ELSEVIER

Journal of Chromatography A, 687 (1994) 1–12

JOURNAL OF CHROMATOGRAPHY A

Retention mechanism and implications for selectivity for a group of dihydropyridines in ionic micellar liquid chromatography

J.M. Saz, M.L. Marina*

Department of Analytical Chemistry, Faculty of Sciences, University of Alcalá de Henares, Ctra. Madrid–Barcelona Km 33.6, 28871 Alcalá de Henares (Madrid), Spain

First received 25 March 1994; revised manuscript received 29 July 1994

Abstract

The retention behaviour of a group of dihydropyridines in micellar liquid chromatography was studied using sodium dodecyl sulphate and hexadecyltrimethylammonium bromide as surfactants in the mobile phase containing 5% of *n*-butanol and a C_{18} column. When the surfactant concentration in the mobile phase is increased, a tendency to change from a three partition equilibria mechanism to direct transfer of solutes from micelles to the stationary phase is observed for both surfactants. This progressive change in the retention mechanism is explained through the large micellar phase–water partition coefficients of these compounds and the increase produced in the fraction of solute molecules in the micellar phase due to the increase in the volume of this phase originating from the increase in surfactant concentration. As a result, the selectivity coefficients show a tendency to match the ratio of the stationary phase to micellar phase partition coefficients of these compounds, constituting further proof of the progressive change in the retention mechanism when the surfactant concentration is increased.

1. Introduction

The use of micellar systems as mobile phases in high-performance liquid chromatography (HPLC) has given rise to micellar liquid chromatography (MLC) [1]. This confers on HPLC the unique properties of micelles, allowing the analysis of ionic solutes [2,3] and of polar and non-polar solutes simultaneously [4] and improving the selectivity through variations of the surfactant nature and concentration [5–7].

Micelles constitute a different phase or pseudo-phase in the bulk mobile phase and retention is determined by the solute affinity toward the aqueous mobile phase, the stationary phase and the micellar mobile phase. A three partition equilibria mechanism has been proposed to explain retention in MLC [8]. Each solute undergoes partitioning between the stationary phase, the aqueous phase and the micellar pseudo-phase. Two equations that arise from this mechanism have been developed to predict retention in MLC [8,9]:

$$\frac{V_s}{(V_e - V_m)} = \frac{v(P_{mw} - 1)}{P_{sw}} \cdot C_M + \frac{1}{P_{sw}} \quad (1)$$

$$\frac{1}{k'} = \frac{V_m K_2}{V_s K_1 [L]} \cdot C_M + \frac{V_m}{V_s K_1 [L]} \quad (2)$$

* Corresponding author.

0021-9673/94/$07.00
SSDI 0021-9673(94)00716-0

where k' is the capacity factor of the solute, K_1 and K_2 the solute–stationary phase and –micelle association constants, C_M the micellized surfactant concentration (total surfactant concentration minus the critical micellar concentration, cmc), [L] the stationary phase concentration, V_s, V_m, V_e and v the stationary and mobile phase volume, the eluting volume of the solute and the molar volume of the surfactant, respectively, and P_{mw} and P_{sw} the micelle–water and stationary phase–water partition coefficients of the solute, respectively.

Borgerding et al. [10] have proposed a limit theory for those compounds whose affinity towards the micellar phase is large enough to experience a direct transfer from this phase to the stationary phase. These solutes only undergo partitioning between the micellar pseudo-phase and the stationary phase, as the amount of solute in the aqueous phase is almost negligible. The capacity factor (k') for these compounds is defined by

$$k' = \frac{V_s}{V_m} \cdot \frac{P_{sm}}{vC_M} \quad (3)$$

The implications of this direct transfer for chromatographic parameters such as selectivity have not been considered in the data published previously.

In this study, new evidence of the direct transfer theory is presented to help interpret the chromatographic behaviour of a group of dihydropyridines (DHPs) in an MLC system in which sodium dodecyl sulphate (SDS) and hexadecyltrimethylammonium bromide (CTAB) are used as surfactants in the mobile phase. The results of the application of this theory to selectivity and some supporting data are presented.

2. Experimental

The HPLC system consisted of a Model 510 pump, U6K injector, Model 481 variable-wavelength UV–Vis detector and Model 740 data module (all from Waters). The analytical columns (150 mm × 3.9 mm I.D.) were packed by a column packing company (Tracer, Barcelona, Spain) using a commercially available C_{18} packing material (e.g., 5-μm Spherisorb ODS-2). The column was water-jacketed and temperature controlled (30 ± 1°C) by a circulating bath.

All reagents (e.g., SDS, CTAB, *n*-butanol and sodium phosphate buffer) were purchased from Merck. DHPs were synthesized in the Department of Organic Chemistry, University of Alcalá de Henares, Spain. Fig. 1 groups the structures of the DHPs studied and their identification numbers used through the paper.

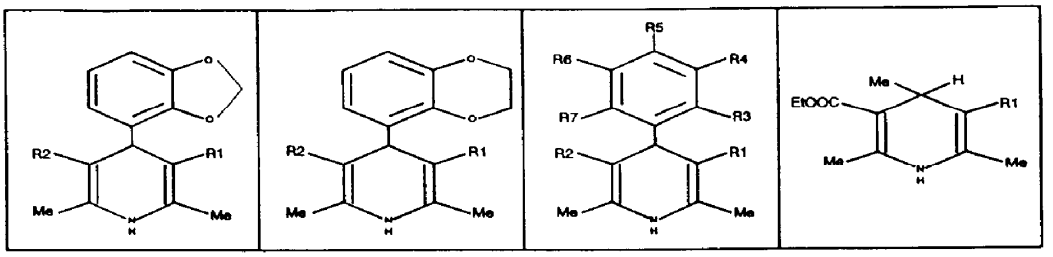
Mobile phases were prepared by dissolving in HPLC-grade water the appropriate amounts of surfactant, *n*-butanol and sodium phosphate buffer in an ultrasonic bath followed by filtration through a 0.45-μm filter. Mobile phases were degassed in the ultrasonic bath prior to their utilization. Stock solutions of test solutes were prepared in the mobile phase itself and injected directly (20 μl) into the chromatographic system. The solute concentration was arbitrarily adjusted to permit detection. Solutes were injected in triplicate for every mobile phase condition used and the mean value of the retention times was used for calculations. The void volume was determined from the first deviation of the baseline and the stationary phase volume was taken as the difference between the total volume of the column and the void volume.

