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Journal of Chromatography A, 719 (1996) 15–26

JOURNAL OF
CHROMATOGRAPHY A

A model describing the effect on retention of the addition of alcohols to the mobile phase in micellar liquid chromatography

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Abstract

A physico-chemical model relating the capacity factor of a solute to micellized surfactant and organic modifier concentrations in micellar liquid chromatography with hybrid eluents is proposed. The equation derived from this model and some simplified equations were tested by using retention data in micellar mobile phases containing hexadecyltrimethylammonium bromide and sodium dodecyl sulphate as surfactants and *n*-propanol and *n*-butanol as organic modifiers. Good agreement between calculated and experimental capacity factors was found and the use of this model to predict the retention behaviour of solutes in micellar liquid chromatography is proposed.

1. Introduction

Micellar liquid chromatography (MLC) is a separation technique of widespread application owing to its advantages compared with conventional reversed-phase liquid chromatography (RPLC). The primary advantages are low cost and non-toxicity of surfactants versus expensive and flammable solvents of chromatographic grade [1–4], unique selectivity [4–9], compatibility of mobile phases with salts and water-insoluble compounds [7] and shorter equilibrium times for gradient elution. On the other hand, the main drawback of this separation technique is its lower efficiency compared with RPLC [4–7,10,11].

The addition of short-chain alcohols to the mobile phase improves the chromatographic

efficiency and permits control of the solute retention time [12]. It seems clear that solute retention depends mainly on micelle and organic modifier concentrations and nature, the nature of the solute, pH and ionic strength, etc., but more work is needed to clarify the solute retention mechanism and to establish, if possible, an equation that permits the prediction of the retention behaviour of solutes in such complicated systems, thus enabling us to exploit the full potential advantages of this separation technique in a more judicious way.

Some efforts have been made in order to find an equation to predict the retention behaviour of solutes in MLC with hybrid eluents as a function of surfactant and alcohol concentrations. As a consequence, some empirical equations have been proposed. Some of the equations derived from the empirical models are the following [13–15]:

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$$\log k' = A\mu + B\varphi + C$$

$$1/k' = A\mu + B\varphi + C\mu\varphi + D$$

$$1/k' = A\mu + B\varphi^2 + C\varphi + D\mu\varphi + E$$

$$\log k' = A\mu + B\varphi + C\mu\varphi + D$$

where μ is the total surfactant concentration in the mobile phase, φ is the volume fraction of organic modifier and A, B, C, D and E are model parameters that depend on the nature of the solute, the surfactant and the alcohol.

There is no general agreement about which of these equations explains more adequately the retention behaviour of solutes in MLC with hybrid eluents because it seems that it depends on the balance among the interactions that take place among the species present in the system.

The objectives of this work were first to propose a general physico-chemical model to relate solute retention in MLC with hybrid eluents as a function of surfactant and alcohol concentrations based on chemical equilibria and second to check the validity of the equation derived from it using the experimental retention data for fifteen benzene and naphthalene derivatives and eight polycyclic aromatic hydrocarbons in micellar mobile phases with different concentrations of hexadecyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) modified with different percentages of *n*-propanol and *n*-butanol in a C_8 column.

2. Theory

Arunyanart and Cline Love [16] reported that reversed-phase micellar liquid chromatography can be described by two principal equilibria, one being a reversible equilibrium of solute in the bulk solvent mobile phase, E_m , with the stationary phase sites, L_s , to form a complex, EL_s , and the second a reversible equilibrium of solute in the bulk solvent mobile phase, E_m , with the surfactant in the micelle in the mobile phase, M_m , to form the complex, EM_m . The equilibria proposed were as follows:



They neglected a third equilibrium involving the direct transfer of solute in the micelle, EM_m , to the stationary phase because it is dependent of the other two.

The expression for the capacity factor when these two equilibria are taken into account is

$$k' = \frac{\phi[L_s]k_1}{(1 + k_2[M_m])} \quad (3)$$

where ϕ is the phase ratio (the ratio of the stationary phase volume, V_s , to the volume of mobile phase, V_m , in the column), $[L_s]$ is the stationary phase site concentration and $[M_m]$ is the concentration of surfactant in the micelle in the mobile phase (total surfactant concentration minus critical micelle concentration).

If an alcohol is introduced into the mobile phase as an organic modifier, we can assume that this compound will interact with both the stationary phase [12,14] and the micelles [8,12,17], thus influencing the solute retention. In other words, we can consider two additional equilibria:



where A_m is the alcohol in the mobile phase, AL_s is the complex formed by the alcohol and the stationary phase sites and AM_m is the complex formed between the alcohol and the surfactant in the micelle in the mobile phase.

Some other equilibria could be considered but they are dependent on those cited above, so we can neglect them.

