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Binaphthyl-based amphiphile as a reagent for dynamically modified silica and fluorescence detection in high-performance liquid chromatography

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Abstract

The modification of bare silica with a binaphthyl-containing surfactant is described. The effects of several factors on the amount of binaphthyl amphiphile adsorbed on the silica surface are reported and the retention mechanisms of solutes are discussed. The separation of non-ionic aromatic compounds shows a clear reversed-phase mechanism, even at very low coverage of silica (below 10 nmol m^{-2}, 3 μmol g^{-1}), which indicates an extremely strong interaction between binaphthyl moieties of the adsorbed surfactant and aromatic rings of the solutes. The ion-pair reversed-phase mechanism appears to be major process responsible for the retention of anionic solutes, especially at higher amphiphile concentrations in mobile phase. The concept of the application of fluorescent amphiphiles in liquid chromatography is discussed, and an example of the detection of non-fluorescent analytes using the "visualization effect" is also presented.

1. Introduction

Surfactants or amphiphilic compounds are valuable mobile phase additives in high-performance liquid chromatography (HPLC). In reversed-phase ion-pair chromatography, separations of ionic compounds are achieved due to the presence of relatively low concentrations of surfactant in the mobile phase [below the critical micelle concentration (CMC)] [1–5]. The use of aqueous surfactant solutions at concentrations above the CMC provides a new separation technique, micellar liquid chromatography [6–10]. The third approach to the use of surfactants in HPLC is the dynamic modification of bare silica with surfactant solutions, giving chromatographic separations similar to those obtained with chemically bonded reversed-phase (RP) materials. It has been shown that these RP-HPLC systems exhibit an excellent reproducibility of selectivity and also superior peak shapes of amine solutes [11–13].

Surprisingly, only a very limited number of surfactants have been applied in such chromatographic separations, mainly conventional, such as cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS), Tweens and Brij 35 [13–15]. The reason for the application of alkyl chain-type surfactants exclusively is limitations with regard to the spectrophotometric detection widely used in HPLC, which needs an optically transparent mobile phase. However, one can take advantage of the presence of light-absorbing surfactants in mobile phase, *e.g.*, monitoring of "transparent" species by an indirect technique used in ion-pair chromatography [16].

We are trying to introduce into analytical

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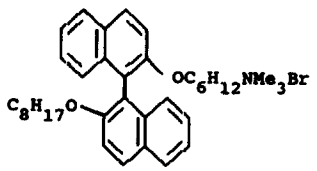

C_8BNC_6N

practice functionalized surfactants bearing a fluorescent aromatic moiety. The binaphthyl-based cationic amphiphile C_8BNC_6N has been successfully used for monitoring iodine in the indirect determination of ascorbic acid [17]; the aggregates of the amphiphile show a high affinity for hydrophobic solutes, especially polycyclic aromatic hydrocarbons (PAHs), and can serve as efficient collective energy donors. The sensitized emission of a particular PAH is then observed [18].

The concept of the application of C_8BNC_6N in chromatographic techniques takes advantages of the presumably strong interactions of the surfactant with the silica surface, which allows surface modification at low surfactant concentrations in the mobile phase; additionally, the presence of a fluorescent amphiphile in the mobile phase can be exploited for indirect detection.

In this paper, the modification of bare silica with the binaphthyl-containing surfactant C_8BNC_6N is reported. The effects of the content of methanol in the mobile phase, pH, buffer concentration and temperature on the amount of amphiphile adsorbed on the silica surface were studied. The retention mechanism of solutes is discussed, and an example of the detection of non-fluorescent analytes using the "visualization effect" is presented.

