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THE RÔLE OF THE STATIONARY PHASE IN MICELLAR LIQUID CHROMATOGRAPHY

ADSORPTION AND EFFICIENCY

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SUMMARY

In micellar liquid chromatography a surfactant solution containing micelles is used as a mobile phase. Ionic surfactants strongly adsorb on chromatographic stationary phases. This adsorption can be modified by adding various organic solvents in the micellar mobile phase: the organic modifier, *e.g.*, *n*-pentanol can also adsorb on the stationary phase and replace a part of the adsorbed surfactant. Efficiency in micellar liquid chromatography seems to be linked with the rigidity of the organic layer (bonded moiety + adsorbed molecules) coating the silica surface. Organic modifiers can decrease this rigidity and increase the solute diffusion coefficients in the stationary phase layer. This increase of mass-transfer rate improved the efficiency. *n*-Propanol and tetrahydrofuran were the most effective organic solvents to improve micellar chromatographic efficiencies. Micellar efficiency was shown to be solute-dependent. Quaternary ammonium salts exhibited low efficiency, even with *n*-propanol in the micellar phase, when other solutes (caffeine, toluene) were separated in the same experiment with good efficiency.

INTRODUCTION

The use of a micellar solution as a mobile phase in reversed-phase liquid chromatography (RP-HPLC) was first performed by Armstrong and Terrill[1]. The usefulness of these non-flammable, non-toxic and inexpensive mobile phases was demonstrated[2,3], and an increasing number of applications have been reported[4–9]. Nevertheless, in spite of the advantages of micellar liquid chromatography (MLC), it has not yet achieved widespread usage among practising chromatographers[10]. The main problem is a serious loss of efficiency when compared to traditional hydro-organic mobile phases. Dorsey *et al.*[11] explained that the efficiency problem was due to a poor mass transfer on bonded stationary phases due to the high water content of the micellar phases. They showed that the addition of 3% (v/v) *n*-propanol in a micellar mobile phase and the use of a column temperature of 40°C greatly improved the

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efficiency for non-ionic solutes with micellar mobile phases containing an anionic, a cationic or a non-ionic surfactant[12].

Different authors presented worthwhile improvements of the efficiency in MLC[12,13], but no fundamental study fully explained why the efficiency in MLC is so poor. The aim of the present work was to point out the importance of the stationary phase in MLC. Surfactants adsorb on stationary phases, so surfactant adsorption isotherms were extensively studied[14–17]. The change in surfactant adsorption induced by the addition of methanol, *n*-propanol, *n*-pentanol and tetrahydrofuran (THF) were investigated in this work.

The retention time of a solute allows one to obtain the dimensionless partition coefficients, K_{MW} and K_{SW}, between micelles (M) and bulk water (W) and between the stationary phase (S) and bulk water, respectively. The Armstrong–Nome equation was[18]

$$\frac{1}{k'} = \frac{1}{\varphi}\left[\frac{V\ (K_{MW} - 1)}{K_{SW}} \cdot C_m + \frac{1}{K_{SW}}\right] \tag{1}$$

in which k' is the capacity factor of the solute, φ is the phase volume ratio V_s/V_0 (where V_s is the stationary phase volume and V_0 the dead volume), V is the molar volume of the surfactant and C_m is the concentration of the surfactant in the micellar form, *i.e.*, the total surfactant concentration minus the critical micelle concentration (CMC).

The K_{MW} values measure the affinity of a solute for a micelle; K_{MW} should be dependent only on the mobile phase and be independent of the nature of the stationary phase. The K_{SW} values give information about the affinity of the solute for the surfactant-covered stationary phase. It may be fruitful to associate these partition coefficients with the observed efficiency for various solutes. Additives to the micellar mobile phase affect the two partition coefficients and the peak efficiency. The effects of some additives added to ionic micellar mobile phases is presented and discussed.

EXPERIMENTAL

Materials

Mobile phases were prepared with deionized and distilled water. Sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB) were obtained from Merck (Darmstadt, F.R.G.); SDS was biochemistry grade and CTAB was analytical grade. Micellar mobile phases were prepared by dissolution of the appropriate amount of surfactant in pure water, in alcoholic or in electrolytic solutions. Then, the solution was aspirated through 0.5-μm cellulose acetate filters (Millipore, Bedford, MA, U.S.A.) and degassed in an ultrasonic bath.