The combination of Eqs. 1–5 yields the following expression for the capacity factor:

$$k' = \frac{\phi k_1 [L_s] (1 + k_4 [A_m])}{1 + (k_3 + k_4) [A_m] + k_2 [M_m] (1 + k_3 [A_m]) + k_3 k_4 [A_m]^2} \quad (6)$$

This general expression can be reduced to simpler models depending on the values of the constants. Some of the reduced models and the approximations to obtain them are given in

Table 1
Simplified expressions derived from the general Eq. 6 and the approximations made to obtain them

Eq. No.	Simplified expressions ^a	Approximatory
7	$\frac{1}{k'} = \frac{1}{a} + \frac{k_3}{a} [A_m] + \frac{k_2}{a} [M_m] + \frac{k_2 k_3}{a} [M_m][A_m]$	$k_4 [A_m] \ll 1$ $k_3 \gg k_4$ $k_3 k_4 [A_m]^2 \ll 1$
8	$\frac{1}{k'} = \frac{1}{a} + \frac{k_3 + k_4}{a} [A_m] + \frac{k_2}{a} [M_m] + \frac{k_2 k_3}{a} [M_m][A_m] + \frac{k_3 k_4}{a} [A_m]^2$	$k_4 [A_m] \ll 1$
9	$\frac{1}{k'} = \frac{k_2}{a} [M_m] + \frac{k_2 k_3}{a} [M_m][A_m]$	$k_4 [A_m] \ll 1$ $k_2 \uparrow \uparrow$ $k_3 \downarrow$
10	$\frac{1}{k'} = \frac{1}{a} + \frac{k_3}{a} [A_m] + \frac{k_2}{a} [M_m] + \frac{k_2 k_3}{a} [M_m][A_m] + \frac{k_3 k_4}{a} [A_m]^2$	$k_4 [A_m] \ll 1$ $k_3 \gg k_4$
11	$\frac{1}{k'} = \frac{1}{ak_4} \frac{1}{[A_m]} + \frac{k_3 + k_4}{ak_4} + \frac{k_2}{ak_4} \frac{[M_m]}{[A_m]} + \frac{k_2 k_3}{ak_4} [M_m] + \frac{k_3}{a} [A_m]$	$k_4 [A_m] \gg 1$

^a $a = k_1 \phi [L_s]$.

Table 1, where some linear models derived from the general equation (Eq. 6) depending on two, three and four independent parameters are shown.

It can be observed that some of these expressions have similar forms to the empirical models proposed by Torres-Lapasió et al. [14] and studied by us previously [15], so we consider that depending on the nature of the solute and on the balance among the different interactions it should be possible to find an expression (the general Eq. 6 or some of the simplified equations

derived from it) to explain the solute retention in MLC with hybrid eluents by means of chemical equilibrium constants.

3. Experimental

3.1. Chromatographic data

Retention data for 23 compounds (obtained previously [15,18]) on a C₈ column (Teknokroma, Barcelona, Spain) were used. The solute

Table 2
Summary of experimental data used in this study

Experiment No.	Compounds	Surfactant and concentration range (M)	Alcohol and concentration range (M)	Ref.
1	1–15	CTAB (0.05–0.12)	<i>n</i> -Propanol (0–1.331)	[18]
2	1–15	CTAB (0.05–0.12)	<i>n</i> -Butanol (0–1.092)	[18]
3	1–15	SDS (0.035–0.14)	<i>n</i> -Propanol (0–1.331)	[18]
4	1–15	SDS (0.035–0.14)	<i>n</i> -Butanol (0–1.092)	[18]
5	16–23	CTAB (0.05–0.12)	<i>n</i> -Propanol (0.399–1.331)	[15]
6	16–23	CTAB (0.05–0.12)	<i>n</i> -Butanol (0.328–1.092)	[15]
7	16–23	SDS (0.05–0.14)	<i>n</i> -Propanol (0.399–1.331)	[15,18]
8	16–23	SDS (0.05–0.14)	<i>n</i> -Butanol (0.328–1.092)	[15,18]

capacity factors were determined in micellar mobile phases containing CTAB and SDS (both from Merck, Darmstadt, Germany) as surfactants and modified with *n*-propanol and *n*-butanol (both from Merck). The experimental retention data used are summarized in Table 2.

Benzene derivatives and polycyclic aromatic hydrocarbons were as follows: (1) benzene, (2) benzylic alcohol, (3) benzamide, (4) toluene, (5) benzonitrile, (6) nitrobenzene, (7) phenol, (8), 2-phenylethanol, (9) chlorobenzene, (10) phenylacetonitrile, (11) 3,5-dimethylphenol, (12) naphthalene, (13) 1-naphthol, (14) 2-naphthol, (15) 1-naphthylamine, (16) pyrene, (17) phenanthrene, (18) 2,3-benzofluorene, (19) fluorene, (20) fluoranthene, (21) acenaphthylene, (22) acenaphthene and (23) anthracene.

3.2. Data manipulation

Data manipulations were carried out using the Sigma Plot System [19].

4. Results and discussion

We worked with the retention data for 23 compounds (benzene derivatives and polycyclic aromatic hydrocarbons) in a C₈ column with hybrid eluents in which CTAB and SDS (concentration ranges 0.05–0.12 and 0.035–0.14 M, respectively) are used as the surfactants and *n*-propanol and *n*-butanol are used as the organic modifiers (concentration ranges 0–1.331 and 0–1.092 M, respectively.)