3. Results and discussion

3.1. Retention mechanism

The predicted linear relationship between $1/k'$ or $V_s/(V_e - V_m)$ versus C_M according to Eqs. 1 and 2 has been demonstrated in literature for many different types of solutes, surfactants and stationary phases [10–12]. Further, good agreement has been found between the partition or binding constants obtained from these equations and those determined by alternative methods [9,13].

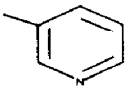
As predicted by theory, a linear relationship between $1/k'$ and C_M is also shown in Fig. 2a–d for the studied DHPs when SDS or CTAB is



Group 1 Group 2 Group 3 Group 4

Group 1	$-R_1$	$-R_2$
1	$-COOCH_2-$(1)	$-COOCH_3$
2	$-COOCH_3$	$-COOCH_3$
3	$-COOCH_2CH_2OCH_3$	$-COOCH_2CH_2OCH_3$
5	$-COOCH_2CH_3$	$-COOCH_2CH_3$
6	$-COOCH_2CH_2OCH_3$	-COOIsp
7	-COOIsp	$-COOCH_2CH_3$
12	$-COOCH_2CH_3$	$-COOCH_3$
14	-COOIsp	-COOIsp
17	-COOIsp	$-COOCH_3$

(1)



Group 2	$-R_1$	$-R_2$
4	$-COOCH_2CH_3$	$-COOCH_3$

Group 3	$-R_1$	$-R_2$	$-R_3$	$-R_4$	$-R_5$	$-R_6$	$-R_7$
8	$-COOCH_2CH_3$	$-COOCH_3$	-H	$-NO_2$	-H	-H	-H
9	$-COOCH_2CH_3$	$-COOCH_3$	-Cl	-Cl	-H	-H	-H
10	$-COOCH_2CH_3$	$-COOCH_3$	$-OCH_2OCH_3$	-H	-H	-H	-H
11	$-COOCH_2CH_3$	$-COOCH_3$	-H	$-OCH_3$	-H	$-OCH_3$	-H
13	$-COOCH_2CH_3$	$-COOCH_3$	-H	-H	-H	-H	-H
15	$-COOCH_2CH_3$	$-COOCH_3$	-H	$-OCH_3$	$-OCH_3$	-H	-H
16	$-COOCH_2CH_3$	$-COOCH_3$	$-OCH_3$	$-OCH_3$	-H	-H	-H
18	$-COOCH_2CH_3$	$-COOCH_3$	-H	$-OCH_3$	-OH	$-OCH_3$	-H
19	$-COOCH_2CH_3$	$-COOCH_3$	-H	$-OCH_3$	$-OCH_3$	$-OCH_3$	-H
20	$-COOCH_2CH_3$	$-COOCH_2CH_3$	-Cl	-H	-H	-H	-Cl
21	$-COOCH_2CH_3$	$-COOCH_2CH_3$	-Cl	-H	-H	-H	-H

Group 4	$-R_1$
22	$-COOCH_3$
23	$-COOCH_2CH_2-$(2)
24	$-COOCH_2CH_3$

(2)

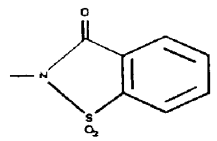


Fig. 1. Structures of the DPHs studied and the number assigned to each.