ODS Hypersil (Shandon, Runcorn, U.K.) was mainly used as the stationary phase. This bonded silica was made up of spherical 5-μm particles with a monolayer coverage of octadecyl groups (ODS)[17]. The physico-chemical characteristics of the ODS Hypersil silica were 104 m^2/g, 8.5% (w/w) and 2.5 $\mu mol/m^2$ for the silica surface, the carbon percentage and the bonding coverage, respectively. Columns (100 mm × 4.6 mm I.D.) were slurry packed in the laboratory using about 1 g of stationary phase. The chromatographic apparatus consisted of two Altex Model 110A pumps, a Model 70-10 six-port Rheodyne injection valve and a Altex Model 153 analytical UV detector.

Solutes of various polarities were tested. Toluene (Prolabo, Rhone-Poulenc, France) was chosen as an apolar solute. Caffeine (Serva, Hedelberg, F.R.G.) was chosen as a polar but non-ionic solute. Benzoic acid (Prolabo) ($pK_a = 4.2$) was an anionic solute at mobile phase pH values between 5.5 and 6.5. Benzyltrimethylammonium bromide (BTAB) was a cationic quaternary ammonium solute. Sodium *p*-octylbenzenesulphonate (SOBS) ($pK_a = 0.8$) was prepared by sulphonation of *p*-octylbenzene (Fluka, Italy) and neutralization by sodium carbonate. Cetylpyridinium chloride (CPC) was obtained from Merck. SOBS and CPC were chosen as ionic solutes having surfactant properties. They have an hydrophobic tail of the same length as that of SDS and CTAB, respectively. In the case of SOBS, the benzene ring of the hydrophobic tail is classed as a four-methylene sequence, as is usually done by industrial surfactant chemists. All experiments were performed at 25°C with a flow-rate of 1 ml/min, unless otherwise indicated.

Methods

The adsorption isotherms for SDS and CTAB were determined at 30°C by pumping the appropriate concentration of surfactant in the mobile phase through the column until constancy of the detector baseline with time. Methanol was used fully to desorb the surfactant, which was determined by selective titration. The procedure was described previously[14].

The column efficiency is commonly calculated by assuming a Gaussian model for peak shape. The general equation to obtain the number, N, of plates per column is

$$N = (t_R/\sigma)^2 \tag{2}$$

where t_R is the retention time for the peak and σ is the standard deviation or σ^2 is the variance measured in time units and related to various peak width measurements. In the case of a perfect Gaussian peak profile, the peak width at 60% of peak height, $W_{0.6}$, is two times the standard deviation. So, the formula most commonly used to calculate the column efficiency is:

$$N = 4(t_R/W_{0.6})^2 \tag{3}$$

The problem in MLC was that the peak shape of many solutes deviated from the ideal Gaussian shape by the appearance of a tail. To obtain the exact efficiency, it was necessary to use statistical methods: whatever the peak shape, (i) the retention time t_R is expressed as the first statistical moment of the elution curve and it occurs at the centre of mass of the peak, and (ii) the peak variance, σ^2, is the second central moment[19]. The moment method requires the use of computers and data acquisition techniques, and full calculations are not possible in case of slightly fused peaks. Foley and Dorsey have recently derived a simple and accurate manual method for the calculation of plate counts[20]. Their equation, which corrects for the asymmetry of skewed peaks, is

$$N = 41.7(t_R/W_{0.1})^2/(B/A + 1.25) \tag{4}$$

in which $W_{0.1}$ is the peak width measured at 10% of the peak height, and B/A measures the peak asymmetry, B and A are measured by using the peak maximum and

$A + B = W_{0.1}$. This equation was used in all the micellar efficiency calculations in this work.