In order to check the validity of the general equation proposed in the Theory section, the constants ($\phi k_1[L_s]$, k_2 , k_3 and k_4) and the predicted capacity factors for each solute in each medium were determined by means of a non-linear fitting [19]. Also, the Eqs. 7–10 (Table 1) were applied to the experimental data and both parameters (or equilibrium constants) and the predicted capacity factors were calculated. In Tables 3, 4, 5 and 6 the best-fit equations (that best explain the experimental data with the minimum number of parameters) are shown together with the values of the parameters (or constants) for the CTAB–propanol, CTAB–

butanol, SDS–propanol and SDS–butanol systems, respectively. In Fig. 1 the mean relative errors of fitting (in absolute values) for the same systems are shown.

In Tables 3–6 it can be observed that the equation that best explains the experimental results depends on the nature of the solute, the surfactant and the organic modifier. Perhaps for this reason in the literature, references to different models that explain the behaviour of some particular solutes in a particular system (hybrid eluent) can be found. Thus, Torres-Lapasió et al. [14], studying the behaviour of some catecholamines, proposed the model

$$1/k' = A\mu + B\varphi + C\mu\varphi + D$$

formally similar to Eq. 7 in Table 1. Moreover, in an earlier paper [15] we proposed the model

$$1/k' = A\mu + B\varphi^2 + C\varphi + D\mu\varphi + E$$

because it fitted best the behaviour of the most hydrophobic compounds studied by us; this equation is similar to Eqs. 8 and 10 in Table 1. This seems to indicate that the models proposed so far are particular cases of a more general equation (Eq. 6) and valid only in particular situations. If we want to predict the retention behaviour of a compound in MLC with a hybrid system we could obtain different equilibrium constants and, depending on the balance among them, we could identify the equation that best explains the experimental results.

The k_2 values obtained in hybrid systems containing CTAB are higher than those obtained with SDS. This can be explained for the favourable electrostatic interactions between the positively charged CTAB head groups and the unlocated charge of the aromatic ring(s) of the solutes [20].

The $\phi k_1[L_s]$ values for the most hydrophobic compounds are great and the retention mechanism in the absence of alcohol can be explained by a direct transfer between the micelle solute species and the surfactant-coated stationary phase [12,21,22]. With CTAB micelles and in the presence of propanol (at different concentrations), these hydrophobic compounds follow an equivalent mechanism, as is shown in Fig. 2 by

Table 3

Equilibrium constants or parameters (standard deviations in parentheses) relating to the equations that best fit the solute retention behaviour with CTAB–propanol eluents

Compound	Best-fit equation	A^a	B^b	C^c	D^d
1	7	52.2 (2.8)	44.0 (3.2)	0.259 (0.011)	–
2	6	13.8 (0.52)	14.6 (1.1)	0.916 (0.084)	0.024 (0.087)
3	7	8.80 (0.30)	10.61 (0.80)	1.052 (0.029)	–
4	7	232 (53)	179 (44)	0.222 (0.014)	–
5	6	27.7 (1.1)	26.5 (1.5)	0.829 (0.098)	0.35 (0.12)
6	6	50.9 (3.6)	44.7 (4.2)	0.61 (0.12)	0.15 (0.11)
7	7	58.5 (7.7)	50.8 (8.7)	0.947 (0.042)	–
8	6	23.4 (1.1)	24.6 (1.8)	0.884 (0.096)	0.085 (0.088)
9	7	520 (230)	406 (186)	0.246 (0.013)	–
10	7	41.3 (2.7)	41.1 (3.6)	0.635 (0.020)	–
11	9	0.7683 ($8.5 \cdot 10^{-3}$)	0.499 (0.020)	–	–
12	9	0.7369 ($6.1 \cdot 10^{-3}$)	0.178 (0.010)	–	–
13	9	0.6938 ($9.7 \cdot 10^{-3}$)	0.450 (0.023)	–	–
14	9	0.7130 ($9.5 \cdot 10^{-3}$)	0.495 (0.023)	–	–
15	9	0.9142 ($8.2 \cdot 10^{-3}$)	0.554 (0.019)	–	–
16	9	0.534 (0.013)	0.233 (0.018)	–	–
17	9	0.528 (0.013)	0.216 (0.018)	–	–
18	9	0.468 (0.015)	0.212 (0.021)	–	–
19	9	0.587 (0.013)	0.182 (0.017)	–	–
20	9	0.544 (0.015)	0.224 (0.020)	–	–
21	9	0.676 (0.012)	0.208 (0.015)	–	–
22	9	0.585 (0.013)	0.157 (0.017)	–	–
23	9	0.572 (0.015)	0.209 (0.020)	–	–

^a $A = \phi k_1 [L_s]$.

^b $B = k_2$.

^c $C = k_3$.

^d $D = k_4$ except when Eq. 9 is considered.