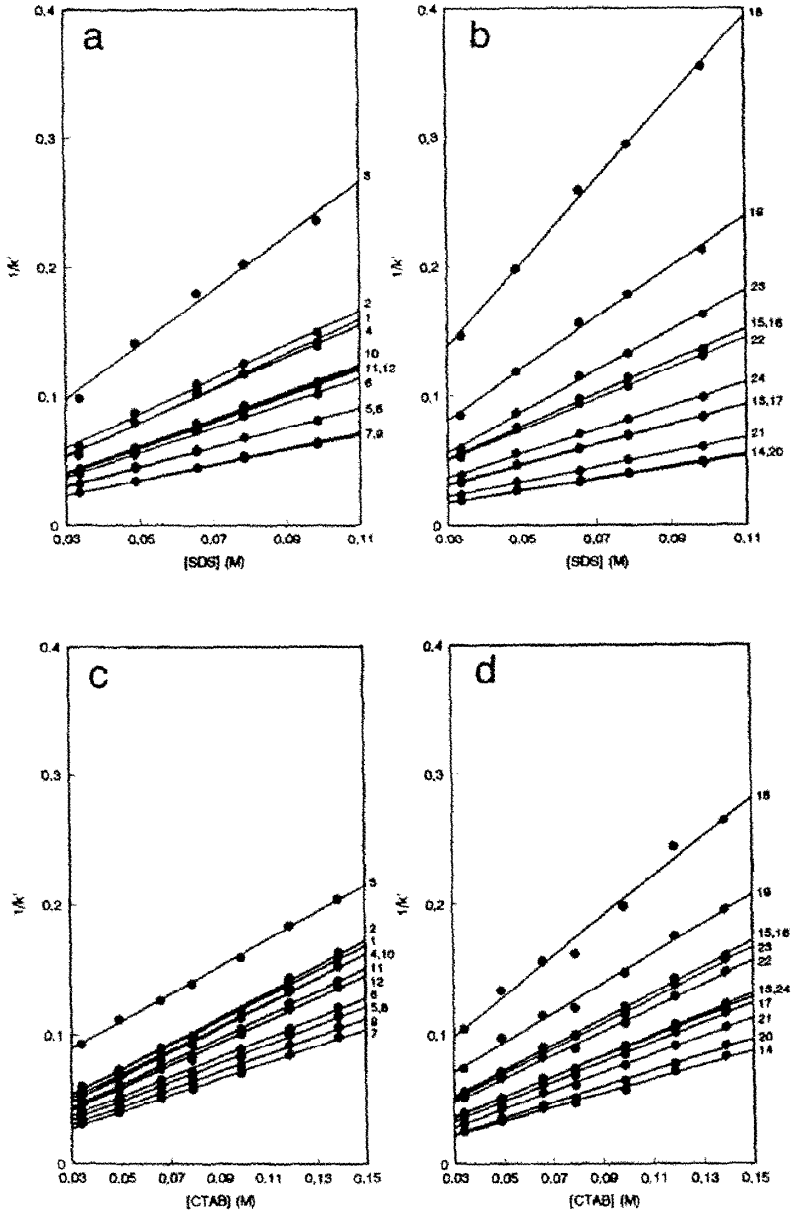


Fig. 2. Inverse of capacity factor ($1/k'$) versus micellized surfactant concentration (C_M) in the mobile phase (total surfactant concentration minus its critical micellar concentration) for each DHP. The composition of mobile phases was 0.01 *M* sodium hosphate buffer (pH 6.7)–5% (v/v) *n*-butanol with a total surfactant concentration ranging from 0.035 to 0.1 *M* for SDS and 035 to 0.14 *M* for CTAB.

esent in the mobile phase above their cmc. A all amount of an organic additive (e.g., *n*-anol) and phosphate buffer of pH 6.7 were added to the mobile phase to decrease the retention of solutes and to control the pH, as these types of compound present a large re-

tention and are quoted in the literature as alkaloid compounds [14]. A similar linear relationship also exists for $V_s/(V_e - V_m)$ versus C_M (data not shown). The parameters of these straight lines are given in Tables 1 and 2 and were used to determine K_2, P_{sw} and P_{mw} using Eqs. 1 and 2. The stationary phase–micellar phase partition coefficients (P_{sm}) were obtained from the ratio P_{sw}/P_{mw}.

The relative error for the solute–micelle association constants shown in Tables 1 and 2 was determined statistically. The means ± standard deviations were 26 ± 7% for SDS and 16 ± 7% for CTAB. In general terms, we observed that the error increased when the intercept of straight lines in Fig. 2a–d decreased. This is primarily due to the fact that the K_2 constants are determined from the slope/intercept ratio of these straight lines and, therefore, small intercept values produce large statistical errors in the determination of solute–micelle association constants.

In general terms, the K_2 constants and the related P_{mw} coefficients shown in Tables 1 and 2 and in Fig. 3 are larger for SDS than CTAB. SDS and CTAB possess a long hydrocarbon chain with twelve and sixteen carbons, respectively. This means that hydrophobic interactions between DHPs and SDS or CTAB should be higher, or at least similar (depending on the molecular size of the solute), in magnitude for CTAB than SDS. If DHPs bind to SDS and CTAB micelles only through hydrophobic forces, then the solute–micelle association parameters (e.g., K_2 and P_{mw}) should also be higher for CTAB or at least similar for both. As

Table 1
Parameters of straight lines obtained when retention factors of Eqs. 1 and 2 using SDS are plotted versus the micellized surfactant concentration and the equilibrium constants calculated from these parameters

DHP	Eq. 1				Eq. 2						
	Slope	Intercept ($\times 10^2$)	r	K_2	Slope	Intercept ($\times 10^2$)	r	K_2	P_{sw}	P_{mw}	P_{sm}
1	1.32	1.37	0.9937	96.16	1.64	1.70	0.9936	96.01	58.64	391.24	0.15
2	1.32	2.06	0.9971	63.95	1.63	2.56	0.9971	63.97	39.10	261.04	0.15
3	2.10	3.44	0.9932	61.07	2.61	4.26	0.9932	61.22	23.46	249.86	0.09
4	1.25	1.74	0.9965	71.63	1.54	2.16	0.9964	71.50	46.25	291.65	0.16
5	0.75	0.86	0.9983	86.83	1.01	0.64	0.9989	158.73	156.84	646.24	0.24
6	0.95	0.90	0.9979	105.37	1.18	1.13	0.9978	104.29	88.63	424.94	0.21
7	0.59	0.56	0.9988	104.02	0.73	0.69	0.9988	105.26	144.48	428.89	0.34
8	0.76	0.69	0.9991	110.52	0.95	0.85	0.9990	111.10	117.08	452.63	0.26
9	0.61	0.49	0.9990	125.27	0.76	0.61	0.9990	123.43	163.24	502.75	0.32
10	1.03	1.03	0.9984	99.85	1.28	1.28	0.9985	99.91	78.11	407.14	0.19
11	1.00	0.98	0.9993	102.37	1.24	1.22	0.9994	102.12	82.19	416.12	0.20
12	1.00	1.11	0.9979	90.00	1.24	1.37	0.9980	90.83	73.01	370.23	0.20
13	0.77	0.90	0.9993	85.73	0.95	1.11	0.9993	85.62	89.76	349.05	0.26
14	0.45	0.40	0.9990	112.68	0.56	0.50	0.9991	112.37	200.65	457.79	0.44
15	1.25	1.42	0.9986	87.79	1.54	1.76	0.9985	87.64	56.74	357.26	0.16
16	1.25	1.42	0.9985	87.53	1.55	1.77	0.9985	87.38	56.50	356.20	0.16
17	0.78	0.75	0.9991	103.90	0.97	0.92	0.9990	104.81	108.21	427.06	0.25
18	3.21	4.18	0.9988	76.81	3.98	5.19	0.9988	76.80	19.31	313.20	0.06
19	1.97	2.19	0.9980	90.01	2.45	2.73	0.9980	89.75	36.65	365.84	0.10
20	0.47	0.37	0.9990	125.71	0.58	0.47	0.9990	124.06	212.74	505.31	0.42
21	0.57	0.53	0.9984	106.02	0.70	0.65	0.9984	107.99	153.05	439.98	0.35
22	1.18	1.47	0.9985	80.56	1.46	1.82	0.9985	80.33	54.82	327.54	0.17
23	1.57	0.89	0.9988	176.66	1.95	1.10	0.9988	177.54	91.00	722.71	0.13
24	0.91	0.99	0.9987	92.31	1.13	1.23	0.9986	91.61	81.03	373.40	0.22