It should be noted that the observed variance, σ^2, is the sum of independent variances arising from the column effects, but also from injector, connecting tubing or dispersion in the detector[21]:

$$\sigma^2 = \sigma^2_{\text{col}} + \sigma^2_{\text{inj}} + \sigma^2_{\text{tube}} + \sigma^2_{\text{detec}} + \sigma^2_{\text{other}} \tag{5}$$

The time constants of the electronic amplifiers of the detector and the recorder are represented by σ^2_{other}. The use of a modern injection valve, a low-volume detector cell and narrow bore (0.1 mm I.D.) connecting tubes reduced the extra-column band broadening but did not fully eliminate it. The major source of the extra-column variance was likely the detector time constant (about 1 s). We made the assumption of similar extra-column band broadenings when a classical hydroalcoholic mobile phase was used or when a micellar phase was used with exactly the same hardware (pumps, injector, column and detector). We compared the plate count, N, or the height equivalent to a theoretical plate, H (= L/N where L is the column length) obtained with a micellar phase to that obtained with an hydroorganic phase.

RESULTS AND DISCUSSION

Adsorption of ionic surfactant on various stationary phases

All the adsorption isotherms of ionic surfactants studied, except for the one of SDS on non-bonded silica, had the same shape. The amount of surfactant adsorbed increases rapidly and reaches a plateau for any surfactant concentration higher than the CMC (Fig. 1). We showed that (i) the quantity of surfactant adsorbed reached similar values (4–5 μmol/m²) on different alkyl (C_1, C_8 or C_{18}) monolayer bonded phases, and that (ii) the plateau was not strictly horizontal in many cases[14]. The last

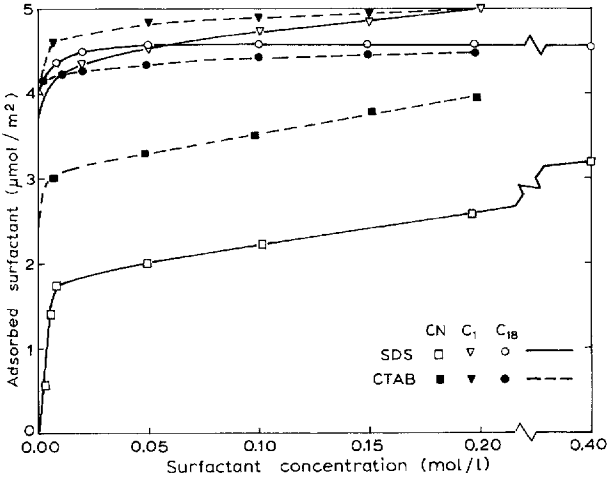

Fig. 1. Surfactant adsorption on three stationary phases: C_1 = SAS Hypersil; C_{18} =ODS Hypersil; CN = CPS Hypersil. Data from ref. 14.

point means that an additional adsorption occurred above the CMC. This further increase of adsorbed surfactant may be as high as 20% of the CMC value in the case of SDS on cyanopropyl bonded silica. A similar comportment was noted by Borgerding and Hinze[7] using the non-ionic surfactant Brij 35 and a Waters Radial-Pak C_{18} bonded stationary phase.

In other work[17] we studied the effect of the addition of 5% (v/v) methanol or 0.1 *M* sodium chloride on the SDS and CTAB adsorption isotherms on two monolayer alkyl (C_1 and C_{18}) bonded silica. 5% Methanol decreased the quantity of surfactant adsorbed by about 15%. The global effect of sodium chloride was an increase or a decrease in the amount adsorbed depending on the surfactant and the stationary phase. Other organic modifiers (*n*-propanol, *n*-pentanol and THF) added to the micellar solution produced a decrease in the plateau concentration of the adsorption isotherms. This decrease was proportional to the mole fraction of the organic modifier added, as shown by Fig. 2.

The adsorption of both SDS and CTAB did not seem to be directly related to the micelle state. The CMC of each surfactant was modified by the addition of organic solvent (Fig. 3). However, the variation of the free surfactant concentration, *i.e.*, the CMC, did not correspond to the isotherm plateau-concentration variations. The organic solvent seemed to compete with the surfactant for adsorption on the stationary phase. Scott and Simpson[22] showed that the longer the alkyl chain of an alcohol, the stronger is the adsorption on C_{18} phases. According to these results, *n*-pentanol was adsorbed on the C_{18} stationary phase more strongly than was *n*-propanol. Thus, it desorbed more surfactant molecules than did propanol. The order of surfactant desorption strength was the same as the order of stationary phase affinity: pentanol > propanol > methanol. The effect of THF, up to 5% (v/v) or a molar fraction, $X = 0.0116$, was similar to the effect of propanol (Fig. 2). The two solvents were given comparable properties when used as chromatographic effluents[21].

