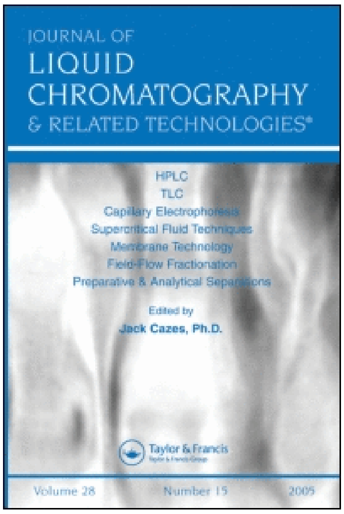

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PREDICTION AND MODELLING STUDIES FOR CAPACITY FACTORS OF A GROUP OF DIHYDROPYRIDINES IN MICELLAR LIQUID CHROMATOGRAPHY WITH HYBRID ELUENTS

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ABSTRACT

Empirical equations were used to predict the retention behaviour of a group of twenty-seven dihydropyridines in Micellar Liquid Chromatography with hybrid eluents on an octylsilica column. A theoretical model was also used to study their retention mechanism. Hexadecyltrimethylammonium bromide and sodium dodecyl sulphate were used as surfactants in the mobile phase and as organic modifiers n-propanol and n-butanol were employed.

INTRODUCTION

Micellar Liquid Chromatography (MLC) can be considered an attractive separation technique due to the special characteristics of the surfactant molecules. Ionic surfactants in aqueous solutions posses two zones, an ionic head group and a hydrophobic core, both capable of binding the solutes and the stationary phase,[1] and modifying the solute retention behaviour when introduced in the mobile phase of a chromatographic system.

Thus, micellar systems can bind a variety of solutes as a result of favourable electrostatic, pi, H-bonding, hydrophobic, or combination of such interactions, making such mobile phases much more versatile than any of the conventional mobile-phase systems.[2-3]

Moreover, different advantages that this technique presents when compared to conventional Reverse Phase High Performance Liquid Chromatography (RP-HPLC), can be cited. Among these, we can expect low cost and nontoxicity of the surfactants *versus* conventional solvents in RP-HPLC,[4-7] a unique selectivity,[3,7-11] compatibility of mobile phases with salts and water-insoluble compounds,[10] shorter equilibration times for gradient elution and the possibility of controlling retention times and selectivity,[12] modifying the mobile phase composition when hybrid eluents (micellar phases containing low percentages of an organic modifier, generally short-chain alcohols) are used.

To exploit the full advantages of MLC with hybrid eluents in a more judicious way, it should be desirable to know the equation that relates the solute capacity factor with surfactant and alcohol concentrations. As stated by Massart *et al.*,[13] mechanistic models should be used if systems are adequately understood and there is some guarantee that the systems will not deviate greatly from their expected behaviour. Otherwise, mechanistic models might be seriously misleading for predictive purposes; unbiased empirical models might prove to be better choices. Consequently, in this article some empirical models and a theoretical model have been employed from different points of view.

The empirical models are as follows:

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

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

$$\lg k' = A\mu + B\varphi + C\mu\varphi + D \qquad (3)$$

where k' is the solute capacity factor, μ is the total surfactant concentration, φ is the volume fraction of organic modifier and A, B, C, D and E the model parameters.

These equations have been used earlier by Torres-Lapasió *et al.*[14] and by our research team,[15] to predict the retention behaviour of catecholamines (using sodium dodecyl sulphate (SDS) as the surfactant and n-propanol as the organic modifier),[14] benzene derivatives and polycyclic aromatic hydrocarbons (using hexadecyltrimetilammoniumbromide (CTAB) and SDS as the surfactants and n-propanol and n-butanol as the organic modifiers in the mobile phase).[15] For catecholamines, the best results were obtained with equation (1) and for benzene derivatives and polycyclic aromatic hydrocarbons, the results showed that equation (2) was of more general applicability. In this work, one of our objectives is to expand the studies of solute retention prediction by means of empirical models with another family of organic compounds (dihydropyridines) and to propose, if it is possible, a general equation that permits to carry out the capacity factor prediction in any mobile phase (in MLC with hybrid eluents) for solutes of different nature with the minimum effort.

