-butylphenol is retained more strongly than 2-*sec.*-butylphenol. The *tert.*-butyl group in the *ortho*-position probably gives better shielding for the hydroxyl group than does the *sec.*-butyl group in the same position. This may effect either a stronger adsorption of the analyte on the solid surface or a weaker solvation in the bulk liquid phase. In the case of isomeric alkyl phenols substituted in the *para*-position the opposite elution order is observed: *tert.*-butyl isomer earlier than the *sec.*-butyl isomer. This has been found also for isomeric alcohols[18]. For dibutyl-substituted phenols with isomeric alkyl chains in *ortho*- and *para*-position, the effect of the branching in the *para*-substituent is predominant.

To evaluate the best separation conditions for butyl-substituted phenols with binary mixtures of methanol and water as the eluents, the retention data of the twelve test compounds in Table I have been used. The experimental capacity factors were correlated with the mobile phase composition by use of the well known semilogarithmic equation

$$\ln \kappa_i = \ln \kappa_{0i} - S_i \varphi_{MeOH} \tag{1}$$

where κ_i is the capacity factor of analyte i and φ_{MeOH} is the volume fraction of

TABLE II

LINEAR REGRESSION COEFFICIENTS, $\ln \kappa_{0i}$ AND S_i IN EQN. 1, CORRELATION COEFFICIENTS, r, AND REGRESSION ERRORS

$\Delta\ln \kappa$ is the difference between the logarithms of the experimental and the calculated capacity factors. Numbering of compounds as in Table I.

Code	S_i	$\ln \kappa_{0i}$	r	$\Delta\ln \kappa_i$				
				$\varphi = 0.55$	$\varphi = 0.60$	$\varphi = 0.70$	$\varphi = 0.80$	$\varphi = 0.90$
1	5.84	3.00	−0.998451	−0.03	−0.03	0.06	0.00	0.00
2	9.07	6.98	−0.999929	0.02	−0.02	−0.01	−0.01	0.00
3	9.08	7.02	−0.999931	0.02	0.00	−0.02	0.01	0.00
4	10.09	7.85	−0.999914	−0.01	−0.00	0.02	−0.01	−
5	9.42	7.47	−0.999943	0.01	−0.01	0.01	−0.02	0.03
6	9.65	7.77	−0.999925	−0.01	−0.01	0.03	−0.02	0.00
7	11.82	10.17	−0.998287	−	−	0.04	−0.08	0.03
8	12.23	10.81	−0.999612	−	−	0.02	−0.04	0.02
9	13.09	11.59	−0.999905	−	−	0.01	−0.03	0.00
10	13.07	11.63	−0.999521	−	−	0.03	−0.04	0.02
11	12.35	11.25	−0.998122	−	−	0.04	−0.09	0.04
12	15.42	14.58	−0.999997	−	−	0.01	0.00	0.01

methanol in the mobile phase. The values κ_{0i} and S_i are obtained by linear regression and are presented in Table II together with the correlation coefficient, r. Also given are the differences between the logarithms of the experimental capacity factors and those calculated by eqn. 1: an excellent agreement is obtained in the concentration range investigated for all compounds tested. This correlation is illustrated in Fig. 1.

The knowledge of the dependence of the capacity factors of the analytes on the mobile phase composition allows one to calculate the optimum separation conditions. This optimization, by varying the content of the organic component in a binary mixture with water, is based on (sometimes small) differences in the S_i values of the analytes, as has been pointed out by several authors[19-22]. The minimum theoretical plate number, N_{ji}, required to achieve a given resolution, R_{ji}, for the most difficult pair of compounds to separate, i and j, has been selected as the optimization criterion

$$N_{ji} = \left[\frac{R_{ji}(\kappa_i + 1)}{(r_{ji} - 1)\kappa_i}\right]^2 \qquad (2)$$

where R_{ji} is the desired chromatographic resolution and r_{ji} is the selectivity coefficient. Here the resolution of the solute pair i and j is defined by means of the standard deviation of the first eluted peak i. According to this definition, baseline separation for peaks of about equal heights is achieved with $R_{ji} = 6$. The chromatographic resolution R_{ji} is related to R_S, given by Snyder and Kirkland[23], by the simple relationship $R_{ji} = 4R_S$.