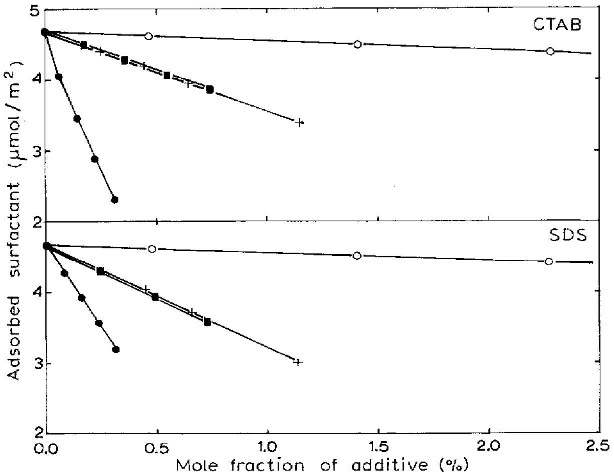

Fig. 2. Additive effects on surfactant adsorption. SDS concentration: 0.05 *M*; CTAB concentration: 0.02 *M*. $X = 2.28\%$ corresponds to 5% (v/v) methanol, $X = 1.15\%$ is 5% (v/v) THF, $X = 0.739\%$ is 3% (v/v) propanol, $X = 0.338\%$ is 2% (v/v) pentanol. Additives: ○ = methanol; + = THF; ■ = propanol; ● = pentanol.

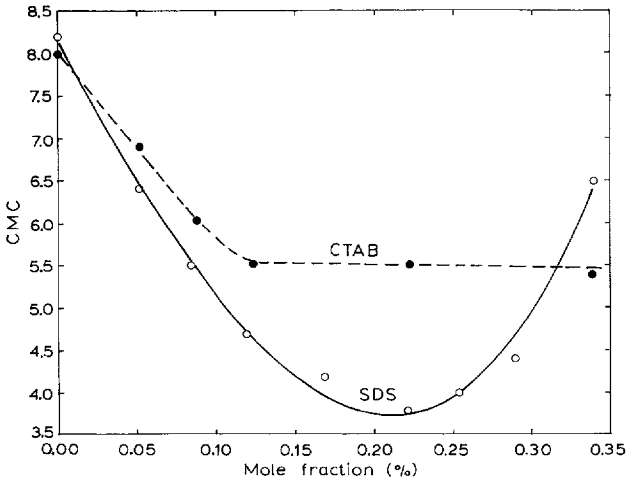

Fig. 3. Pentanol influence on CMC measured by conductimetry. ○, full line: SDS scale in 10^{-3} *M*. ●, dashed line: CTAB scale in 10^{-4} *M*. *X* =0.338% corresponds to 2% (v/v) pentanol.

Efficiency obtained with solutes of various polarities

As stated above, one of the early problems with MLC was rather poor chromatographic efficiency. This low efficiency was shown to be caused by slow mass transfer due principally to poor wetting of the stationary phase[11]. Fig. 4A shows a classical chromatogram obtained with a hydroalcoholic mobile phase. The peak of benzophenone, with a retention time of 3.3 min ($k' = 2.15$), allowed calculation of the