Some theoretical models to explain the solute retention behaviour in liquid chromatography with micellar mobile phases have been proposed in the literature,[16] but when hybrid eluents are considered, the complexity is greater because the alcohol can compete with the solutes for the interaction with micelles and with the stationary phase.[12,14]

In order to explain the mechanism of solute retention in such complicated media, our research team proposed a physico-chemical model[18] that accounts for the interactions between the solute and the stationary phase, the solute and the surfactant in the micelle and those between the alcohol (organic modifier) and the stationary phase and/or the surfactant in the micelle. The equation derived from this model that relates to the solute capacity factor and the micellized surfactant and alcohol concentrations in the mobile phase is as follows:

$$k' = \frac{\phi\, k_1\, [L_s]\,(1 + k_4\,[A_m])}{1 + (k_3 + k_4)\,[A_m] + k_2[M_m]\,(1 + k_3[A_m]) + k_3 k_4 [A_m]^2} \qquad (4)$$

where k_1, k_2, k_3 and k_4 are different equilibrium constants (corresponding to solute/stationary phase, solute/micelle, alcohol/stationary phase and alcohol/micelle interactions, respectively), ϕ is the phase ratio, $[L_s]$ is the stationary phase sites concentration, $[A_m]$ is the alcohol concentration in the mobile phase and $[M_m]$ is the micellized surfactant concentration.

This equation can be reduced to more simple models depending on the equilibrium constant values. Thus, some of the simplified equations are the following:

$$\frac{1}{k'} = \frac{1}{a} + \frac{k_3}{a}[A_m] + \frac{k_2}{a}[M_m] + \frac{k_2 k_3}{a}[M_m][A_m] \qquad (5)$$

$$\frac{1}{k'} = \frac{1}{a} + \frac{k_3 + k_4}{a}[A_m] + \frac{k_2}{a}[M_m] + \frac{k_2 k_3}{a}[M_m][A_m]$$

$$+\frac{k_3k_4}{a}[A_m]^2 \tag{6}$$

$$\frac{1}{k'}=\frac{k_2}{a}[M_m]+\frac{k_2k_3}{a}[M_m][A_m] \tag{7}$$

$$\frac{1}{k'}=\frac{1}{a}+\frac{k_3}{a}[A_m]+\frac{k_2}{a}[M_m]+\frac{k_2k_3}{a}[M_m][A_m]$$
$$+\frac{k_3k_4}{a}[A_m]^2 \tag{8}$$

$$\frac{1}{k'}=\frac{1}{ak_4}\frac{1}{[A_m]}+\frac{k_3+k_4}{ak_4}+\frac{k_2}{ak_4}\frac{[M_m]}{[A_m]}+\frac{k_2k_3}{ak_4}[M_m]$$
$$+\frac{k_3}{a}[A_m] \tag{9}$$

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

The model has been checked with a limited number of compounds (fifteen benzene derivatives and eight polycyclic aromatic hydrocarbons),[18] all of them with one or more aromatic rings, and employing CTAB and SDS as surfactants and n-propanol and n-butanol as organic modifiers. The second objective of this work is to check the model with solutes of different nature, such as dihydropyridines, and to extract information about their retention mechanism in MLC with hybrid eluents.

In order to achieve our purposes, retention data obtained in a MLC system for twenty-seven dihydropyridines by using CTAB and SDS as surfactants and n-propanol and n-butanol as organic modifiers, have been used.[19]

EXPERIMENTAL

Chromatographic Data

Retention data for 27 dihydropyridines[19] on a C_8 column (Technokroma, Barcelona, Spain) have been used. The solute capacity factors were determined in micellar mobile phases containing CTAB and SDS as surfactants and n-propanol and n-butanol as organic modifiers (all from Merck, Darmstad, Germany). The experimental retention data used have been summarized in Figure 1.