2. Experimental

2.1. Apparatus

The chromatographic system was composed of a Model 1440 liquid chromatograph (ISCO, Lincoln, NB, USA) and an RF 5000 spectrofluorimeter (Shimadzu, Kyoto, Japan) equipped with a sample flow cell. The solutes were detected as follows ($\lambda_{ex}/\lambda_{em}$): naphthalene and 1,2-dimethylnaphthalene, 260/320 nm; anthracene and benzo[*a*]pyrene, 380/400 nm; and 3-hydroxynaphthoate and quinine, 380/450 nm.

Separations were performed on 100 × 4.6 mm I.D. columns which were packed with LiChrosorb Si 100 (Merck, Darmstadt, Germany), $d_p = 10$ μm, by the slurry technique at 300 bar with a Knauer pneumatic high-pressure pump.

A precolumn packed with silica gel (35–40 μm) (Merck) was located between the pump and sample injector, in order to saturate the mobile phase with silica. The analytical column was thermostated at 25°C unless stated otherwise.

2.2. Reagents

The amphiphile compound, C_8BNC_6N, was prepared and purified as described elsewhere [19]. A stock standard solution of C_8BNC_6N ($5 \cdot 10^{-3}$ *M*) was prepared by dissolving the weighed sample in methanol. All other chemicals were of analytical-reagent grade and were used as received. Water filtered through a Milli-Q system (Millipore, Bedford, MA, USA) was used throughout.

2.3. Procedures

The adsorption isotherms were determined from the breakthrough curves recorded with the spectrofluorimeter (λ_{ex} = 340 nm, λ_{em} = 380 nm). The concentration of C_8BNC_6N in the eluates was determined spectrophotometrically at 340 nm using a Specord M 40 instrument (Carl Zeiss, Jena, Germany).

The columns were modified by two methods:

(i) two-step modification, the column initially being washed (conditioning) with 100 ml of mobile phase containing buffer, but without amphiphile additive, followed by modification with amphiphile-containing mobile phase without buffer;

(ii) conventional, one step modification, with mobile phase containing buffer solution and appropriate amounts of amphiphile.

2.4. Determination of critical micelle concentration (CMC)

The CMC of C_8BNC_6N in methanol–water was measured in the presence of varied amounts of phosphate by the method based on energy transfer [20] using perylene as an energy acceptor.

3. Results and discussion

3.1. Adsorption isotherms

In order to examine factors governing amphiphile adsorption, modifications of silica gel were performed by two general procedures as indicated under Experimental, varying the pH of the "conditioning mobile phase" and the content of methanol in the mobile phase in the two-step procedure, and changing the composition of the mobile phase in the one-step procedure. The results are presented in Fig. 1.

The pH of the "conditioning mobile phase" during the initial treatment of silica is a crucial factor governing surface coverage by the amphiphile in the two step-procedure (Fig. 1A). The adsorption isotherms do not show Langmuir behaviour, and exhibit saturation at higher amphiphile concentrations. The amount of amphiphile adsorbed increases as the pH of the mobile phase during the washing step increases. As expected, higher surface coverages were obtained for columns pretreated at pH 8.5 (curve 4, Fig. 1A), even when a higher content of methanol in the mobile phase was used [methanol–water (5:5, v/v)]. The courses of the isotherms reflect the two-step procedure applied. The washing step is responsible for the initial amount of ionized silanols accessible for ion-pair formation with amphiphile molecules. The modification step, with mobile phase without buffer, causes the gradual protonation of silanols, yielding a final surface coverage that depends on the pH of initial washing and the duration of the modification step.

The curves in Fig. 1B represent adsorption isotherms obtained by the one-step procedure.