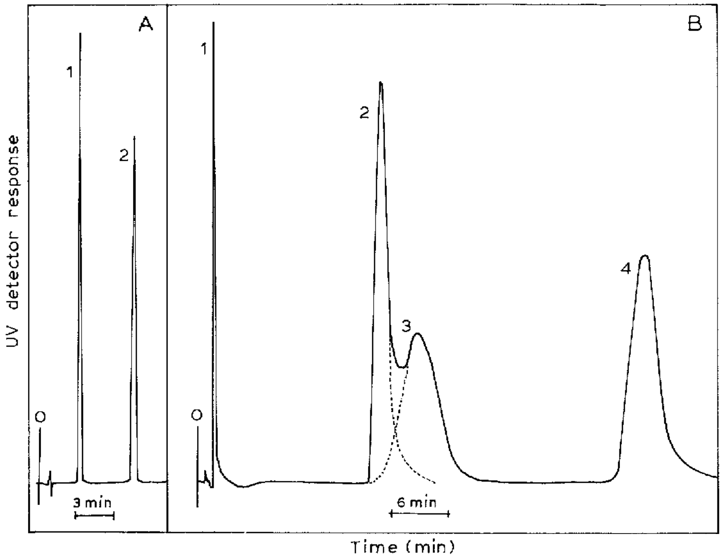

Fig. 4. Chromatograms on a 10-cm ODS Hypersil 5 μm column. A, Mobile phase methanol–water (75:25, v/v). Peaks: 1 = benzophenone; 2 = biphenyl (≈ 1 nmol). B, mobile phase 0.03 *M* CTAB in water. Peaks: 1 = caffeine (≈ 5 nmol); 2 = benzoic acid (≈ 30 nmol); 3 = CPC (≈ 30 nmol); 4 = toluene (≈ 60 nmol injected).

value of the efficiency, N, to be 3100 plates (H = 32 μm). The second peak (biphenyl), with a retention time of 7.8 min (k' = 6.43), was associated with an efficiency, N, of 4600 plates (H = 22 μm). Eqn. 2 showed that N is related to σ^2 (eqn. 5). Whereas the standard deviation σ_{col}, due to the column itself, was dependent on the elution time, the extra-column standard deviations were not time-dependent. Thus, the extra-column band broadening became less important for the most strongly retained solutes, and the efficiency seemed to increase with increasing retention times. Assuming that the standard deviations, σ_{col}, for benzophenone and biphenyl were strictly proportional to the respective retention times, and using eqns. 2 and 5, it was possible roughly to estimate the extra-column variance to be 1400 μl^2 (corresponding to a global extra-column dead volume of about 37 μl). This value was about 40% of the total variance for benzophenone which was 3500 μl^2 (eqn. 2), but only 10% of the total variance for biphenyl (13 300 μl^2). It was clear that extra-column band broadening had a less significant effect on highly retained solutes. This means that, given the characteristic of our system and with the ODS (C_{18}) column, only k' values greater than 7 were really significant for efficiency study. Fortunately, with high-water-content micellar mobile phases and ODS-bonded stationary phases, capacity factors, k', were higher than 7 for most of the solutes studied.

Fig. 4B shows a chromatogram obtained with the same hardware as for Fig. 4A, but with a micellar mobile phase comprising of 0.03 *M* CTAB. Table I lists the retention times, capacity factors and efficiencies for the solutes separated with CTAB (Fig. 4B) and SDS micellar mobile phases.

As stated in the literature[3–5,7,10–13], the efficiency was much lower with both anionic (SDS) and cationic (CTAB) micellar mobile phases, than with hydroalcoholic mobile phases. However, Table I and Fig. 4 show that the efficiency was strongly solute dependent. So, it seemed to be of interest to try to determine which parameters were involved in micellar efficiency.

TABLE I

CHROMATOGRAPHIC DATA WITH AQUEOUS MICELLAR PHASES

Column: 10 cm × 4.6 mm I.D., ODS Hypersil 5 μm, V_0 = 0.9 ml. Flow-rate: 1 ml/min. Average of three measurements, reproducibility 20%.

Mobile pase	*Solute*	t_R *(min)*	k'	N	H *(µm)*	B/A
0.05 *M* SDS	Caffeine	2.8	2.1	250	400	4.2
	Toluene	39.6	43.0	1350	74	3.4
	BTAB	46.7	50.9	160	625	2.1
	SOBS	6.7	6.4	1650	61	1.5
0.03 *M* CTAB	Caffeine	1.8	1.0	200	500	1.3
	Toluene	46.5	50.7	800	125	1.7
	Benzoic acid	19.5	20.6	490	200	2.2
	CPC	22.5	24.0	180	560	1.2