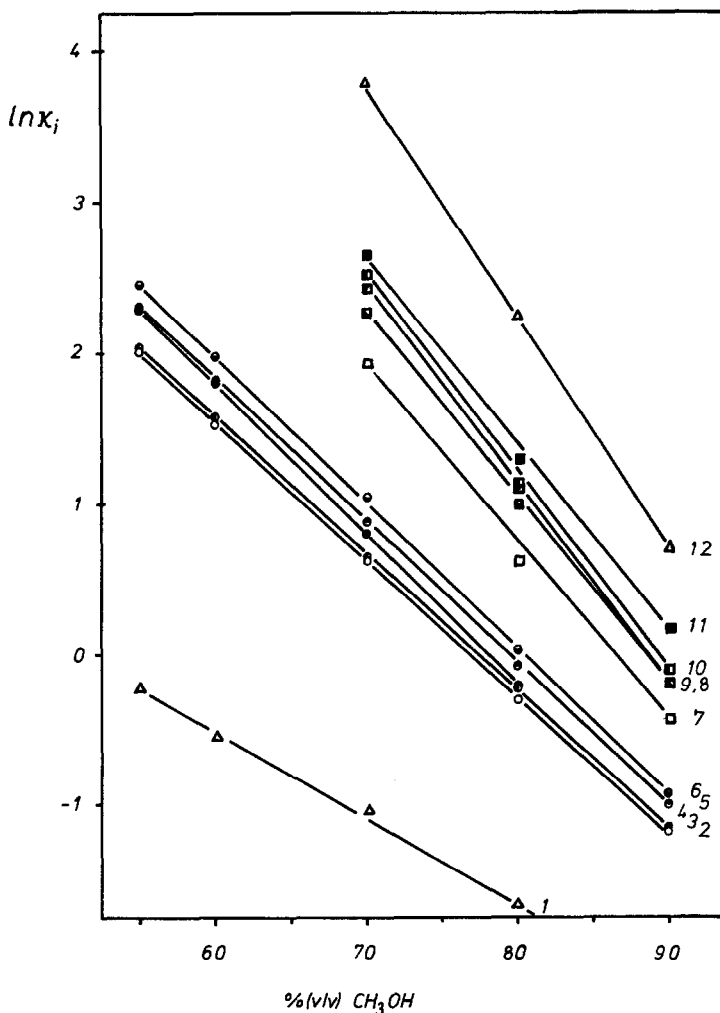An additional condition for a rapid separation is that the value of the capacity

Fig. 1. Dependence of the capacity factors of butylphenols on an octadecylsilica column on the volume fraction of methanol in eluents consisting of water and methanol. Compound numbers as in Table I.

factor of the last compound eluted is as small as possible. In isocratic elution, quite often the capacity factors of all components cannot be maintained within a sufficiently narrow range.

Great differences in the retardation between mono-, di- and tributylphenols allow only one of these groups to be adjusted within an appropriate capacity factor range of *e.g.*, $1.5 < \kappa < 4$. Examples of mobile phases for which either mono- or dibutylphenols satisfy this requirement are shown in Table III. A methanol content between 80 and 82.5% (v/v) provides a suitable elution range for the dibutylphenols. For monobutylphenols the desired capacity factor range is obtained with a methanol content between 66 and 72.5% (v/v). The optimum mobile phase composition cannot be determined only by means of an appropriate capacity factor range, but must be

TABLE III

CAPACITY FACTORS, κ_i, OF BUTYLPHENOLS CALCULATED FROM TABLE II BY EXTRA-POLATION FOR VARIOUS CONTENTS OF METHANOL IN THE MOBILE PHASE

Code	Compound	κ_i			
		$\varphi = 0.660$	$\varphi = 0.725$	$\varphi = 0.800$	$\varphi = 0.825$
1	Phenol	0.42	0.29	0.19	0.16
2	3-*tert.*-Butylphenol	2.70	1.50	0.76	0.60
3	4-*tert.*-Butylphenol	2.79	1.55	0.78	0.62
4	4-*sec.*-Butylphenol	3.29	1.71	0.80	0.62
5	2-*sec.*-Butylphenol	3.50	1.90	0.95	0.74
6	2-*tert.*-Butylphenol	4.05	2.60	1.05	0.83
7	3,5-Di-*tert.*-Butylphenol	10.68	4.96	2.04	1.52
8	4-Octylphenol	15.46	6.98	2.79	2.05
9	2,4-Di-*tert.*-butylphenol	19.12	8.16	3.04	2.20
10	2,4-Di-*sec.*-butylphenol	20.16	8.62	3.23	2.33
11	2,6-Di-*tert.*-butylphenol	22.17	9.94	3.94	2.89
12	2,4,6-Tri-*tert.*-butylphenol	81.68	29.98	9.43	6.41
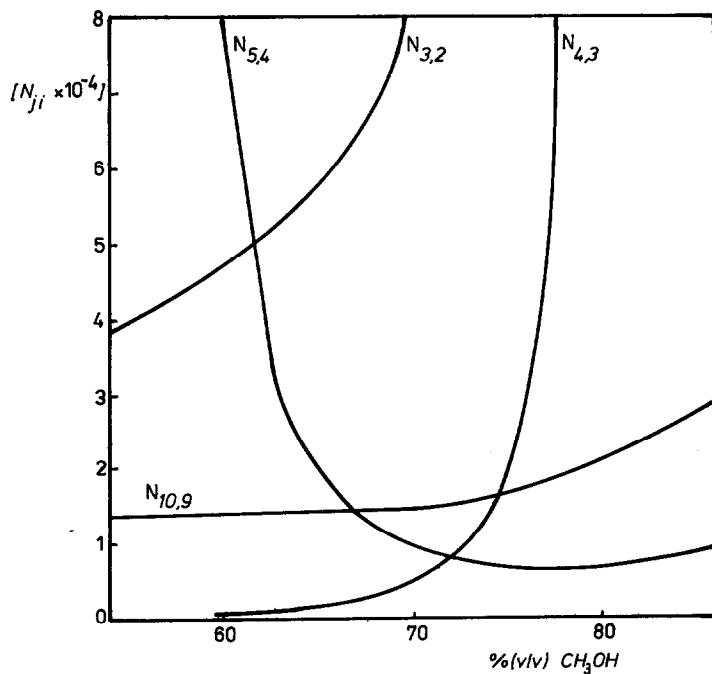
Fig. 2. Influence of the methanol content of the eluent on the number of theoretical plates, N_{ji}, required for a resolution, $R_{ji} = 6$. Phase system: octadecylsilica/water–methanol. Compound numbers as in Table I.