In this case $A = k_2 / \phi k_1 [L_s]$ and $B = k_3 k_4 / \phi k_1 [L_s]$.

the zero or negative intercepts obtained (in Fig. 2 the variation of the reciprocal of the experimental capacity factors for chlorobenzene and naphthalene is plotted as a function of the micellized surfactant concentration at different concentrations of alcohol in the mobile phase in a CTAB–propanol system). This behaviour (negative intercepts) was explained earlier [22] and it is thought that these values are zero rather than negative. The alcohol in these systems can only compete with the solute for the stationary phase.

The values obtained for k_3 when using butanol are greater than those obtained with propanol as organic modifier, which is in agreement with Borgerding et al. [12], who reported that the amount of surfactant desorbed by such additives increases as their hydrophobicity increases.

The k_4 values obtained show that the organic modifier does not interact appreciably with the micelle in the presence of the most hydrophobic solutes (16–23), that is, the equilibrium between the alcohol and the stationary phase takes place to a greater extent than the equilibrium between

Table 4

Equilibrium constants or parameters (standard deviations in parentheses) relating to the equations that best fit the solute retention behaviour with CTAB–butanol eluents

Compound	Best-fit equation	A^a	B^d	C^d	D^d
1	6	41.2 (5.2)	31.9 (5.8)	1.35 (0.27)	0.03 (0.20)
2	6	15.23 (0.53)	17.7 (1.1)	5.02 (0.29)	3.27 (0.50)
3	6	9.70 (0.34)	13.25 (0.95)	4.71 (0.27)	3.76 (0.66)
4	7	100 (27)	68 (22)	1.393 (0.088)	–
5	6	29.6 (2.5)	29.6 (3.7)	4.31 (0.61)	2.39 (0.72)
6	6	64.3 (8.6)	60 (10)	7.3 (1.2)	5.1 (1.2)
7	6	81 (18)	77 (20)	18.4 (4.4)	16.6 (5.1)
8	6	27.6 (2.0)	31.7 (3.4)	6.56 (0.68)	4.59 (0.92)
9	7	130 (44)	90 (35)	1.422 (0.090)	–
10	6	54.6 (7.1)	59.4 (9.7)	9.5 (1.5)	6.9 (1.6)
11	7	152 (62)	102 (48)	2.70 (0.15)	–
12	7	265 (168)	181 (124)	1.464 (0.094)	–
13	7	293 (156)	189 (109)	2.66 (0.11)	–
14	7	213 (100)	137 (72)	2.62 (0.40)	–
15	7	160 (69)	132 (63)	2.28 (0.11)	–
16	7	243 (121)	120 (65)	1.84 (0.28)	–
17	7	206 (101)	108 (58)	1.74 (0.27)	–
18	7	293 (164)	126 (76)	2.18 (0.36)	–
19	7	193 (101)	98 (57)	1.78 (0.33)	–
20	7	233 (115)	117 (63)	1.82 (0.28)	–
21	7	146 (61)	85 (40)	1.57 (0.26)	–
22	7	160 (79)	78 (44)	1.72 (0.36)	–
23	7	187 (89)	96 (51)	1.73 (0.30)	–

^a $A = \phi k_1 [L_s]$.

^b $B = k_2$.

^c $C = k_3$.

^d $D = k_4$ except when Eq. 9 is considered.

In this case $A = k_2 / \phi k_1 [L_s]$ and $B = k_2 k_3 / \phi k_1 [L_s]$.

the alcohol and the micelle in the mobile phase. Moreover, the k_4 values obtained for butanol are greater than those for propanol; in other words, butanol interacts with the micelles to a greater extent than does propanol. This is in agreement with Khaledi et al. [17], who reported larger S_{hyb} values for butanol than propanol.

The relative errors of fitting when using the general equation (Eq. 6) or the simplified equations (Fig. 1) depend on the system studied and range between 2.5% (CTAB–propanol) and 10.3% (SDS–butanol) (mean values of $|E_r|$ over all the compounds). The highest values obtained for the SDS–butanol system must be investigated further but in the other three systems (CTAB–propanol, CTAB–butanol and SDS–propanol)

the fitting errors are acceptable. With respect to the high error values obtained with micellar mobile phases containing SDS and modified with butanol, as mentioned earlier, we think that they are probably due to changes in the retention mechanism as the alcohol concentration increases. Thus, in Fig. 3a and b the reciprocals of the experimental capacity factors are plotted versus the micellized surfactant concentration for compounds 12 and 18, respectively. It can be observed that at low alcohol concentration the retention mechanism is a direct transfer between the micelles and the modified stationary phase and at the highest alcohol concentrations, perhaps owing to an enhancement of the solubility of the solutes, this test solutes in the bulk solvent

Table 5

Equilibrium constants or parameters (standard deviations in parentheses) relating to the equations that best fit the solute retention behaviour with SDS–propanol eluents