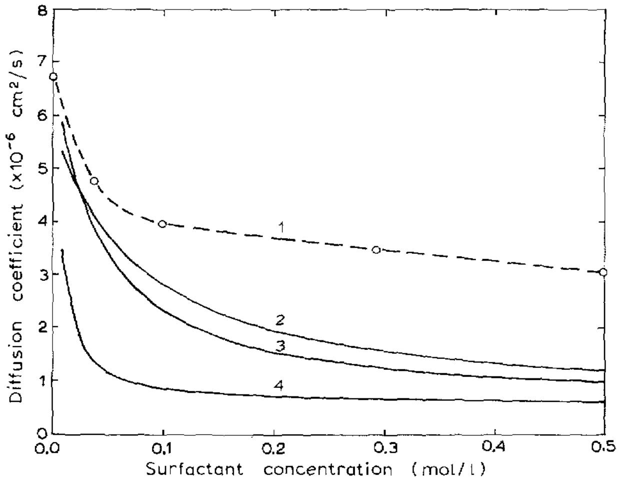

Fig. 5. Effect of micelles on solute diffusion coefficients. From data (compound 1, dashed line) and equations (compounds 2, 3 and 4) of ref. 24. 1 = Sodium 2,6-naphthalenedisulphonate; 2 = *p*-nitrophenol; 3 = *p*-nitroaniline; 4 = naphthol.

According to Snyder and Kirkland[21], the contributions to band broadening in a column can be represented by

$$H = C_e d_p + \frac{C_m d_p^2 u}{D_m} + \frac{C_d D_m}{u} + \frac{C_{sm} d_p^2 u}{D_m} + \frac{C_s d_f^2 u}{D_s} \qquad (6)$$

in which the C values are constant plate height coefficients related to eddy diffusion (e), mobile phase mass transfer (m), longitudinal diffusion (d), stagnant mobile phase mass transfer (sm) and stationary phase mass transfer (s), d_p is the diameter of the packing particles, d_f the thickness of the stationary phase layer, D_m the solute diffusion coefficient in the mobile phase layer, D_s is the solute diffusion coefficient in the stationary phase layer and u is the mobile phase velocity.

The first solute-dependent parameter is the diffusion coefficient, D_m, in the mobile phase (terms 2, 3 and 4 in eqn. 6). In recent work[23] we showed that D_m was strongly dependent on the K_{MW} values. Fig. 5 shows the D_m evolution *versus* the surfactant concentration for three binding solutes of similar polarities, and a non-binding solute. Table II lists the efficiencies obtained with these solutes.

There were no significant differences in efficiency between the slow-diffusing solutes and the rapidly diffusing one. Furthermore, there were no significant efficiency differences at different surfactant concentrations[23]. These results indicated that the mobile phase mass-transfer effects were not mainly responsible for the poor efficiency obtained with micellar mobile phases.

The last term of eqn. 6 involves stationary phase mass transfer. It seems to be the most important term, overshadowing the other factors in the case of micellar mobile phases. The thickness, d_f, of the stationary phase layer was significantly increased by surfactant adsorption[7], and the structure of the layer was modified by the insertion of surfactant molecules. This may increases the viscosity of the stationary phase layer and

TABLE II

EFFICIENCY AND DIFFUSION COEFFICIENTS

Column: 30 cm × 4.6 mm I.D., polynitrile 10 μm (Varian). Flow-rate 1 ml/min; 20°C. A 3000-plate efficiency was obtained with a hydroalcoholic mobile phase and the same hardware, from ref. 23.

Solute	K_{MW}	K_{SW}	*0.005 M SDS*		*0.5 M SDS*	
			D_m (10^{-6} cm^2/s)	*N* (*plates*)	D_m (10^{-6} cm^2/s)	*N* (*plates*)
Naphthol	370	30	1.1	530	0.62	540
p-Nitroaniline	87	4.6	3.3	760	0.97	660
p-Nitrophenol	48	4	3.6	460	1.18	510
Sodium 2,6-naphthalene-disulphonate	*	*	4.5	560	3.06	560

* Non-micelle binding solute.

decrease the diffusion coefficient, D_s, of the solute in the liquid crystal-like layer[23].

The surfactant adsorption was not very different on four monolayer bonded stationary phases[14]. Table III lists the efficiency obtained with the solutes studied compared with the respective K_{SW} values which measure the solute affinity for the

TABLE III

EFFECT OF THE STATIONARY PHASE ON EFFICIENCY

Mobile phase: 0.03 *M* CTAB. Columns: 10 cm × 4.6 mm I.D., packed with Hypersil monolayer bonded stationary phases 5 μm; 25°C. Average of three measurements, reproducibility 20%.