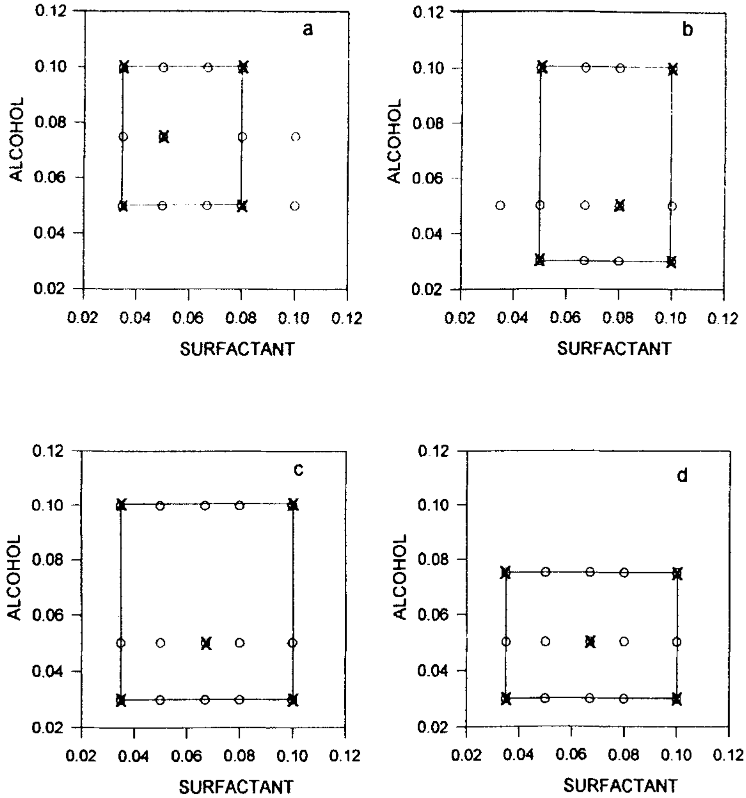
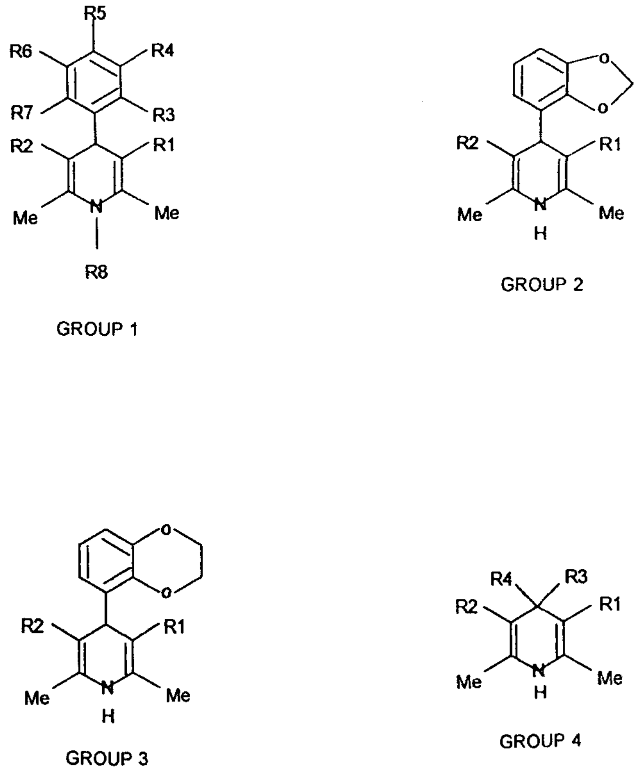


Figure 1. Mobile phase composition when CTAB-propanol (Fig. 1a), CTAB-butanol (Fig. 1b), SDS-propanol (Fig. 1c) and SDS-butanol (Fig. 1d) were used as hybrid eluents. Alcohol concentrations are expressed as the volume fraction of the organic modifier and the surfactant concentration is the total surfactant concentration in the mobile phase. Data points in and inside the square have been used in the studies with the empirical model, being the data marked with X the five mobile phases of the factorial design. All the data showed in these Figures have been employed in the studies with the theoretical model.