Table 2
Parameters of straight lines obtained when retention factors of Eqs. 1 and 2 using CTAB are plotted versus the micellized surfactant concentration and the equilibrium constants calculated from these parameters.

DHP	Eq. 1				Eq. 2						
	Slope	Intercept ($\times 10^2$)	r	K_2	Slope	Intercept ($\times 10^2$)	r	K_2	P_{sw}	P_{mw}	P_{sm}
1	0.97	2.49	0.9997	38.85	1.20	3.09	0.9997	38.89	32.28	106.22	0.30
2	0.99	2.49	0.9997	39.88	1.23	3.09	0.9997	39.87	33.53	114.02	0.29
3	1.05	5.81	0.9983	18.03	1.30	7.20	0.9992	18.00	13.89	50.50	0.28
4	0.93	2.38	0.9989	38.90	1.15	2.96	0.9989	38.81	35.16	112.13	0.31
5	0.73	1.17	0.9992	62.61	0.91	1.46	0.9992	62.40	68.38	171.85	0.40
6	0.76	1.46	0.9998	52.00	0.94	1.82	0.9998	51.94	57.64	150.86	0.38
7	0.64	0.78	0.9989	82.66	0.80	0.97	0.9990	82.44	103.25	227.26	0.45
8	0.73	1.24	0.9995	59.30	0.91	1.53	0.9995	59.22	69.34	174.57	0.40
9	0.69	0.92	0.9986	74.43	0.85	1.15	0.9986	74.29	87.36	206.05	0.42
10	0.95	1.95	0.9990	48.68	1.18	2.42	0.9990	48.74	41.32	134.65	0.31
11	0.89	1.74	0.9998	51.38	1.11	2.16	0.9998	51.28	48.83	150.23	0.33
12	0.87	1.59	0.9999	54.70	1.08	1.96	0.9999	54.79	53.67	160.23	0.33
13	0.81	1.11	0.9999	73.13	1.00	1.38	0.9999	72.95	76.66	212.89	0.36
14	0.55	0.59	0.9999	92.13	0.68	0.74	0.9999	92.45	149.25	278.03	0.54
15	1.01	2.11	0.9996	47.68	1.25	2.62	0.9996	47.62	38.23	132.04	0.29
16	0.99	2.25	0.9991	44.12	1.23	2.79	0.9991	44.17	35.88	122.51	0.29
17	0.76	1.05	0.9991	72.33	0.95	1.13	0.9988	84.39	88.08	231.74	0.38
18	1.54	5.20	0.9920	29.55	1.90	6.46	0.9920	29.45	15.49	81.99	0.19
19	1.16	3.50	0.9990	33.06	1.44	4.33	0.9990	33.18	22.22	87.43	0.25
20	0.62	0.40	0.9988	153.64	0.76	0.50	0.9988	153.31	200.11	421.80	0.47
21	0.71	0.66	0.9992	107.54	0.88	0.82	0.9992	107.51	122.91	297.29	0.41
22	0.91	2.02	0.9994	45.37	1.13	2.50	0.9994	45.28	41.34	130.15	0.32
23	0.97	2.19	0.9993	44.41	1.20	2.72	0.9993	44.34	39.90	133.86	0.30
24	0.78	1.26	0.9994	61.99	0.96	1.56	0.9994	61.85	64.18	171.19	0.37

these parameters are much larger for SDS than CTAB, it is most likely that differences in the intensity of hydrophilic interactions between DHPs and the ionic surface of SDS and CTAB micelles could be responsible for the higher affinity of DHPs to SDS than CTAB. This result is in accordance with the reported alkaline properties of this class of compounds [14], which could indicate the possibility that these DHPs will be positively charged under the experimental conditions used. This idea is also supported by the fact that SDS micelles, owing to their anionic surface, produce an increase in the local concentration of protons on their surface by a factor of ca. 100 [15], which can lead to an increase in the pK_a of a given compound of between 0.5 and 3.0 units [16]. For other compounds such as benzene and naphthalene derivatives under similar experimental conditions, larger solute–micelle association constants with CTAB have been reported [12]. This may be due to the diverse molecular structures of these derivatives and DHPs. In fact, benzene and naphthalene deriva-

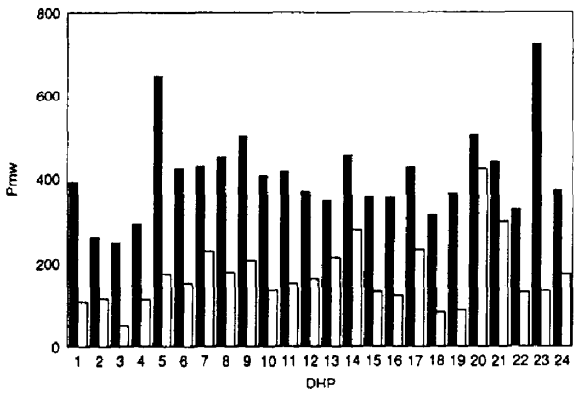


Fig. 3. P_{mw} coefficients of DHPs for either SDS (■) and CTAB (□).

tives have π-electrons which can interact with the positive surface of CTAB micelles.