Stationary phase		*Caffeine**	*Toluene*	*Benzoic acid*	*CPC*	*Biphenyl***
CPS cyanopropyl	k'	1.8	27	33	27	3.6
	K_{SW}	2.0	63	490	910	–
	N	430	1210	330	100	4000
	H (μm)	230	83	300	1000	25
SAS C_1	k'	2.4	18	37	26	3.9
	K_{SW}	3.6	55	870	850	–
	N	300	630	200	15	3400
	H (μm)	330	160	500	6700	29
MOS C_8	k'	1.3	39	23	21	5.2
	K_{SW}	1.8	190	760	1000	–
	N	160	600	150	70	3300
	H (μm)	620	170	670	1430	30
ODS C_{18}	k'	1	50.7	20.6	24	6.4
	K_{SW}	2.3	190	550	610	–
	N	200	800	490	180	4600
	H (μm)	500	130	200	560	22

* Efficiency values of caffeine were not very significant given its low retention time (high extra-column effects).

** Biphenyl was used to check the column efficiency with methanol–water (75:25, v/v) on ODS and MOS Hypersil and methanol–water (70:30, v/v) on SAS and CPS Hypersil.

TABLE IV

EFFECT OF SOME ADDITIVES ON EFFICIENCY IN MLC

Column: 10 cm × 4.6 mm I.D., ODS Hypersil 5 μm; 25°C. Average of three measurements, reproducibility 20%, 4600 plates were obtained with biphenyl and a methanol–water (75:25, v/v) mobile phase. Results obtained with caffeine were not very significant because the k' values were lower than 1.5.

Mobile phase	*Solute*	*Additive*					
		None	*0.1 M NaCl*	*5% Methanol*	*3% Propanol*	*0.5% Pentanol*	*3% (v/v) THF*
0.05 *M* SDS	Caffeine	250	230	260	800	450	1100
	Toluene	1350	1000	1000	4400	2300	1400
	BTAB	160	110	120	400	150	160
	SOBS	1650	1000	1300	1900	1300	1500
0.02 *M* CTAB	Caffeine	180	190	210	2000	140	2800
	Toluene	750	1100	800	3900	1100	4000
	Benzoic acid	380	420	600	2200	600	2000
	CPC	200	220	300	370	300	380

surfactant-covered stationary phase. It is apparent that, whatever the stationary phase, the lowest efficiency occurred with CPC and the highest with toluene. At this point, it seems that the higher the K_{SW} value, the lower is the efficiency. The surfactant adsorption on bonded stationary phases was significantly affected by additives in the micellar mobile phase[16,17]. The efficiencies obtained with each additive are listed in Table IV for SDS and CTAB micellar mobile phases.

As stated by Dorsey[10–12], the best improvement in micellar efficiency was obtained with the addition of 3% *n*-propanol in the micellar mobile phase. Although, the efficiency obtained for BTAB and CPC, with SDS and CTAB as micellar mobile phases, respectively, remained low, even when propanol was present (Table IV). These two compounds are quaternary ammonium salts. Amine and ammonium salts have an high affinity for residual surface silanols, which was the reason for the high K_{SW} values (Table III)[15,16]. The first reason for the significantly low efficiency noted with these solutes is the heteroenergetic retention process from the mixed partition–adsorption

TABLE V

EFFICIENCY EVOLUTION OF A COLUMN EXPOSED TO SURFACTANTS

A, New column; B, after 2 days of work with CTAB mobile phases and about 3 h of rinse with methanol (200 ml); C, after 2 days of work with SDS mobile phases and about 3 h of rinse with methanol (200 ml); D, after a couple of working days with CTAB + pentanol mobile phases and rinse with methanol; E, after 2 days of work with CTAB + propanol and rinse with methanol. Column: 10 cm × 4.6 mm I.D., ODS Hypersil 5 μm. Mobile phase: methanol–water (75:25, v/v), 25°C.