The structure of the dihydropyridines used in this work as well as their assigned numbers are shown in Figure 2. This Figure groups the four basic structures considered and in Tables 1, 2, 3, and 4, the assigned numbers for each solute and the substituting groups are tabulated for these four structures.



GROUP 1

GROUP 2

GROUP 3

GROUP 4

Figure 2. Structures of the dihydropyridines used in this work and their assigned values.

Data Manipulation

First, some empirical models (equations (1), (2), and (3) in the introduction) have been applied to the chromatographic data, in order to check which of them was the best to predict the solute capacity factors. In this work, the model parameters were calculated[20] by using only five capacity factors according to the factorial design shown in Figure 1.

In this case, the capacity factors were calculated for all the mobile phases excepting those outside the squares shown in Fig. 1 and, in this way the prediction relative errors were obtained.

Table 1

Assigned Numbers and the Corresponding Substituting Groups for the Dihydropyridines Belonging to Group 1 in Figure 2

Solute	R1	R2	R3	R4	R5	R6	R7	R8
1	COOIsp	$COOCH_2CH_2OMe$	H	NO_2	H	H	H	H
9	COOEt	COOMe	H	NO_2	H	H	H	H
10	COOMe	COOEt	Cl	Cl	H	H	H	H
11	COOEt	COOMe	OCH_2OMe	H	H	H	H	H
12	COOEt	COOMe	H	OMe	H	OMe	H	H
14	COOEt	COOEt	H	H	H	H	H	H
16	COOEt	COOMe	H	OMe	OMe	H	H	H
17	COOEt	COOEt	OMe	OMe	H	H	H	H
19	COOEt	COOMe	H	OMe	OH	OMe	H	H
20	COOEt	COOMe	H	OMe	OMe	OMe	H	H
21	COOEt	COOEt	Cl	H	H	H	Cl	H
22	COOMe	COOMe	NO_2	H	H	H	H	CH_2OEt
23	COOEt	COOEt	Cl	H	H	H	H	H

Table 2

Assigned Numbers and the Corresponding Substituting Groups for the Dihydropyridines Belonging to Group 2 in Figure 2

Solute	R1	R2
2	$COOCH_2Py$	COOMe
3	COOMe	COOMe
4	$COOCH_2CH_2OMe$	$COOCH_2CH_2OMe$
6	COOEt	COOEt
7	$COOCH_2CH_2OMe$	COOIsp
8	COOIsp	COOEt
13	COOMe	COOEt
15	COOIsp	COOIsp
18	COOIsp	COOMe

Second, the physico-chemical model reported by us in an earlier article[18] and the simplified equations derived from it, were applied to all the chromatographic data (shown in Figure 1). The equilibrium constants were calculated using the Sigma Plot System[21] and, with them, the relative errors were obtained for all the mobile phases studied and for all the equations under study (equations (4) to (9) in the introduction section).