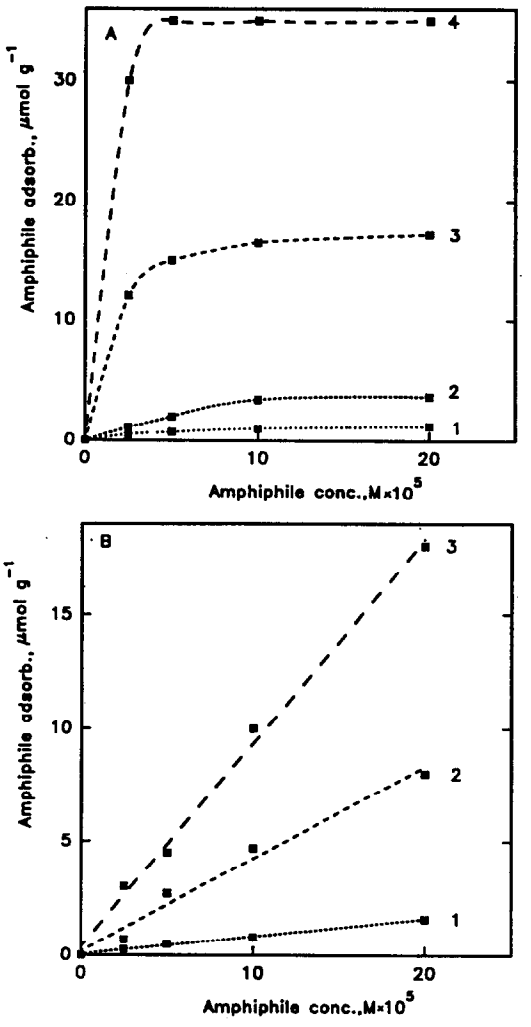

Fig. 1. Adsorption of C_8BNC_6N amphiphile by LiChrosorb Si 100 as a function of C_8BNC_6N concentration in the mobile phase for different modification procedures. (A) Two-step procedure. Eluent, methanol–water (1)–(3) (30:70) and (4) (50:50); pH of conditioning mobile phase, (1) 0.1 *M* H_3PO_4, (2) 5.0, (3) 6.4 and (4) 8.5. (B) One-step procedure. Mobile phase, methanol–water–0.2 *M* phosphate buffer, (1), (2) (30:65:5) and (3) (30:20:50); pH of buffer, (1) 5.0, (2) 6.4 and (3) 2.1.

As expected, an increase in the pH of the mobile phase causes an enhancement of the adsorption of the surfactant on the silica gel, but the unexpected efficient adsorption at pH 2.1 (curve 3) should be noted. In pure methanol–water (3:7, v/v), one would expect domination of

monomeric molecules of the amphiphile, but the presence of a high concentration of counter ions (phosphate) should improve micelle formation. Indeed, the determined CMC value at 0.1 *M* phosphate buffer concentration is $1 \cdot 10^{-4}$ *M*, which indicates the presence in the mobile phase (pH 2.1) at least of premicellar aggregates. The low pH decreases the ionization of silanols, thus making them inaccessible for ion-pair interactions with cationic amphiphile molecules. Taking into account the dissociation constant of silanols, $pK = 7.1$ [21], one can calculate that only 1% of silanols is dissociated at pH 5.0, and markedly less at pH 2.1. The abnormally high adsorption of the amphiphile at low pH can be explained in the terms of micellar phenomena, by the formation of multilayers of amphiphile on the silica surface.

From the comparison of two modification procedures, the significant effect of the presence of phosphate buffer in the mobile phase is clear. Buffer at a concentration of $1 \cdot 10^{-2}$ *M* decreases the adsorption of the amphiphile by about 50%, probably as the result of competitive interaction of buffer cations with silanols, which has been reported by Hansen *et al.* [22], and also competitive ion-pair equilibria of phosphate ions with amphiphile molecules. The two-step procedure seems to be more convenient for the flexible regulation of the amount of C_8BNC_6N adsorbed on silica, because by changing the pH of the washing phase, and the composition of mobile phase used for modification, one can obtain reproducible surface coverages below 10 nmol m^{-2} (pH < 5) and highly coated silica, containing above 600 nmol m^{-2} (column washed with the mobile phase containing $2 \cdot 10^{-2}$ *M* ammonia). Moreover, the absence of buffer ions in the mobile phase will be advantageous for the indirect detection of ionic solutes.