Compound	Best-fit equation	A ^a	B ^b	C ^c	D ^d
1	6	36.6 (3.3)	23.0 (3.9)	0.83 (0.26)	0.53 (0.43)
2	6	10.60 (0.46)	17.2 (1.6)	2.35 (0.22)	2.10 (0.53)
3	6	7.30 (0.16)	12.63 (0.69)	2.61 (0.13)	2.58 (0.40)
4	6	128 (25)	67 (18)	1.45 (0.72)	0.97 (0.85)
5	6	21.49 (0.47)	19.23 (0.85)	1.493 (0.091)	0.94 (0.17)
6	6	33.4 (1.6)	25.8 (2.3)	1.40 (0.20)	0.84 (0.30)
7	6	9.04 (0.44)	12.4 (1.5)	1.12 (0.18)	0.57 (0.38)
8	6	17.54 (0.38)	19.68 (0.84)	1.73 (0.11)	0.77 (0.17)
9	6	177 (32)	87 (20)	1.76 (0.78)	1.01 (0.79)
10	6	29.7 (1.3)	29.1 (2.3)	2.03 (0.21)	1.45 (0.34)
11	6	59.7 (3.0)	50.6 (3.7)	1.43 (0.22)	0.52 (0.21)
12	6	242 (45)	93 (22)	0.78 (0.39)	0.12 (0.30)
13	6	204 (38)	147 (33)	4.0 (1.3)	2.3 (1.1)
14	6	168 (20)	118 (17)	2.08 (0.43)	0.59 (0.29)
15	6	687 (509)	567 (440)	29 (22)	25 (20)
16	9	0.324 (0.013)	0.099 (0.018)	–	–
17	9	0.368 (0.013)	0.106 (0.018)	–	–
18	9	0.266 (0.011)	0.097 (0.016)	–	–
19	9	0.408 (0.013)	0.083 (0.017)	–	–
20	9	0.3187 (8.9 · 10 ⁻³)	0.106 (0.012)	–	–
21	9	0.485 (0.014)	0.105 (0.019)	–	–
22	9	0.440 (0.017)	0.065 (0.021)	–	–
23	9	0.362 (0.019)	0.099 (0.017)	–	–

^aA = ϕk_1 [L_s].

^bB = k_2 .

^cC = k_3 .

^dD = k_4 except when Eq. 9 is considered.

In this case A = $k_2/\phi k_1$ [L_s] and B = $k_2 k_3/\phi k_1$ [L_s].

can interact with both the micelle and the stationary phase.

The modification to the solute retention mechanism when an alcohol is introduced into the mobile phase has been reported earlier [10,14,23], that is, the addition of alcohols increases the hydrophobic character of the bulk liquid (the bulk aqueous phase becomes less polar) in the mobile phase and concomitantly shifts the solute equilibrium from the micelle to bulk liquid and also from the stationary phase to the bulk liquid phase. It seems that this effect becomes more important as the hydrophobicity of the alcohol increases. Thus, it can be observed that when propanol is used as the organic modifier only at the highest alcohol concentration is

the mechanism change produced whereas when butanol is employed even at relatively low alcohol concentrations this change in mechanism is produced.

In order to investigate the validity of the model proposed in this paper, the capacity factors calculated when using the best-fit equation (Tables 3 and 5) versus the experimental values for compounds 1–15 are plotted in Fig. 4 for (a) the CTAB–propanol system and (b) the SDS–propanol system. The equations of these straight lines are

$$k'_{\text{calc.}} = 0.992k'_{\text{exp.}} + 0.092 \quad (r = 0.998)$$

$$k'_{\text{calc.}} = 0.990k'_{\text{exp.}} + 0.13 \quad (r = 0.996)$$

Table 6

Equilibrium constants or parameters (standard deviations in parentheses) relating to the equations that best fit the solute retention behaviour with SDS–butanol eluents.

Compound	Best-fit equation	A^a	B^b	C^c	D^d
1	6	36.3 (3.3)	22.2 (3.8)	2.38 (0.66)	1.13 (0.94)
2	6	10.68 (0.54)	17.5 (1.9)	5.48 (0.64)	4.0 (1.5)
3	6	7.25 (0.27)	12.4 (1.1)	6.06 (0.54)	4.8 (1.7)
4	6	125 (23)	64 (16)	6.9 (2.0)	5.2 (2.6)
5	6	21.7 (1.1)	19.7 (1.9)	4.01 (0.48)	2.62 (0.89)
6	6	33.5 (2.7)	25.8 (3.7)	4.05 (0.76)	2.6 (1.2)
7	6	9.11 (0.63)	12.7 (2.1)	2.64 (0.58)	1.2 (1.1)
8	6	17.78 (0.85)	20.3 (1.9)	5.30 (0.64)	2.9 (1.1)
9	6	171 (35)	83 (22)	9.8 (2.8)	7.6 (3.4)
10	6	29.7 (1.9)	29.2 (3.3)	5.73 (0.81)	3.6 (1.3)
11	6	64.6 (7.8)	56.8 (9.7)	7.1 (1.5)	4.7 (1.8)
12	7	188 (33)	66 (16)	2.23 (0.19)	–
13	6	230 (64)	169 (55)	20.8 (6.6)	14.6 (6.4)
14	6	211 (52)	155 (45)	21.9 (6.6)	14.4 (6.0)
15	6	597 (390)	489 (337)	80 (53)	65 (48)
16	9	0.217 (0.059)	0.88 (0.14)	–	–
17	9	0.259 (0.066)	0.91 (0.15)	–	–
18	9	0.171 (0.056)	0.84 (0.14)	–	–
19	9	0.276 (0.071)	0.93 (0.16)	–	–
20	9	0.213 (0.060)	0.89 (0.14)	–	–
21	9	0.348 (0.077)	0.98 (0.17)	–	–
22	9	0.287 (0.072)	0.94 (0.16)	–	–
23	9	0.247 (0.065)	0.90 (0.15)	–	–