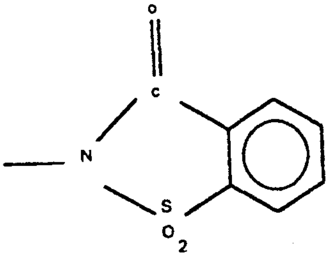
Table 3

Assigned Numbers and the Corresponding Substituting Groups for the Dihydropyridines Belonging to Group 3 in Figure 2

Solute	R1	R2
5	COOEt	COOMe

Table 4

Assigned Numbers and the Corresponding Substituting Groups for the Dihydropyridines Belonging to Group 4 in Figure 2



Solute	R1	R2	R3	R4
24	CN	CN	Me	Me
25	COOMe	COOEt	H	Me
26	COO(1)	COOEt	H	Me
27	COOEt	COOEt	H	Me

RESULTS AND DISCUSSION

In this work, we have worked with the retention data for a group of twenty-seven dihydropyridines on a C_8 column using hybrid eluents in which CTAB and SDS (total concentration range: 0.035-0.100 M) are used as surfactants, and n-propanol and n-butanol are used as organic modifiers (concentration range: 0.399-1.331 M and 0.328-1.092 M, respectively). The empirical models presented in the introduction of this article have been checked, in order to clarify what is the best equation to predict the retention behaviour of dihydropyridines in a MLC system. Also, the theoretical physico-chemical model has been used because it can help us to understand the retention mechanism of these compounds.

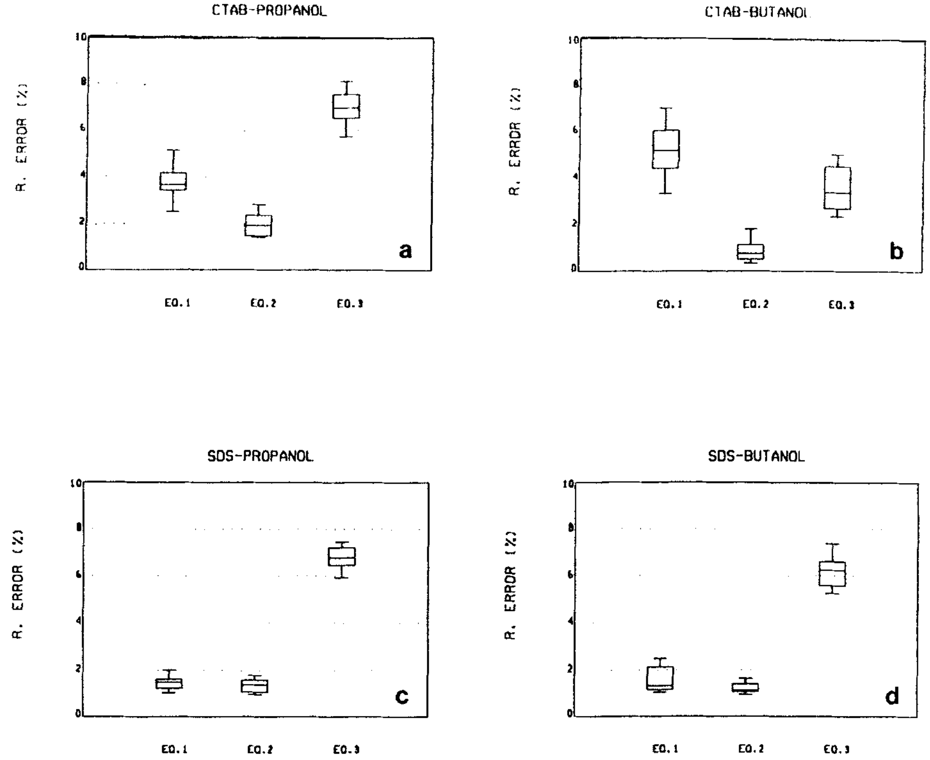


Figure 3. Mean relative errors (as absolute values) *versus* the equation used for mobile phases: CTAB-propanol (Fig. 3a), CTAB-butanol (Fig. 3b), SDS-propanol (Fig. 3c) and SDS-butanol (Fig. 3d).

A. Empirical Models

In this section, equations (1), (2), and (3) (see introduction) have been used to predict the solute capacity factors for the dihydropyridines. These equations relate the reciprocal of the capacity factors (1/k') or their logarithm (log k') with the total surfactant concentration in the mobile phase (μ) and the volume fraction of the organic modifier (φ).