3.2. Retention studies

The columns modified under different conditions were tested by retention studies, using solutes chosen to represent anionic [3-hydroxynaphthoic acid (3HNA)], cationic [quinine (Q)] and non-ionic [naphthalene (N), 1,2-dimethylnaphthalene (DMN) and anthracene (A)]. The dependences of capacity factors (k') as a function of C_8BNC_6N concentration are presented in Fig. 2.

The clear correlation between the retention of non-ionic solutes and the amount of adsorbed C_8BNC_6N can be seen in all instances. The concentration of C_8BNC_6N in the mobile phase and the presence of buffer solution play a negligible role for non-polar solutes. Approximately the same k' value is observed for different columns and different mobile phase compositions, providing similar amounts of C_8BNC_6N adsorbed. The separations show a clear reversed-phase mechanism even for low coverages of silica (Fig. 2B and C), which indicates an extremely strong adsorptive interaction between binaphthyl moieties of the adsorbed surfactant and aromatic rings of the solutes. Quinine is not retained over the full range of amphiphile concentrations used (Fig. 2A); in contrast, 3-hydroxynaphthoic acid shows a strong dependence on the concentration of the amphiphile in the mobile phase. The mechanism of the retention of anionic solutes seems to be more complex, and results should be discussed considering a reversed-phase ion-pair mechanism as an additional process. The ion-pair reversed-phase mechanism appears to be major process at higher C_8BNC_6N concentrations in the mobile phase, which is reflected by an abrupt increase in k'. This effect is the most clearly seen in Fig. 2D, where despite the constant amount of amphiphile adsorbed, k' still increases with increasing surfactant concentration.

An increase in the amount of organic modifier, methanol, in the mobile phase causes a normal decreasing effect on retention, as indicated from a comparison of Fig. 2C and D.

The retention of all solutes decreases at elevated temperature (Fig. 3), as would be expected considering the effect of temperature on partition equilibria and the decrease in surface coating by amphiphiles.

The pH effect on k' for non-ionic solutes is simply related to the amount of adsorbed C_8BNC_6N, but with 3HNA the strong increase in retention at higher pH region indicates more