^a $A = \phi k_1$ [L_s].

^b $B = k_2$.

^c $C = k_3$.

^d $D = k_4$ except when Eq. 9 is considered.

In this case $A = k_2/\phi k_1$ [L_s] and $B = k_2 k_3/\phi k_1$ [L_s].

For both systems the slopes are very near unity and the intercepts near zero.

Also, the reciprocals of the capacity factors (experimental and calculated) were plotted as a function of the concentration of both surfactant in the micelles (at different fixed alcohol concentrations) and alcohol (at different fixed total surfactant concentrations) for compounds 4, 5 and 12 in the CTAB–propanol system and the resultant graphs are shown in Fig. 5. These compounds were chosen as examples because, as has been shown in Table 3, they follow three different models. It can be observed that the experimental and the calculated capacity factors DO not differ significantly, so we can conclude

that the general model proposed in this paper is valid for a great variety of compounds and that the simplified equations are also valid for predicting the retention behaviour of these compounds in different situations.

5. Conclusions

From the results obtained in this work several conclusions can be drawn. First, the good agreement between the calculated capacity factors ($k'_{\text{calc.}}$) and the experimental values ($k'_{\text{exp.}}$) is a strong indication that Eq. 6 fits the experimental data and that the physico-chemical model and

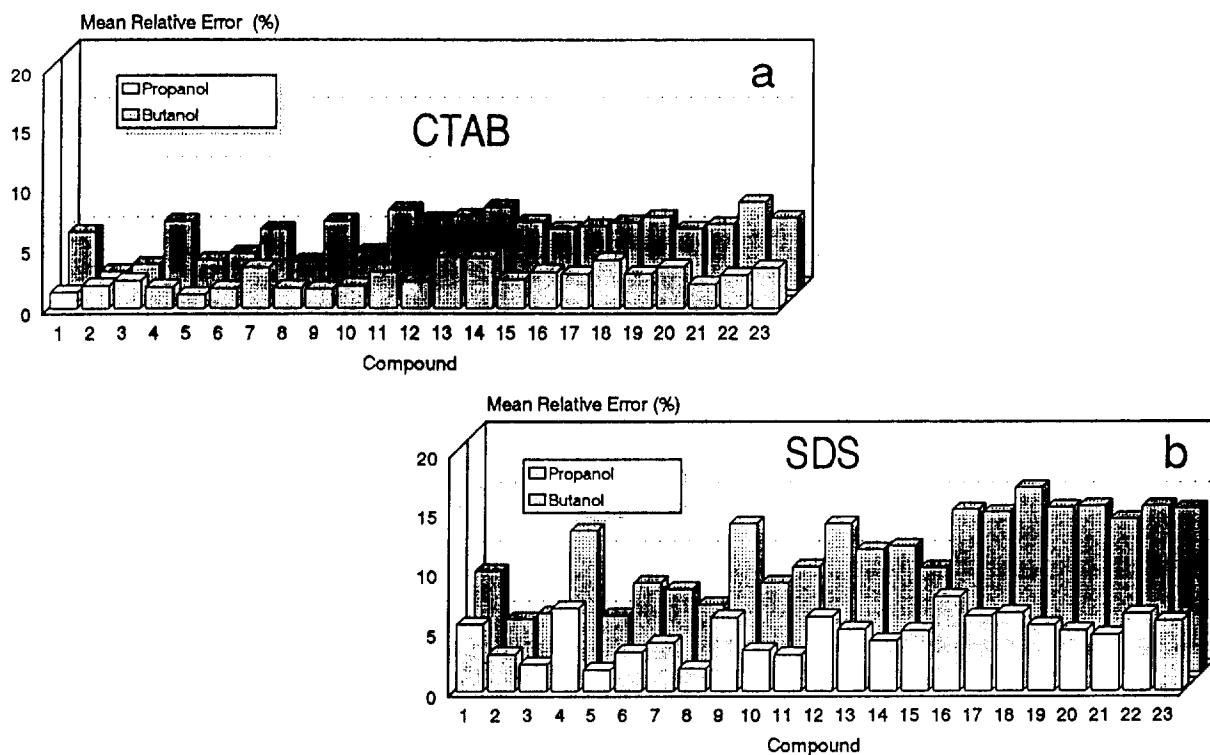


Fig. 1. Mean relative error of fitting (in absolute values) for the test solutes in CTAB–propanol, CTAB–butanol, SDS–propanol and SDS–butanol systems.