As shown in Tables 1 and 2 and Fig. 3, the solute–micelle interaction is much larger for SDS than for CTAB. However, the P_{mw} coefficients with CTAB are also large. This could be mainly due to (i) the high hydrophobicity of these compounds (e.g., log P_{ow} ranges from 2.8 to 5.0 for the DHPs studied in this work) and (ii) the π-electrons which almost all of these DHPs possess in their phenyl ring which could interact with the positive surface of CTAB micelles.

P_{mw} coefficients for either SDS and CTAB, with the exception of three cases, possess values larger than 100 (Tables 1 and 2 and Fig. 3). This indicates the possibility that DHPs will be present in the mobile phase mainly in the micellar pseudo-phase, that is, their chromatographic behaviour could be explained by the direct transfer theory proposed by Borgerding et al. [10]. To demonstrate this idea, the experimental k' values and those obtained by this theory (Eq. 3) need to be the same. We calculated for every DHP and chromatographic condition used the k' values expected by Eq. 3. Fig. 4 shows a representative group of data for DHPs with small, intermediate and large P_{mw} coefficients, and the general pattern is similar in all instances. As shown by Fig. 4, when the surfactant concentration is increased the k' values of the direct transfer theory tend to match the experimental values. Therefore, there is a change from a three partition equilibria mechanism to direct transfer of DHPs from the micellar pseudo-phase to the stationary phase when the surfactant concentration in the bulk mobile phase is increased. This could be explained through the increase in the micellar pseudo-phase volume which, owing to the large P_{mw} coefficients of these compounds (Tables 1 and 2 and Fig. 3), causes an increase in the micellar–water solute molecules fraction. Table 3 shows an estimate of the ratio of molecules between the micellar and aqueous phases for the compounds shown in Fig. 4. These data were obtained from the P_{mw} coefficients and the micellar and aqueous phase volumes.

Fig. 5 shows the DHP P_{sw} coefficients when either SDS or CTAB is present in the mobile phase. The P_{sw} coefficients are slightly higher for SDS than for CTAB. This difference may be evidence of the surfactant adsorption on the stationary phase, at least for one of the two surfactants, otherwise the P_{sw} coefficients of these compounds should be independent of the nature of the surfactant used in the mobile phase. Assuming surfactant adsorption on the stationary phase, as the affinity of DHPs for SDS micelles is higher than for CTAB micelles (Fig. 3), the affinity towards the SDS-modified stationary phase is expected also to be higher than for CTAB, as demonstrated by Fig. 5. The magnitude and difference between the P_{sw} coefficients for both surfactants (Fig. 5) are much lower than for the P_{mw} coefficients (Fig. 3). Therefore, it is likely that the participation of the surfactant molecules adsorbed in the solute retention will be small and then DHPs are retained primarily through interaction with the C_{18} chains.

A linear relationship between P_{mw} and P_{sw} coefficients is clearly shown in Fig. 6 for CTAB but not for SDS. This result could indicate interaction of the solute with the micellar and the surfactant-modified stationary phase similar in nature for CTAB and different for SDS. Assuming that surfactant adsorbed-molecules on the stationary phase for either SDS or CTAB probably participate to a small extent in the retention mechanism (Fig. 5) and solute–stationary phase interaction occurs primarily through the C_{18} chains, the nature of the solute–micelle interaction could be mainly controlled by hydrophobic forces for CTAB. The worse correlation between P_{mw} and P_{sw} coefficients for SDS could be explained by considering the above-mentioned participation of hydrophilic interactions on the DHP–micelle association complex.

3.2. Selectivity coefficients

The selectivity coefficients were calculated for each pair of compounds. Fig. 7 shows a representative group of selected data among those compounds with small, intermediate and large P_{mw} coefficients. The general pattern observed in almost all instances is that the selectivity co-