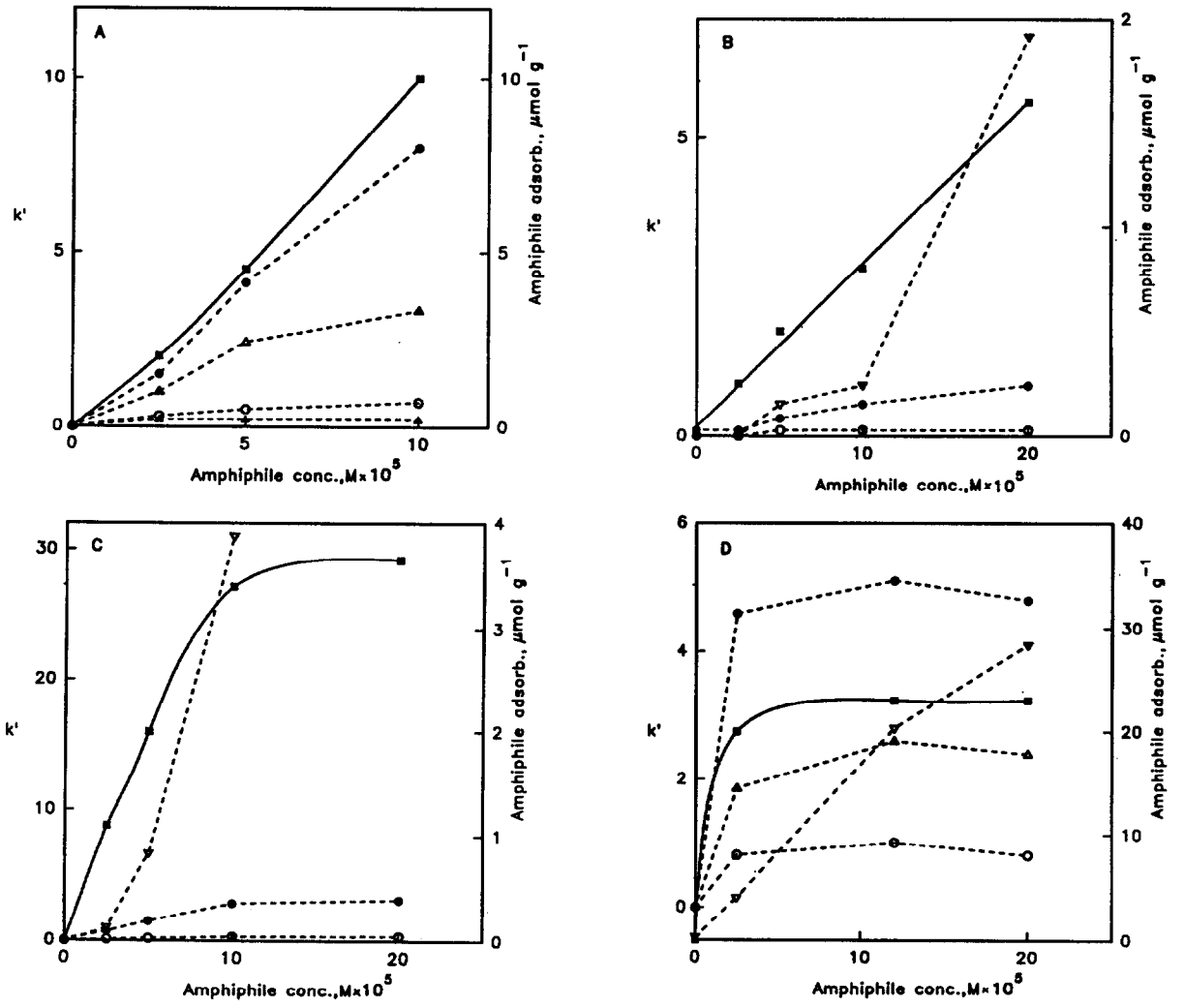

Fig. 2. Relationship between the concentration of C_8BNC_6N in the mobile phase and retention (k' values) for the test solutes: ○ = naphthalene; △ = DMN; ● = anthracene; ▽ = 3HNA; ▲ = quinine; ■ = adsorption isotherm for different experimental conditions. One-step procedure: (A) pH = 2.1, eluent = methanol–water–0.2 *M* buffer (30:20:50); (B) pH = 5.0, eluent = methanol–water–0.2 *M* buffer (30:65:5). Two-step procedure; (C) pH = 5, eluent = methanol–water (30:70); (D) pH = 8.5, eluent = methanol–water (50:50).

complete ionization of the solute, and thus the significance of reversed-phase ion-pair interactions (Fig. 4).

3.3. Retention mechanism

The generally high retention observed for both non-ionic and anionic solutes indicates strong interaction with the adsorbed binaphthyl amphiphiles. Assuming the simple reversed-phase interaction for non-polar solutes, the partition coefficient (P) can be simply calculated from the fundamental chromatographic equation

$$k' = \phi P \quad (1)$$

where k' is capacity factor, and $\phi = v_{ads}/v_m$ is the phase ratio.