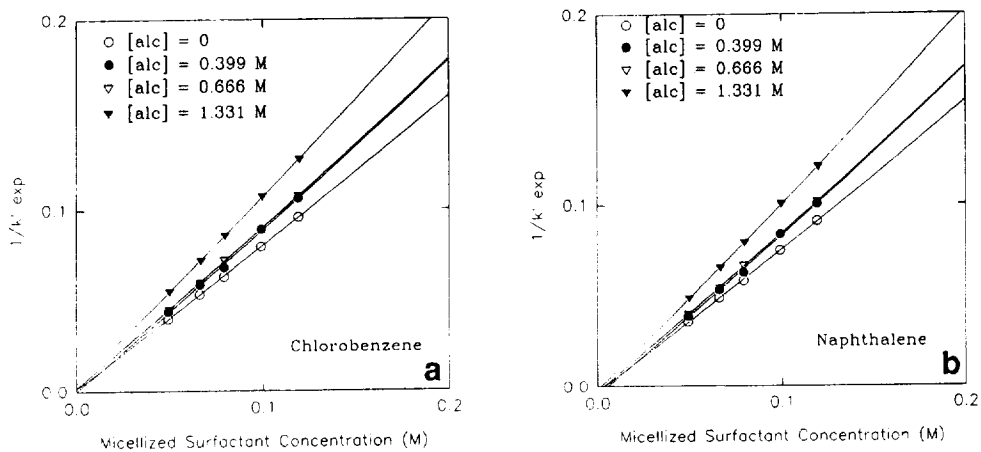


Fig. 2. Variation of the reciprocals of the experimental capacity factors as a function of the micellized surfactant concentration for (a) chlorobenzene and (b) naphthalene in CTAB micellar phases modified with *n*-propanol at different alcohol concentrations.

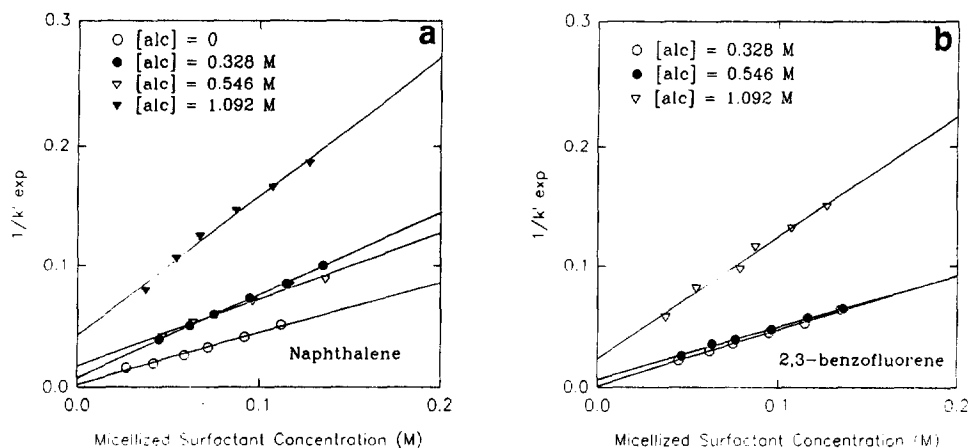


Fig. 3. Variation of the reciprocals of the experimental capacity factors as a function of the micellized surfactant concentration for compounds (a) **12** and (b) **18** in SDS mobile phases modified with *n*-butanol.

equations derived from it describe the system.

On the other hand, it is possible to find an equation (general or simplified) to explain the retention behaviour of solutes in micellar liquid chromatography with hybrid eluents, but it depends on the solute and the system studied, that is, the expression that relates the capacity factor

to both the surfactant and the alcohol concentrations depends on the balance of the interactions among the species present in the system.

Also, it seems that the fitting error depends on the system studied, CTAB and *n*-propanol being the surfactant and modifier, respectively, that allow the relative errors to be decreased.

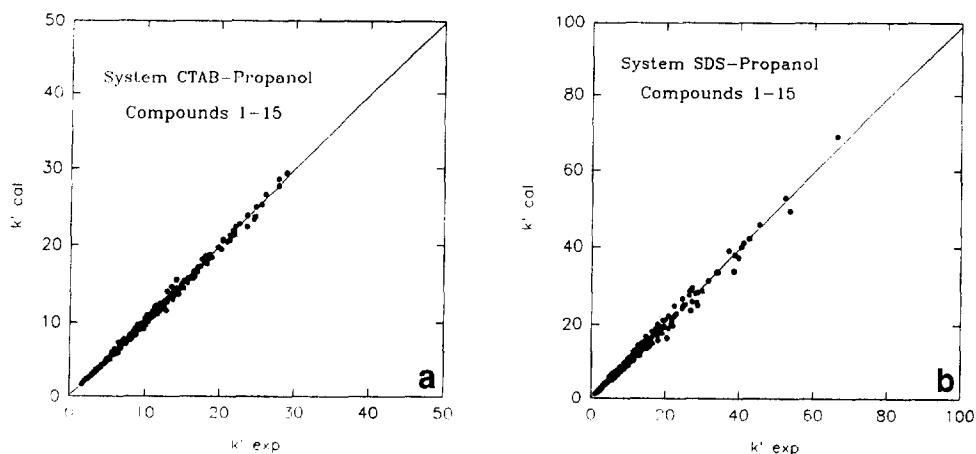


Fig. 4. Calculated capacity factors when using the best-fit equation (Tables 3 and 5) versus the experimental values for compounds **1–15**. (a) CTAB–propanol system; (b) SDS–propanol system.