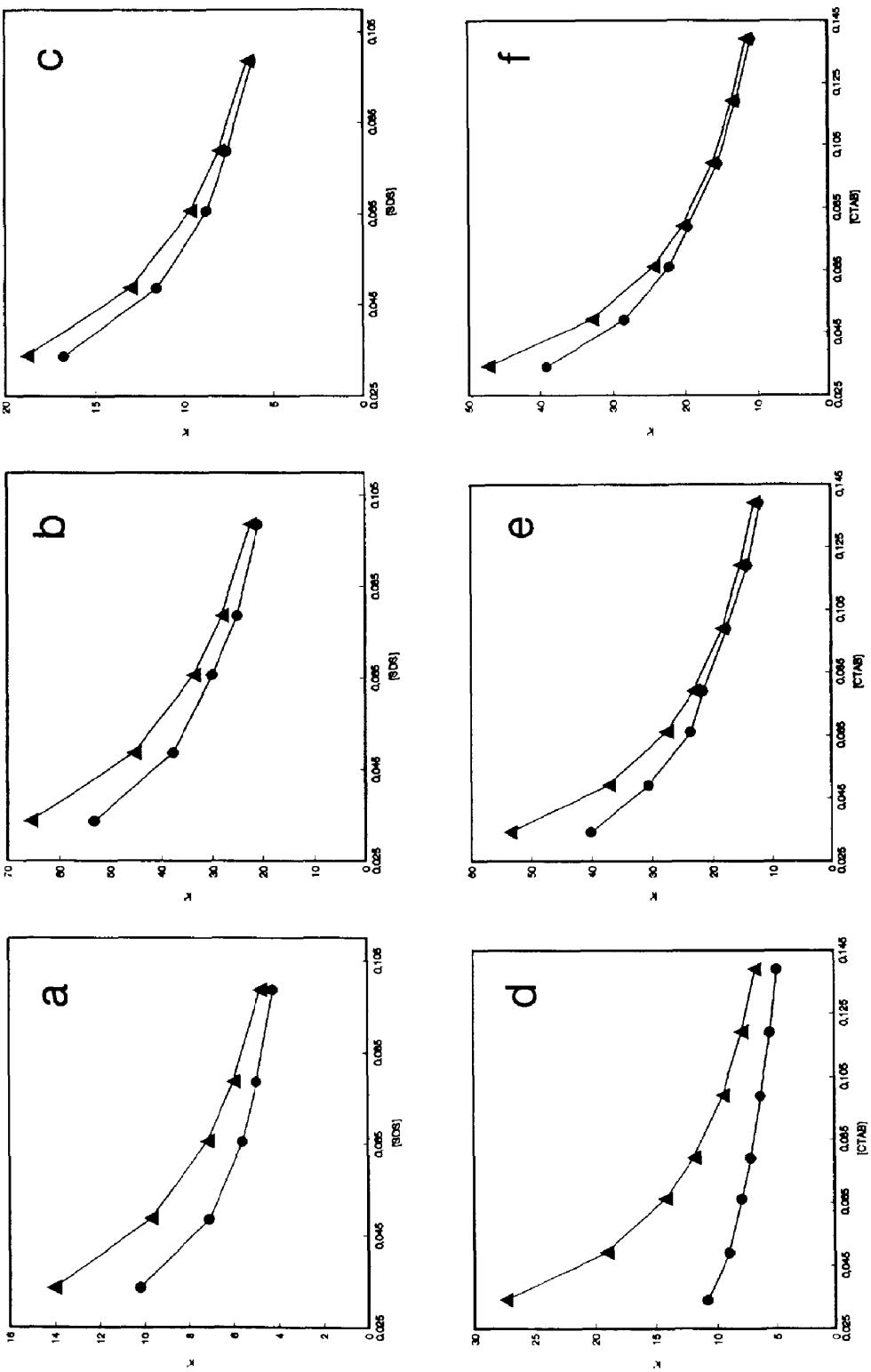


Fig. 4. (●) Experimental and (▲) theoretical capacity factors (k') of three representative groups of DHPs with small, intermediate and large P_{m_w} coefficients as a function of surfactant concentration (M) in the mobile phase for (**a**–**c**) SDS and (**d**–**f**) CTAB. The compounds represented are (**a** and **d**) **3**, (**b** and **e**) **14**, (**c**) **23** and (**f**) **20**.

Table 3
Micellar–water ratio of solute molecules for conditions used in Fig. 4.

		DHP 3	DHP 14	DHP 23	DHP 20
[SDS] (M)	0.035	2.1	3.8	6.0	
	0.050	3.0	5.5	8.8	
	0.067	4.1	7.5	11.9	
	0.080	4.9	9.0	14.3	
	0.100	6.2	11.4	18.0	
[CTAB] (M)	0.035	0.6	3.5		5.3
	0.050	0.9	5.1		7.7
	0.067	1.2	6.8		10.4
	0.080	1.5	8.2		12.5
	0.100	1.9	10.4		15.8
	0.120	2.3	12.6		19.1
	0.140	2.7	14.8		22.5

efficients decrease, tending to the P_{sm} coefficient ratio of solutes, when the surfactant concentration in the mobile phase increases. There are only a few cases for which the tendency is like that shown in Fig. 7a and d: the selectivity coefficients increase when the surfactant concentration increases but also tending to the P_{sm} coefficient ratio of solutes. These results can be explained by Eq. 3 based on the direct transfer of the solute from the micellar phase to the stationary phase postulated above when the

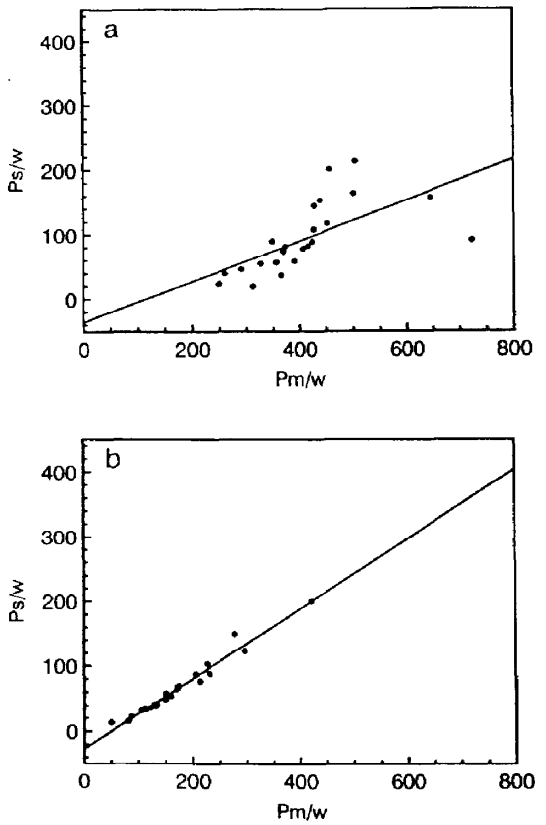


Fig. 6. Correlation between P_{sw} and P_{mw} coefficients of DHPs for (a) SDS and (b) CTAB.

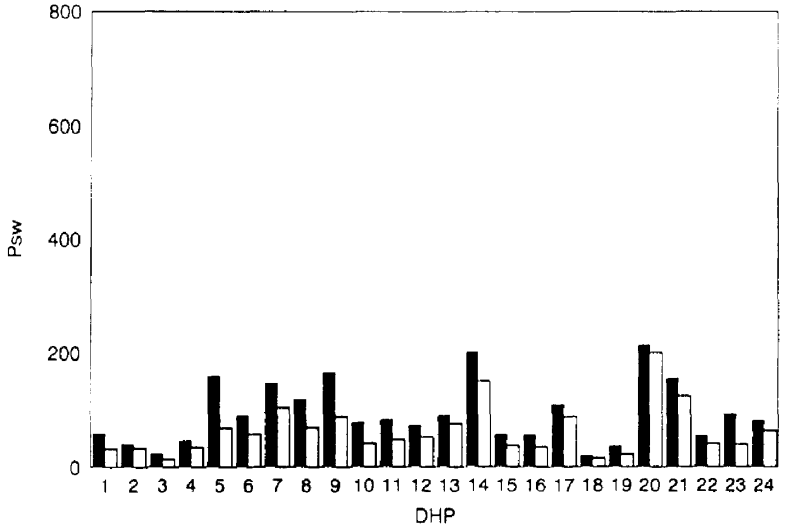


Fig. 5. P_{sw} coefficients of DHPs when SDS (■) or CTAB (□) is used as surfactant modifier in the mobile phase.