The volumes of surfactant adsorbed (v_{ads}) were calculated from breakthrough curves, using a molar volume of the amphiphile of 900 Å^3 [18],

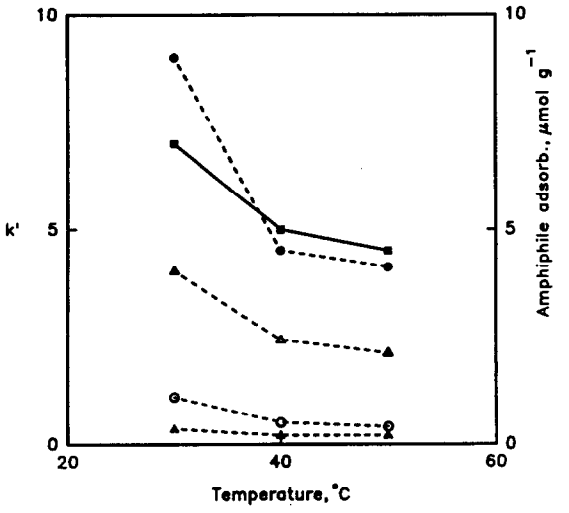

Fig. 3. Effect of temperature on C_8BNC_6N adsorption and retention (k' values). Eluent, methanol–water–0.2 M buffer (30:20:50); pH = 2.1. Symbols as in Fig. 2.

and the dependence of the capacity factor (k') on ϕ for $v_m = 0.85$ ml was plotted. The partition coefficients obtained for particular solutes and mobile phase compositions are given in Table 1. The value for benzo[*a*]pyrene (BaP) was obtained from two experimental points, as in most instances BaP was completely retained on the columns.

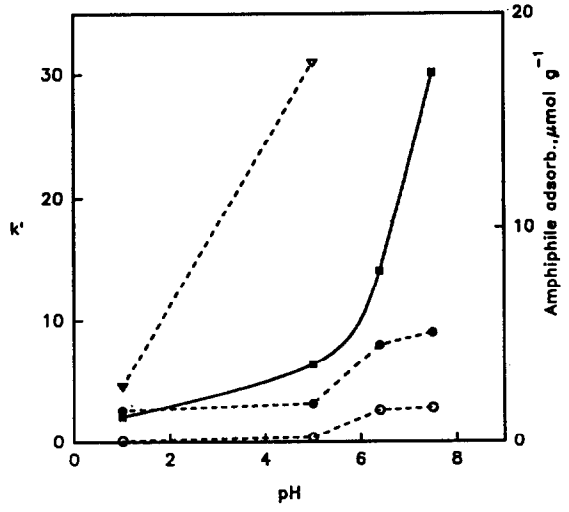

Fig. 4. Effect of pH on C_8BNC_6N adsorption and retention (k' values). Two-step procedure: conditioning solution, methanol–water–0.2 M buffer (30:65:5); eluent, methanol–water (30:70) containing $1 \cdot 10^{-4}$ M C_8BNC_6N. Symbols as in Fig. 2.

An increase in elution power of the mobile phase [methanol–water (5:5)] causes a decrease in the interaction of all non-ionic solutes with the adsorbed surfactant. The addition of methanol should decrease the polarity of the bulk phase without affecting the polarity of the surface coating [23], which in addition to the retention effect, should result in increased mass transfer, this in turn resulting in improved efficiency. As expected, the values of the partition coefficients reflect the hydrophobicity of the solutes, reaching a very high value, $3.1 \cdot 10^3$, for benzo[*a*]pyrene.

With the anionic solute, 3-hydroxynaphthoic acid, ion-pair equilibria should be considered. From the general rules of ion-pair extraction, the following fundamental equilibria were taken into account:

$$R^+S^- \rightleftharpoons \overline{R^+S^-} \qquad P = \frac{\overline{[R^+S^-]}}{[R^+S^-]} \tag{2}$$

$$R^+ + S^- \rightleftharpoons R^+S^- \qquad K = \frac{[R^+S^-]}{[R^+][S^-]} \tag{3}$$

$$R^+ + S^- \rightleftharpoons \overline{R^+S^-} \qquad E = \frac{\overline{[R^+S^-]}}{[R^+][S^-]} \tag{4}$$