found by focusing on the decisive influence of the selectivity which determines the theoretical plate number, N_{ji}, required for the separation of all compounds of the mixture.

Plots of theoretical plate numbers necessary for a given resolution of the critical (poorest resolved) band pairs as a function of the mobile phase composition are shown in Fig. 2. The worst selectivity at all eluent compositions investigated is observed for the pair 4-*tert.*-butylphenol and 3-*tert.*-butylphenol, (3/2). Since the theoretical plate number, $N_{3,2}$, to achieve the specified resolution is rather high (about 40 000), the resolution of this pair of compounds was neglected in the optimization discussion for systems without an activator. It was intended to solve this separation problems by addition of a surface activator.

The progression of the function $N_{ji} = f(\varphi_{MeOH})$ at $R_{ji} = 6$ for the pair 4-*sec.*- and 4-*tert.*-butylphenol, pair (4/3), is found to be opposite to that for 2-*sec.*- and 4-*sec.*-butylphenols, (5/4). The mobile phase composition at the point of intersection of these two curves at 71.8% (v/v) methanol can be considered to be optimum for monoalkylphenols. The remaining compounds of the model mixture are separated under these conditions with an higher resolution than that for the monoalkylphenol pairs (4/3) and (5/4). The only exceptions are the two 2,4-disubstituted phenols, (10/9). The minimum column efficiency required for the resolution of all test compounds, except the pair (3/2), is therefore given by the intersection of the $N_{10,9}$ curve with the $N_{5,4}$ curve in Fig. 2. The intersection corresponds to an optimum mobile

TABLE IV

CAPACITY FACTORS, κ_i, OF BUTYLPHENOLS ON AN OCTADECYLSILICA PACKING WITH METHANOL–WATER ELUENTS AND HEXYL NITRILE AS AN ADDITIVE

Code	Compound	κ_i						
		% (v/v) hexyl nitrile						
		0.00	0.25	0.50	1.00	1.50	2.00	
$\varphi_{methanol} = 0.70$								
2	3-*tert.*-Butylphenol	1.86	2.11	2.14	1.90	1.80	1.73	
3	4-*tert.*-Butylphenol	1.90	2.19	2.24	2.00	1.91	1.82	
4	4-*sec.*-Butylphenol	2.24	–	2.57	2.28	2.18	2.07	
5	2-*sec.*-Butylphenol	2.42	–	2.88	2.56	2.48	2.32	
6	2-*tert.*-Butylphenol	2.83	–	3.36	2.99	2.86	2.71	
7	3,5-Di-*tert.*-butylphenol	6.91	7.33	8.05	7.02	6.55	6.04	
8	4-Octylphenol	9.69	9.94	10.92	9.82	9.21	8.60	
9	2,4-Di-*tert.*-Butylphenol	11.38	11.00	11.89	11.20	10.38	9.60	
10	2,4-Di-*sec.*-butylphenol	12.28	11.64	12.34	11.50	10.58	9.60	
11	2,6-Di-*tert.*-butylphenol	14.08	14.35	15.31	14.35	13.01	12.30	
		0.00	0.50	1.00	1.50	2.00	3.00	4.00
$\varphi_{methanol} = 0.60$								
2	3-*tert.*-Butylphenol	4.58	4.82	4.96	4.99	4.54	4.29	4.20
3	4-*tert.*-Butylphenol	4.83	5.06	5.19	5.21	4.73	4.47	4.37
4	4-*sec.*-Butylphenol	6.01	6.14	6.20	6.22	5.58	5.18	5.02
5	2-*sec.*-Butylphenol	6.10	6.41	6.57	6.89	6.30	6.20	6.19
6	2-*tert.*-Butylphenol	7.17	8.00	8.74	8.90	8.21	8.11	8.09

phase composition of about 67% (v/v) methanol and the requirement of about 15 000 theoretical plates. Since the $N_{5,4}$ curve increases only slightly with increasing methanol content it is preferable to work at that mobile phase composition where an optimum separation of the monosubstituted phenols is achieved, i.e., at 71.8% (v/v) methanol, requiring a minimum theoretical plate number, $N_{ji} = 15\ 780$.

Dynamic surface modification

The results obtained in the eluent optimization for the octadecylsilica/methanol–water system reveal that a theoretical plate number of about 15 000 is needed for a minimum resolution of 6 for the test mixture. This implies a rather long analysis time. The analysis time can be reduced by improving the selectivities between phenols with the same number of carbon atoms in the alkyl substituents.