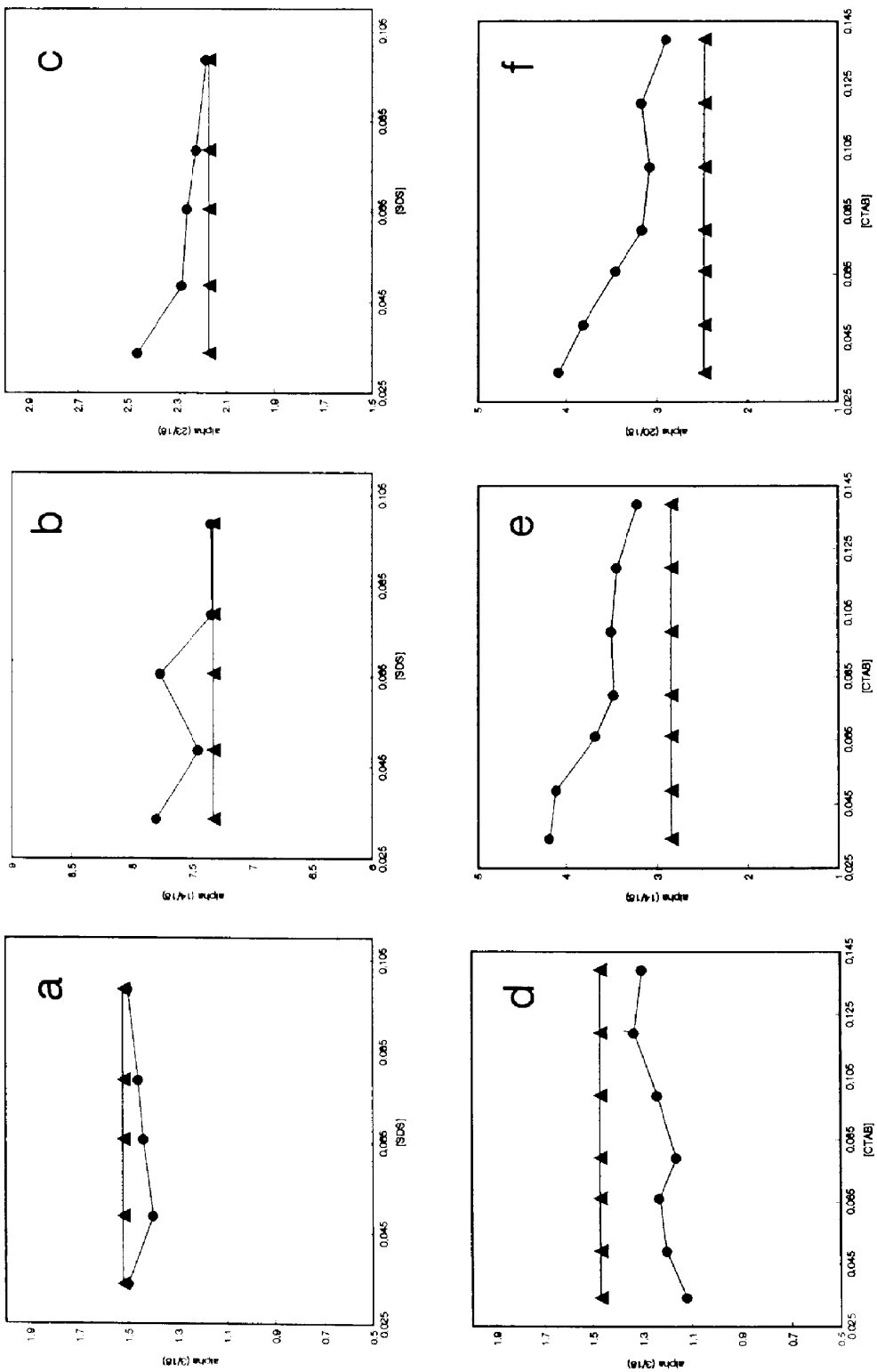


Fig. 7. Selectivity coefficients (●) for some representative pairs of DHPs with small, intermediate and large P_{mw} coefficients versus surfactant concentration (M) in the mobile phase for SDS and CTAB. Horizontal straight lines (▲) represent the ratio of P_{sm} coefficients for each pair for SDS and CTAB.

concentration of surfactant in the mobile phase is high. If Eq. 3 is valid for these compounds when the surfactant concentration is high, then the selectivity should tend to the ratio of P_{sm} coefficients, as demonstrated in Fig. 7.