The global results for these studies are shown in Figure 3. In this Figure, the mean relative errors of prediction are plotted *versus* the equation used for mobile phases containing CTAB-propanol (Figure 3a), CTAB-butanol (Figure 3b), SDS-propanol (Figure 3c) and SDS-butanol (Figure 3d), respectively.

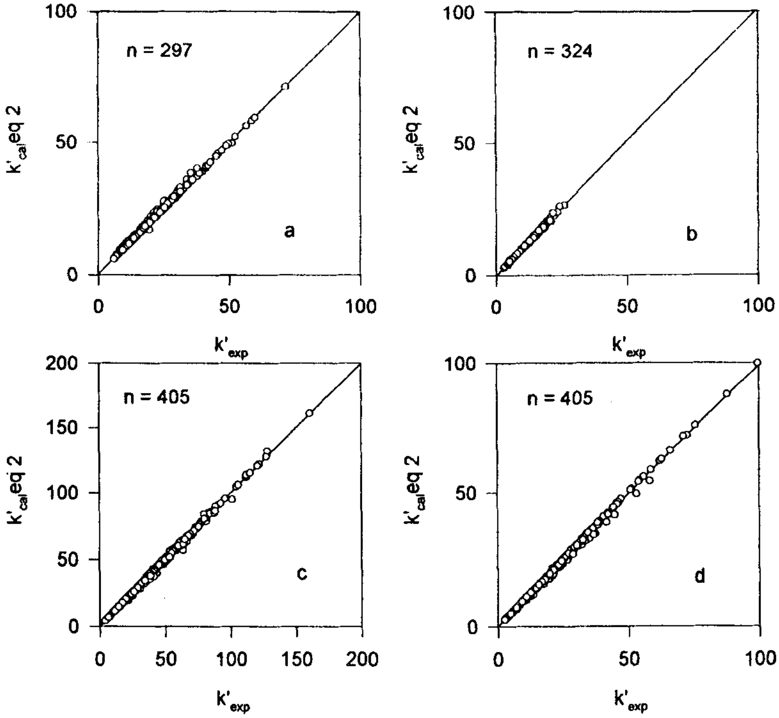


Figure 4. Calculated *versus* experimental capacity factors for systems: CTAB-propanol (Fig. 4a), CTAB-butanol (Fig. 4b), SDS-propanol (Fig. 4c) and SDS-butanol (Fig. 4d), being n the number of experimental data considered.

As can be observed in Figure 3, there are significative differences among the prediction errors for the three equations, with only two exceptions: SDS-propanol and SDS-butanol systems with equations (1) and (2). It seems that equation (2) predicts more adequately the capacity factors of these compounds because the errors obtained are the lowest. This fact is in agreement with an earlier report[15] in which the retention of benzene derivatives and polycyclic aromatic hydrocarbons was modellized. Always, the prediction errors with equation (2) are very low and they range from 1.29 to 3.3 %, 0.22 to 2.32 %, 0.8 to 2.13 % and 0.87 to 1.91 % for mobile phases containing CTAB-propanol, CTAB-butanol, SDS-propanol and SDS-butanol, respectively.

Comparable results were obtained in the case of SDS-propanol and SDS-butanol systems with equation (1) and (2), so, if we want to predict the retention behaviour we ought to use equation (1) because this later depends on a lower number of parameters. To show the good agreement found between the calculated (k'_{cal}, predicted by means of equation (2)) and the experimental capacity factors (k'_{exp}), k'_{cal} *versus* k'_{exp} values for systems CTAB-propanol (Fig. 4a), CTAB-butanol (Fig. 4b), SDS-propanol (Fig. 4c) and SDS-butanol (Fig. 4d) are plotted in Figure 4. The equations for the straight lines corresponding to these systems are the following:

CTAB-propanol $k'_{cal} = 0.410 + 0.995\, k'_{exp}$; $r^2 = 0.9969$ n = 297
CTAB-butanol $k'_{cal} = 0.119 + 1.013\, k'_{exp}$; $r^2 = 0.9974$ n = 324
SDS-propanol $k'_{cal} = 0.164 + 0.996\, k'_{exp}$; $r^2 = 0.9984$ n = 405
SDS-butanol $k'_{cal} = 0.053 + 0.990\, k'_{exp}$; $r^2 = 0.9983$ n = 405

n being the number of experimental data considered.

The intercepts and the slopes of these straight lines are very close to zero and unity, respectively, which is a good indication of the validity of equation (2) to predict capacity factor values in such systems. Also, it is interesting to note that correlation coefficients are very close to unity. These facts make us to think that equation (2) is of more general applicability than equations (1) or (3), which is in agreement with the results reported by us earlier[15] with compounds of different nature.

B. Theoretical Model

In an earlier work,[18] a theoretical model that explains the retention behaviour as a function of micellized surfactant and alcohol concentrations was proposed. The solutes under study were benzene derivatives and polycyclic aromatic hydrocarbons (PAHs). For these compounds, a good agreement between the experimental and the calculated retention data was found and some important aspects about the retention mechanism could be extracted. In this study, our purpose is to check the validity of this model for compounds of different nature (dihydropyridines).

In a first step, the equilibrium constants by using equations (4) to (9) (in the introduction section) for the four hybrid eluents (CTAB-propanol, CTAB-butanol, SDS-propanol and SDS-butanol) were calculated. Then, the calculated capacity factors for the different solutes by means of those equations were obtained and the relative errors were calculated. In order to check the homocedasticity assumption of the model, the residuals obtained for every compound and for every phase composition *versus* the calculated capacity factors, the micellized surfactant concentration and the alcohol concentration in the mobile phase were plotted.

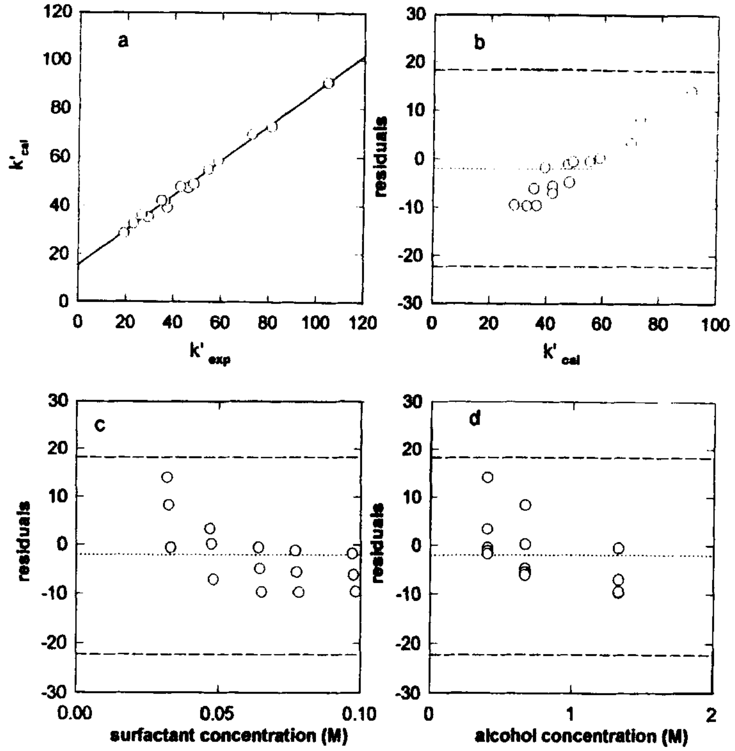


Figure 5. Calculated capacity factor by eq. (9) *versus* experimental capacity factor (Fig. 5a) and residuals *versus* k'_{cal}, micellized surfactant concentration and alcohol concentration (Fig. 5b, 5c, and 5d, respectively) for compound number 1 and for mobile phases containing SDS as the surfactant and n-propanol as the organic modifier.