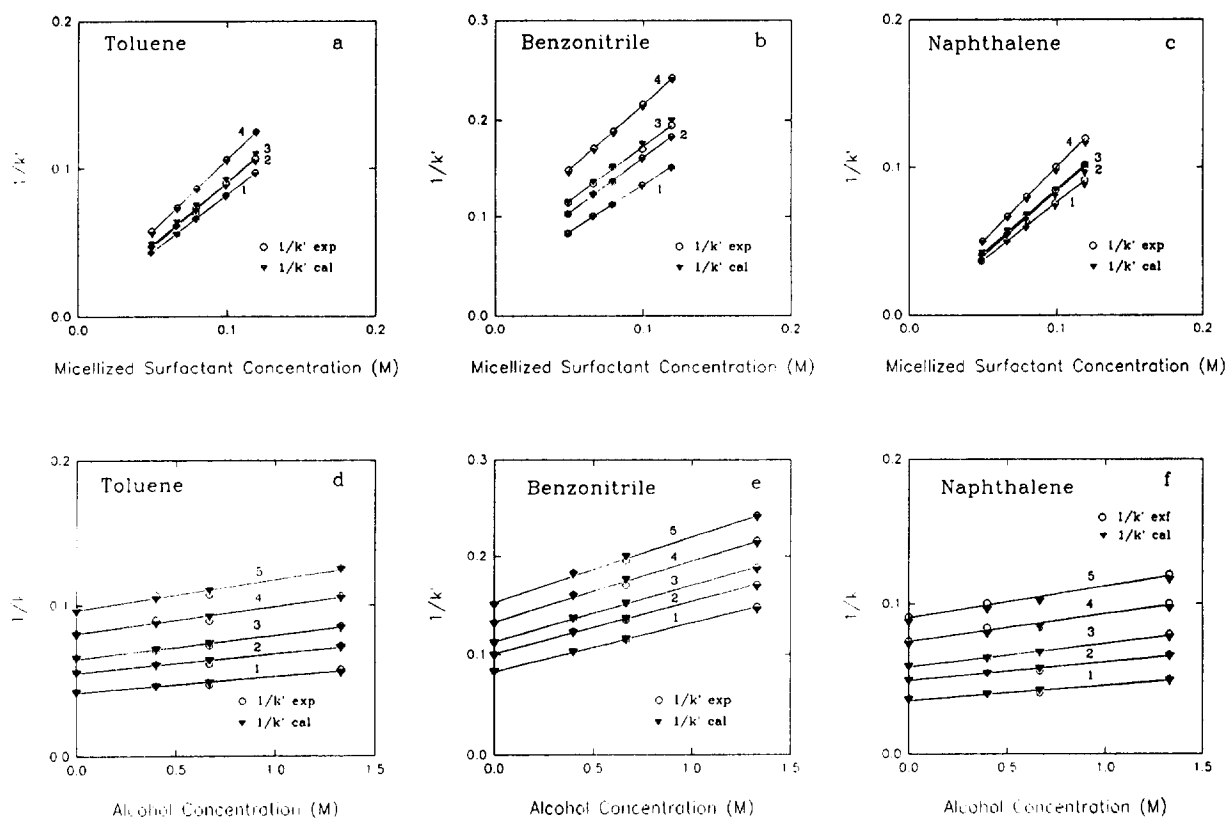


Fig. 5. Variation of the reciprocals of the capacity factors (experimental and calculated) as a function of (a–c) micellized surfactant (CTAB) concentration and (d–f) alcohol (propanol) concentration for compounds 4, 5 and 12. In the $1/k'$ vs. $[M_m]$ plots the numbers on the lines are as follows: 1, $[alc] = 0$; 2, $[alc] = 0.399$; 3, $[alc] = 0.666$; 4, $[alc] = 1.331$ M. In the $1/k'$ vs. alcohol concentration plots the numbers on the lines are as follows: 1, $[M_T] = 0.050$; 2, $[M_T] = 0.067$; 3, $[M_T] = 0.080$; 4, $[M_T] = 0.100$; 5, $[M_T] = 0.120$ M.

Acknowledgements

We gratefully acknowledge the support of this work through a research project from DGICYT (Spain) (reference PS90-0026). Also, we thank Mr. Hidalgo Moreno and Mr. Bronchalo Bronchalo for their assistance with the software used in this work.

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