A change of the selectivity can be achieved by the dynamic modification of the solid surface. In this approach a layer of modifier molecules is adsorbed from the mobile phase. These adsorbates can adsorb the analyte molecules. The surface modifier is added to the mobile phase in such low concentrations that the solvent properties of the eluent are practically unchanged[24–27]. For our purpose, n-hexyl nitrile and n-hexylamine were selected as the modifiers. The changes in the capacity factors and in the selectivity coefficients of the phenols have been measured as a function of the nature and concentration of the additive in the mobile phase. Different elution behaviours of the phenols are observed resulting from the different polar groups in the modifier molecules (CN or NH_2).
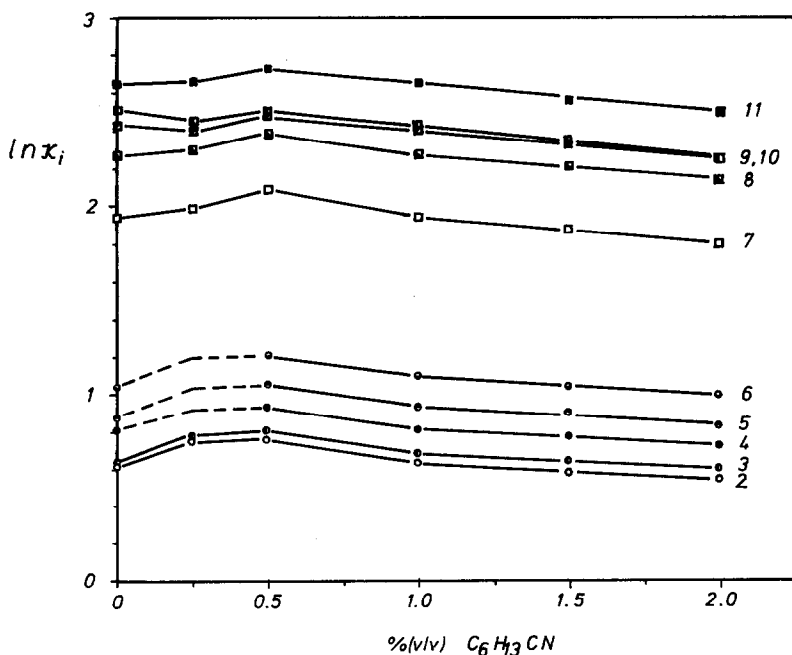

Fig. 3. Dependence of the capacity factors of butylphenols on the volume fraction of the additive hexyl nitrile in the eluent. Phase system: octadecylsilica/water–methanol (30:70). Compound numbers as in Table I.

Activation with hexyl nitrile

Data on the dependence of the capacity factor of the butylphenols on the modifier concentration are given in Table IV, and illustrated by the semilogarithmic plot in Fig. 3. The capacity factor has a maximum at about 0.5% (v/v) modifier which acts as an activator.