where a bar denotes concentration in the stationary phase, concentrations without a bar refer to the mobile phase, P is the partition coefficient, K is the association constant in the mobile phase and E is the extraction constant. These equilibria are not independent, as

$$E = PK \tag{5}$$

An expression for the capacity factor of S^- can be then obtained, considering

$$k' = \phi \frac{\Sigma\,\overline{R^+S^-}}{\Sigma\,S^-} = \phi \frac{\overline{[R^+S^-]}}{[R^+S^-] + [S^-]} + k'_0 \tag{6}$$

where k'_0 is the term for the amphiphilic ion independent retention. Eq. 6 can be rewritten as

$$k' - k'_0 = \phi \frac{PK[R^+]}{K[R^+] + 1} \tag{7}$$

Table 1
Partition coefficients (P) calculated from Eq. 1 for C_8BNC_6N-modified LiChrosorb Si 100

Eluent: MeOH–H_2O (v/v)	Partition coefficient, $P \cdot 10^{-2}$			
	Naphthalene	Anthracene	DMN	Benzo[*a*]pyrene
3:7	1.4	16	–	–
5:5	0.70	3.7	1.7	31

and after rearrangement

$$\frac{\phi}{k' - k'_0} = \frac{1}{P} + \frac{1}{E[R^+]} \quad (8)$$

Assuming that $k'_0 \ll k'$, Eq. 8 simplifies to

$$\frac{\phi}{k'} = \frac{1}{P} + \frac{1}{E[R^+]} \quad (9)$$

This equation is similar to simplified equations proposed by Horváth *et al.* [2], Westerlund and Theodorsen [24] and Knox and Hartwick [25].

A plot of ϕ/k' versus $[R^+]^{-1}$ should result in a straight line. Further, the constants describing the equilibria (K, P and E) can be calculated from the intercept and slope values. Unfortunately, it appeared that calculation of association constant (K) and partition coefficient (P) cannot be performed, as negative intercepts of the plots were obtained. The extraction constant values (E) obtained for methanol–water (3:7 and 5:5, v/v) mobile phases are $5 \cdot 10^7$ and $2 \cdot 10^6$, respectively. Considering the improving effect of a less polar mobile phase on the ion-pair formation equilibria (K), one can suspect a far greater decrease in the partition coefficient (P) than calculated for non-ionic solutes (Table 1).

The negative intercepts indicate contributions from other equilibria, probably connected with the competing effect of counter anions, Br^-, present in the mobile phase, or interactions of the solute with cationic head groups of the surfactant adsorbed on the silica gel and not fully neutralized by ionized silanols. Similar problems with negative intercepts have been observed in micellar chromatography for sparingly soluble solutes, and it was explained by the slow mass transport in the bulk phase [26,27].

The restricted mass transfer between the mobile and stationary phases is reflected by broadening of the chromatographic bands. Large peak widths were observed especially for 3HNA and anthracene. In order to elucidate the effect of entrance–exit rate constants on retention, the random-walk model [28] was applied. The values for the desorption rate constant, k_d, were obtained from the measured chromatographic parameters, substituted into the equation

$$H = \frac{2k'}{(1 + k')^2} \frac{\nu}{k_d} \quad (10)$$

where H is the height equivalent to a theoretical plate and ν is the linear velocity. The adsorption rate constant, k_a, was calculated using the basic chromatographic expression $k' = k_a/k_d$. If both the adsorption and desorption rate constants of a solute with the stationary phase were large, mass transfer would not limit the efficiency, but the rate constants can vary greatly.