Solute	*Test*				
	A	*B*	*C*	*D*	*E*
Benzophenone	3100	2900	2700	3300	3200
Biphenyl	4600	3900	3600	4500	4200

interactions. The second reason is the fact that these silanols lie on the silica surface, which means that quaternary ammonium salts have to pass through the surfactant adsorbed layer and through the bonded layer (Fig. 6) to reach the silanols. This may result in a large d_f value and partly explain the poor efficiency for these solutes (term 5, eqn. 6).

Pentanol was adsorbed more strongly than any other additive studied (Fig. 2 and ref. 22), however, its effect on efficiency was not as good as that of propanol (Table IV). It seemed that an important physico-chemical parameter was the "rigidity" of the organic stationary phase layer. The term "rigidity" was used by De Gennes and Taupin[24] to explain the rôle of medium-chain-length *n*-alcohols on microemulsion formation. They showed that the major effect of those alcohols was to increase the flexibility of the layers separating the aqueous phase from the oil phase. Although the oil phase of a microemulsion is different from the stationary phase in MLC, the aqueous phases are quite similar. Then, in a very crude fashion, we propose to compare the interphases, *i.e.*, the surface of the surfactant-covered bonded phase may resemble the alcohol–surfactant layer separating the oil phase from the aqueous phase in an oil-in-water microemulsion.

With a pure aqueous mobile phase, the bonded layer was in a very rigid "collapsed state"[25] (Fig. 6). Surfactant may be adsorbed on this layer (Figs. 1 and 6, ref. 14) wich still remained rigid. Organic additives may modify and perhaps destroy the crystal-like "collapsed state"[26] (Fig. 6). Propanol seems to be the additive producing the less rigid organic layer which induced high diffusion coefficients, D_s, and higher efficiency. The partial displacement/replacement of adsorbed surfactant molecules by pentanol molecules seems to make up a composite layer less rigid than the pure adsorbed surfactant layer, but more rigid than the propanol–surfactant layer. THF, whose effect on adsorption was similar to that of propanol (Fig. 2), improved the efficiency almost as well as did propanol (Table IV).

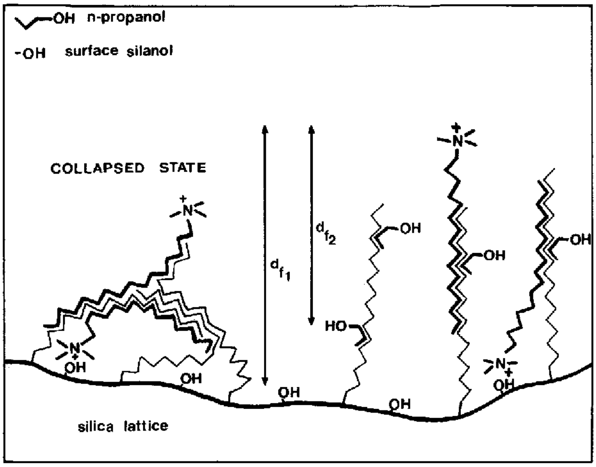

Fig. 6. Oversimplified model of the surfactant-covered stationary phase (CTAB and ODS Hypersil monolayer type). d_{f_1} = Thickness of the layer in the case of quaternary ammonium compounds; d_{f_2} = thickness of the layer in the case of non-polar compounds. Left side: the "collapsed state". Right side: a brush-type layer obtained with 3% (v/v) propanol in the micellar mobile phase.

It was pointed out[7] that the surfactant adsorbed layer was very stable, *i.e.*, it was impossible to desorb the surfactant even after a 24-h dynamic extraction with acetonitrile–water (30:70, v/v). However, pure methanol fully desorbed the entire adsorbed surfactant[14,16]. To confirm this, we determined the efficiency of a column exposed to both anionic and cationic surfactants with intermediate methanol rinsing. The pressure drop remained constant. Table V lists the efficiency evolution of the column. The constancy of the hydroalcoholic pressure drop and efficiency was good evidence of total surfactant desorption on monolayer bonded stationary phases. Indeed, if a part of SDS was irreversibly adsorbed onto the stationary phase, the negative charges would retain the CTA^+ ion during the CTAB exposure, producing a build-up of a thick adsorbed layer that could obstruct the column and/or produce a permanent low efficiency.

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