The solid surface is gradually covered by hexyl nitrile with increasing modifier concentration in the eluent. This leads to a stronger interaction of the alkylphenols with the surface layer and to a stronger retention. Further increase in the modifier concentration above a given limit results in a decrease in retention. It may be assumed that the adsorbed hexyl nitrile molecules in the first layer are oriented towards the
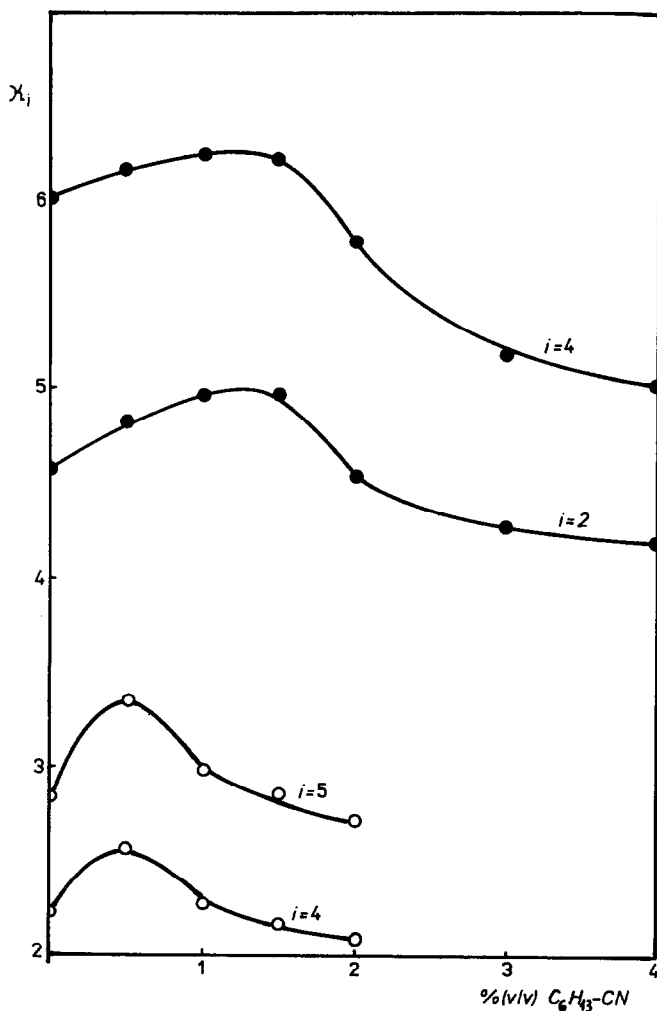
Fig. 4. Change of the capacity factor dependence of butylphenols on the additive (hexyl nitrile) concentration at different methanol contents in the eluent. ●, 60%; ○, 70%. Phase system: octadecyl-silica/water–methanol. Compound numbers as in Table I.
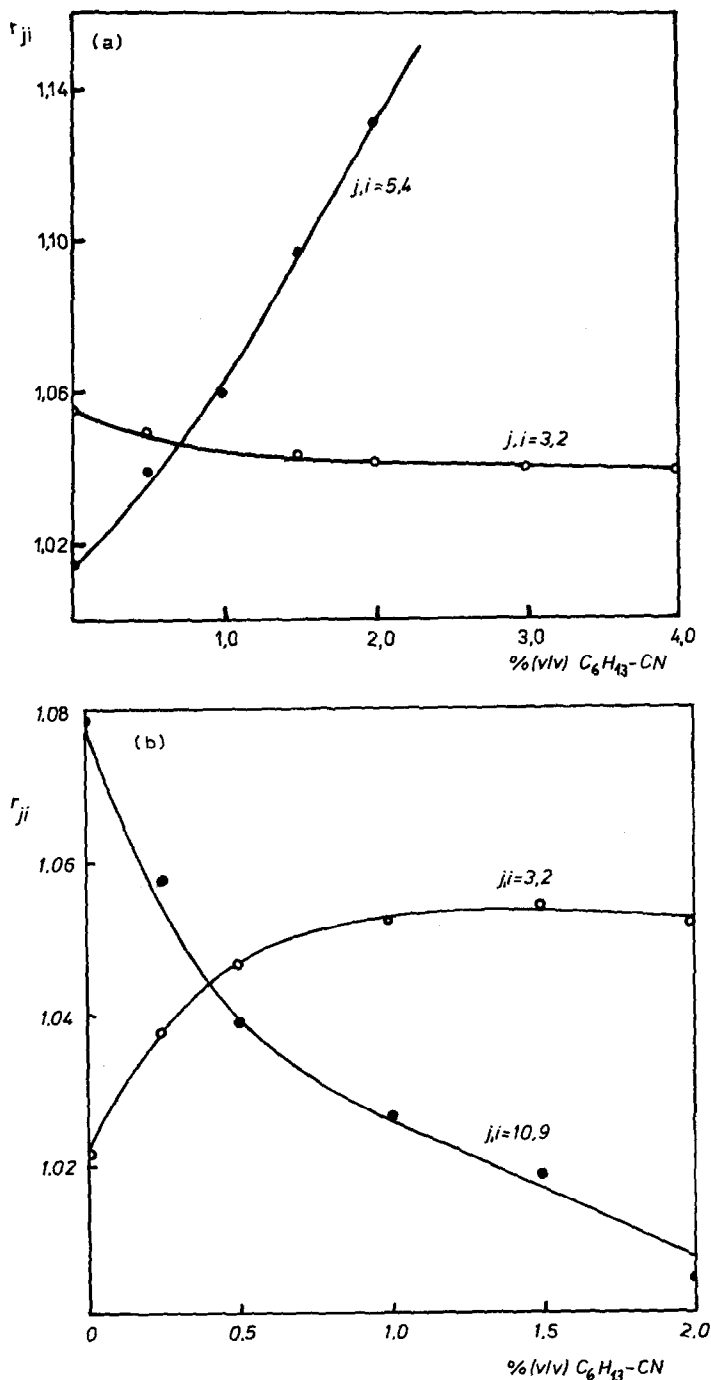
Fig. 5. Dependence of the selectivity coefficients of pairs of butylphenols on the additive (hexyl nitrile) concentration at different methanol contents in the eluent. (a) 60%; (b) 70%. Phase system: octadecylsilica/water-methanol. Compound numbers as in Table IV.

surface with the alkyl group, forming an adsorption layer with the nitrile groups oriented towards the bulk liquid phase. After saturation of the first layer, the second layer of alkyl nitrile will be adsorbed in the opposite direction, resulting in a reduced adsorption of phenolic compounds onto the adsorbate molecules. The hexyl nitrile concentration in the mobile phase corresponding to the maximum activation depends on the methanol content in the mobile phase (see Table IV and Fig. 4). Although an higher content of methanol in the mobile phase is expected to lead to a modifier saturation of the stationary phase at an higher hexyl nitrile concentration in the mobile phase, Fig. 4 shows that the maximum in the capacity factor curve for the phenols is surprisingly obtained at lower concentrations of hexyl nitrile, indicating that the adsorption is more complex than described by the simple model given above.