The values of k_d and k_a were calculated using Eq. 10 for a flow rate of 1.54 mm s^{-1} (0.8 ml min^{-1}). The results are given in Table 2. The k_a values were normalized to the same amount of C_8BNC_6N adsorbed, in order to compare two mobile phases. The values of k_a are surprisingly low (*e.g.*, $k_a = 322$ s^{-1} has been reported for β-naphthol in the presence of SDS below the CMC on an ODS column [29]). Moreover, a higher content of methanol in the mobile phase causes a lowering of the adsorption rate, which is unexpected as the adsorption is diffusion controlled. The very low values of k_a may indicate interaction of the solute with the surfactant in the mobile phase; even below the CMC the formation of premicellar, cluster-like aggregates

Table 2
Adsorption and desorption rate constants for C_8BNC_6N-modified LiChrosorb Si 100

Eluent: MeOH–H_2O (v/v)	Rate constant	Naphthalene	Anthracene	Benzo[*a*]pyrene
3:7	k_a (s^{-1})	6.6	20.4	–
	k_d (s^{-1})	1.81	1.03	–
5:5	k_a (s^{-1})	2.81	10.1	11.6
	k_d (s^{-1})	2.72	1.98	0.27

has been reported [30]. On the other hand, the increase in k_d on going to a methanol-rich mobile phase is in accordance with expectation. This means that a solute with a higher k_d value can return to the bulk phase frequently, and thereby is closer to equilibrium, whereas a much smaller k_d values results in solutes remaining in the stationary phase much longer. As both effects act in the same direction, a marked improvement in efficiency is observed in a methanol-rich mobile phase. It should be noted that the elution of benzo[*a*]pyrene with methanol–water (3:7, v/v) mobile phase was virtually impossible owing to the substantial peak broadening, which was not the case with methanol–water (5:5, v/v).

3.4. Application

As the main reason for undertaking these studies was the application of fluorescent amphiphiles in chromatographic practice, mainly taking advantage of the fluorescence characteristics of the amphiphile, we checked the usefulness of the system for the fluorescence detection of non-fluorescent solutes. Taking into account the ion-pair reversed-phase mechanism of retention of anionic solutes (S^-), one can expect an increase in the fluorescent signal when the $C_8BNC_6N^+S^-$ ion pair is eluted. Pilot studies performed with heptanesulphonate ($C_7SO_3^-$) and pentanesulphonate ($C_5SO_3^-$) appeared to be promising. Fig. 5 shows an example of a chromatogram obtained for these two non-fluorescent solutes injected into an eluent containing the fluorescent C_8BNC_6N amphiphile (ion-pair reagent).

The next approach to be examined is the construction of a sensing energy transfer system, consisting of acceptor molecules incorporated in donor fluorescent aggregates, for monitoring non-fluorescent solutes (spatial perturbation of sensitized emission of acceptor). Benzo[*a*]pyrene and perylene are good candidates for efficient acceptors, as sensitized emission of these solutes in binaphthyl aggregates [18,20] and decreased entrance–exit rate constants have been observed. These studies will be continued, as the system seems to be promising for the separation

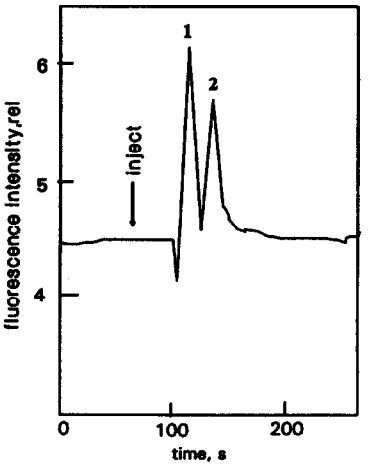

Fig. 5. Separation of alkylsulphonates on LiChrosorb Si 100 modified with C_8BNC_6N amphiphile with fluorescence detection. Excitation and emission wavelengths, 330 nm and 380 nm, respectively; mobile phase, methanol–water (50:50, v/v) containing $1 \cdot 10^{-4}$ *M* C_8BNC_6N; flow-rate, 0.8 ml min^{-1}. Peaks: 1 = pentanesulphonate and 2 = heptanesulphonate (0.5 μg each).

and detection of amino acids, peptides and other bioactive substances.

4. Acknowledgement

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