Developing a mathematical expression for these compounds derived from the three partition equilibria theory, it is possible to explain the tendency of selectivity coefficients to the P_{sm} coefficient ratio when the concentration of surfactant increases:

$$k' = \frac{q_s}{q_{aq} + q_M} = \frac{V_s[XL]}{V_m(1 - vC_M)[X] + V_m vC_M[XM]} \quad (4)$$

where q_s, q_{aq} and q_M are the amounts of solute in the stationary, aqueous and micellar phases, respectively, and [XL], [X] and [XM] are the concentrations of the solute in the stationary, aqueous and micellar phases, respectively. Dividing by [XM]:

$$k' = \frac{V_s P_{sm}}{V_m(1 - vC_M)(1/P_{mw}) + V_m vC_M} = \frac{V_s}{V_m} \cdot \frac{P_{sm}}{vC_M(1 - 1/P_{mw}) + 1/P_{mw}} \quad (5)$$

The selectivity coefficient for a given pair of compounds (e.g., compounds **1** and **2**) will be defined by

$$\alpha = \frac{P_{sm1}[vC_M(1 - 1/P_{mw2}) + 1/P_{mw2}]}{P_{sm2}[vC_M(1 - 1/P_{mw1}) + 1/P_{mw1}]} \quad (6)$$

Eq. 6 shows that if $P_{mw1} > P_{mw2}$ then α will decrease when the surfactant concentration (e.g., C_M) is increased, otherwise α will decrease. This explains the cases for which α increases with C_M. As the P_{mw} coefficients for these compounds are close to or larger than 100 for either SDS or CTAB (Tables 1 and 2), it is possible to consider $(1 - 1/P_{mw}) \approx 1$. Substituting in Eq. 6:

$$\alpha = \frac{P_{sm1}}{P_{sm2}} \cdot \frac{vC_M + 1/P_{mw2}}{vC_M + 1/P_{mw1}} \quad (7)$$

When C_M is increased, vC_M could be large enough to make $(vC_M + 1/P_{mw}) \approx vC_M$, that is

$$\alpha = \frac{P_{sm1}}{P_{sm2}} \quad (8)$$

Therefore, as expected by theory, the results obtained in this work demonstrate that when the surfactant concentration in the mobile phase is increased, the selectivity coefficients tend to a constant value which corresponds to the P_{sm} coefficient ratio of the solutes. This tendency is due to a change in the retention mechanism from a three partition equilibria mechanism to a direct transfer mechanism when the concentration of surfactant in the mobile phase is increased. The general pattern observed in the literature for selectivity versus surfactant concentration in the mobile phase is a decrease in selectivity when the surfactant concentration increases [5,7]. Other workers have observed an increase in selectivity versus surfactant concentration in the mobile phase [7]. However, in all instances, selectivity tends to a limiting value which can be explained by the above-mentioned change to a direct transfer mechanism in the solute retention when the surfactant concentration in the mobile phase increases.

The selectivity coefficients calculated in this work are higher for SDS than for CTAB for every surfactant concentration studied. This result is in good agreement with the hypothesis that solutes can be located in micelles in different microenvironments of different polarity. The selectivity will be larger if the difference in polarity between the mobile phase and stationary phase environment occupied by solutes is also larger [17]. As discussed previously, Fig. 6 could be showing a similar nature for solute–micelle and –stationary phase interaction for CTAB, but not for SDS, which may be the reason for the higher selectivity of SDS.

Finally, the selectivity results are similar to those obtained previously for benzene and naphthalene derivatives under the same chromatographic conditions, for which selectivity is also higher for SDS than for CTAB and improves when the surfactant concentration in the mobile phase decreases [12].

4. Conclusions

A direct transfer from micelles to the stationary phase is presented to explain the retention behaviour and selectivity coefficients for a group of DHPs in MLC when surfactant concentration in the mobile phase increases.

A primarily hydrophobic interaction of these DHPs with CTAB and a hydrophilic interaction with SDS is suggested according to the correlation between P_{mw} and P_{sw} coefficients. The selectivity results are also in good agreement with this hypothesis, as DHPs show larger selectivity coefficients for SDS than for CTAB, which may be due to some differences in the polarity of the microenvironmental of DHPs in SDS and CTAB micelles.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by DGICYT (Spain) (reference PS90-0026). They also thank Ms. Ines Benito for measuring critical micellar concentrations and Professor Dr. Julio Alvarez Builla for the gift of the DHPs used in this work.

References

[1] D.W. Armstrong and S.J. Henry, *J. Liq. Chromatogr.*, 3 (1980) 657.
[2] F.G.P. Mullins and G.F. Kirkbright, *Analyst*, 109 (1984) 1217.
[3] G.F. Kirkbright and F.G.P. Mullins, *Analyst*, 109 (1984) 493.
[4] P. Yarmchuk, R. Weinberger, R.F. Hirsch and L.J. Cline Love, *Anal. Chem.*, 54 (1982) 2233.
[5] M.A. García, S. Vera, M. Bombín and M.L. Marina, *J. Chromatogr.*, 646 (1993) 297.
[6] J.K. Strasters, E.D. Breyer, A.H. Rodgers and M.G. Khaledi, *J. Chromatogr.*, 511 (1990) 17.
[7] M.G. Khaledi, J.K. Strasters, A.H. Rodgers and E.D. Breyer, *Anal. Chem.*, 62 (1990) 130.
[8] D.W. Armstrong and F. Nome, *Anal. Chem.*, 53 (1981) 1662.
[9] M. Arunyanart and L.J. Cline Love, *Anal. Chem.*, 56 (1984) 1557.
[10] M.F. Borgerding, F.H. Quina, W.L. Hinze, J. Bowermaster and H.M. McNair, *Anal. Chem.*, 60 (1988) 2520.
[11] M.L. Marina, S. Vera and A.R. Rodríguez, *Chromatographia*, 28 (1989) 379.
[12] M.A. García, S. Vera and M.L. Marina, *Chromatographia*, 32 (1991) 148.
[13] E. Pramauro and E. Pelizzetti, *Anal. Chim. Acta*, 154 (1983) 153.
[14] P. Mageney, R. Gosmini, S. Raussou, M. Commercon and A. Alexakis, *J. Org. Chem.* 59 (1994) 1877.
[15] I.A. Pastre and M.G. Neumann, *J. Photochem. Photobiol. A*, 79 (1994) 1.
[16] G.S. Hartley, *Trans. Faraday Soc.*, 30 (1934) 444.
[17] M.G. Khaledi, *Anal. Chem.*, 60 (1988) 876.