The addition of hexyl nitrile to the mobile phase is found to influence significantly the selectivity of phenol separation (Fig. 5). Improved separation of some phenols is accompanied, however, by poorer separations of others under the same conditions. Of interest are the compounds with the lowest resolution in the modifier-free mobile phase.

For the mobile phase with 60% (v/v) methanol the selectivity for monosubstituted *sec.*-butylphenols (5/4) improves with increasing concentration of hexyl ni-
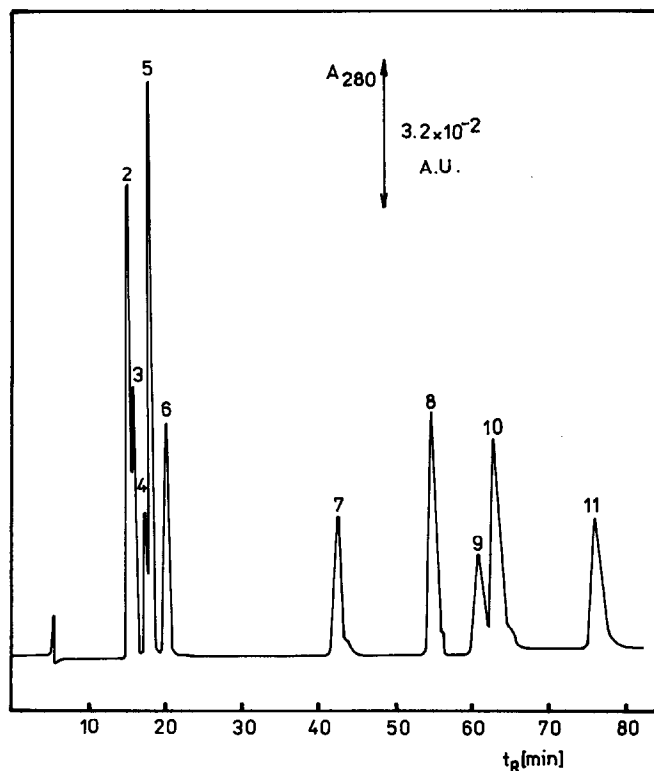

Fig. 6. Chromatogram of a mixture of mono- and disubstituted butylphenols using hexyl nitrile as an additive. Column: 250 mm × 4 mm, octadecylsilica. Eluent: methanol–water (70:30, v/v) + 0.5% (v/v) hexyl nitrile, flow-rate 1 ml/min. Temperature: 25°C. Compound numbers as in Table V.

trile (see Fig. 5a). For the same phase system a slight decrease in the selectivity coefficient of 4-*tert.*- and 3-*tert.*-butylphenol (3/2) occurs (see Fig. 5a). A decrease in selectivity was also observed for the monosubstituted *sec.*- and *tert.*-butylphenols, (4/3) and (6/5). The selectivity coefficients of these two pairs, however, never drop below 1.15 for the hexyl nitrile concentration range investigated. Due to the long analysis time needed for the separation of the whole test mixture, solvents with 60% (v/v) methanol are of little interest, however.

For mobile phases with 70% (v/v) of methanol the addition of the modifier results in improved selectivities for all monosubstituted phenols (see the pair 3/2 in Fig. 5b). The decrease in selectivity for 2,4-disubstituted phenols at increasing hexyl nitrile concentration (see the pair 10/9 in Fig. 5b) limits the application of this modifier to rather low concentrations. At a hexyl nitrile concentration of 0.5% (v/v) the loss in resolution for the pair 10/9 is still acceptable and the separation of monosubstituted phenols is significantly improved. The resolution of disubstituted phenols is still good, as is seen from the chromatogram in Fig. 6.

Deactivation with hexylamine

After addition of hexylamine to an eluent consisting of water and methanol the retention of the investigated phenols was generally reduced (see Table V and Fig. 7). These results suggest that the interaction of the analytes with the octadecyl group
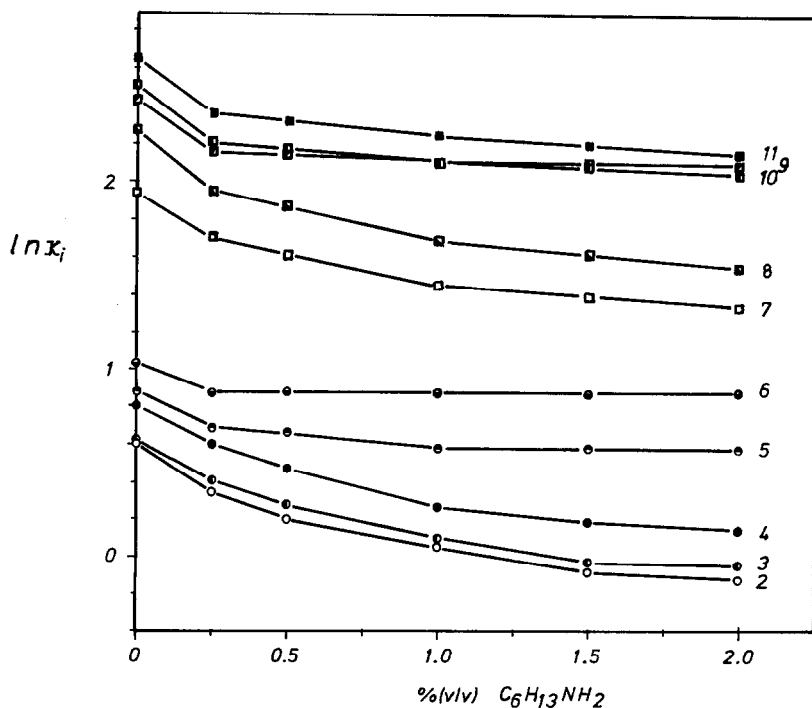

Fig. 7. Dependence of the capacity factors of butylphenols on the volume fraction of the additive (hexylamine) in the eluent. Phase system: octadecylsilica/water–methanol (30:70). Compound numbers as in Table V.

TABLE V

CAPACITY FACTORS, κ_i, OF BUTYLPHENOLS ON AN OCTADECYLSILICA PACKING WITH METHANOL–WATER ELUENTS [70% (v/v) METHANOL] AND HEXYLAMINE AS AN ADDITIVE

| Code	Compound	κ_i					
		% (v/v) hexylamine					
		0.00	0.25	0.50	1.00	1.50	2.00
2	3-tert.-Butylphenol	1.86	1.42	1.22	1.06	0.92	0.88
3	4-tert.-Butylphenol	1.90	1.51	1.32	1.11	0.97	0.95
4	4-sec.-Butylphenol	2.24	1.82	1.61	1.31	1.21	1.15
5	2-sec.-Butylphenol	2.42	2.00	1.95	1.81	1.78	1.77
6	2-tert.-Butylphenol	2.83	2.42	2.41	2.39	2.38	2.39
7	3,5-Di-tert.-Butylphenol	6.91	5.50	5.01	4.25	3.96	3.74
8	4-Octylphenol	9.69	7.06	6.49	5.43	4.99	4.66
9	2,4-Di-tert.-butylphenol	11.38	8.67	8.50	8.21	8.16	7.99
10	2,4-Di-sec.-butylphenol	12.28	9.11	8.75	8.21	7.94	7.65
11	2,6-Di-tert.-butylphenol	14.08	10.57	10.19	9.35	8.94	8.48
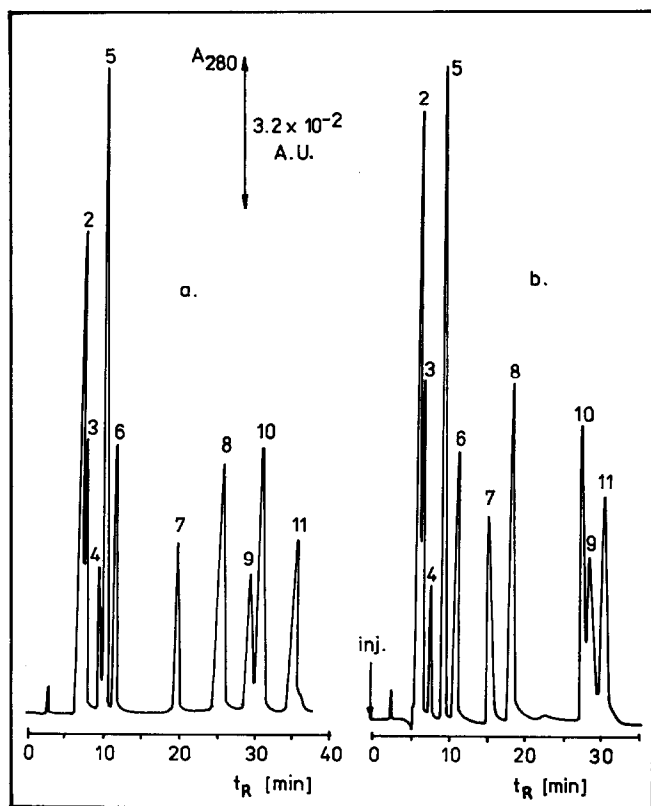
Fig. 8. Chromatograms of a mixture of mono- and disubstituted butylphenols using hexylamine as an additive. Column: 250 mm × 4 mm, octadecylsilica. Eluent:methanol–water (70:30, v/v) + hexylamine (a) 0.5 and (b) 2.0% (v/v), flow-rate 1 ml/min. Temperature: 25°C. Compound numbers as in Table V.
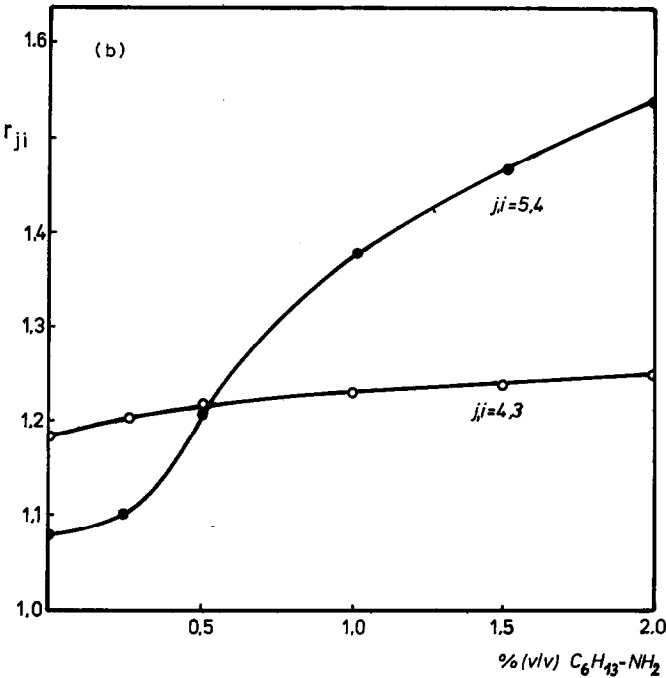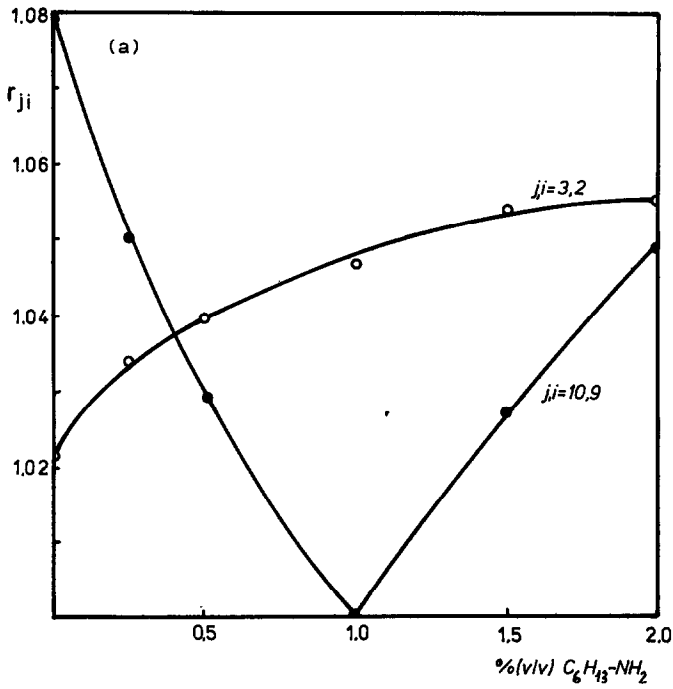
Fig. 9. Change of the selectivity coefficients of pairs of butylphenols with the additive (hexylamine) concentrations in the eluent. Phase system: octadecylsilica/water–methanol. Compound numbers as in Table V.

of the surface is stronger than the interaction with the NH_2 group of the adsorbed modifier. This modifier acts as a deactivator. The decrease in the capacity factor caused by the addition of hexylamine is higher for *meta*- and *para*-substituted phenols than for *ortho*-substituted compounds. The chromatograms in Fig. 8 illustrate the effect of the hexylamine concentration. A change in the elution order was observed only in one case (pair 10/9). It can be concluded from Fig. 7 that these 2,4-disubstituted butylphenols can be separated only at hexylamine concentrations significantly above or below 1% (v/v). The selectivity for these two compounds is therefore decisive for the choice of the optimum modifier concentration in the mobile phase. The chromatograms in Fig. 8 as well as the plots in Fig. 9 show that the selectivity for the pair (10/9) at low hexylamine concentration [0.25% (v/v)] is approximately the same as at high concentration [2% (v/v)]. The increase in the selectivity for mono-substituted phenols with increasing hexylamine content (see Fig. 9) is the reason for the recommendation to use 2% (v/v) hexylamine in the mobile phase. Along with the improved selectivity for the majority of compounds, also the analysis time is reduced.

CONCLUSIONS

Liquid chromatography using an octadecylsilica adsorbent and methanol–water mobile phases is suitable for the separation of mixtures of butyl-substituted phenols. An excellent linear dependence of the logarithm of the capacity factors of the solutes on the volume fraction of the organic solvent component exists which permits the use of simple strategies to establish the optimum mobile phase composition. A good agreement between the calculated and experimental results is obtained. By use of alkyl nitrile and alkylamine modifiers, slight changes in the selectivity of the separation of butyl-substituted phenols can be induced. The type of the polar group in the modifier determines the elution behaviour of the phenols. Whilst the addition of a nitrile modifier causes an increase in retention which is followed by a decrease at higher modifier concentrations, addition of the amine modifier causes a monotonous decrease in retention. The extent of the change in the capacity factor with the modifier concentration depends on the nature of the solute. The selectivity coefficients of the phenols consequently depend on the modifier concentration.

For the separation of a model mixture containing the technologically most important and most commonly used mono- and disubstituted butylphenols, the optimum mobile phase composition corresponds to 30 and 70% (v/v) water and methanol, with 0.5% (v/v) hexyl nitrile or 2% (v/v) hexylamine.

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