With these Figures (not shown), together with the plot of the calculated *versus* the experimental capacity factors, we were able to decide if the model was adequate to explain the retention behaviour and what was the equation that, with the minimum number of parameters, could explain the retention data.

Thus, it can be cited that, for example, these Figures show the inadequacy of the equation (9) in all the cases studied. To illustrate this fact in Figure 5, the plots of k'_{cal} (calculated capacity factor by eq. (9)) *versus* k'_{exp} (experimental capacity factor) (Figure 5a), residuals versus k'_{cal}, micellized surfactant concentration and alcohol concentration in the mobile phase (Figures 5b, 5c and 5d, respectively), are shown for compound 1 when mobile phases containing SDS and n-propanol are considered. The slope and the intercept shown in Figure 5a do not coincide with

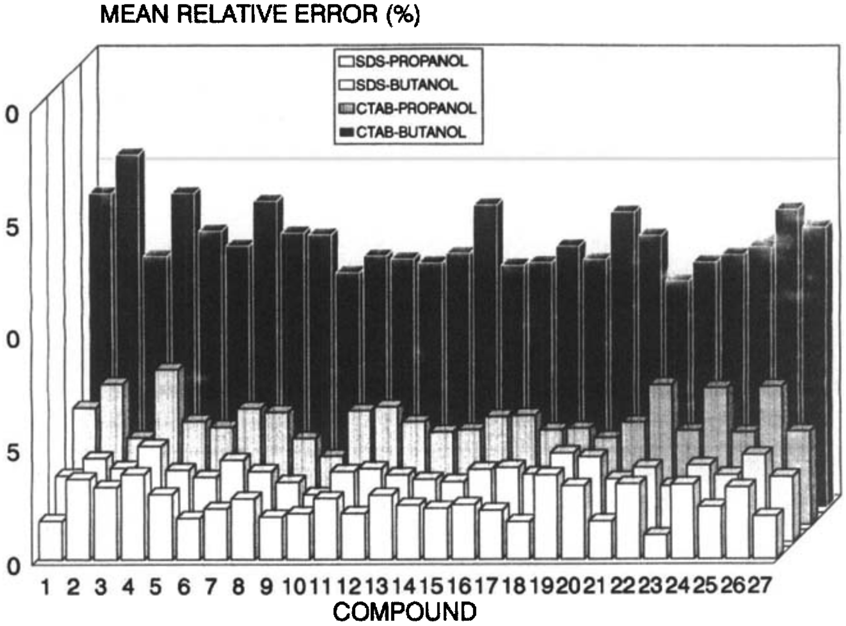


Figure 6. Mean relative errors (in absolute value) obtained for every compound with the best equation in CTAB-propanol, CTAB-butanol, SDS-propanol and SDS-butanol systems.

the unity and zero values, respectively, although the correlation coefficient is very close to unity. Figures 5b, 5c and 5d show that there is not a random distribution of the residuals with the dependent or the independent variables.

In Tables 5, 6, 7 and 8 the calculated values of a ($\phi k_1[L_s]$), k_2, k_3 and k_4 or related parameters (by means of the most adequate equation), for hybrid eluents containing CTAB and propanol, CTAB and butanol, SDS and propanol, and SDS and butanol, respectively, are presented.

For mobile phases containing CTAB as the surfactant, the more adequate equation for explaining the dihydropyridine retention behaviour is generally equation (7). This fact suggests, that in these systems the solutes suffer a direct transfer from the micellar mobile phase to the modified stationary phase. In these cases, the alcohol influences the solute retention due to its interaction with the stationary phase. The values of k_4 are negligible, so we can consider that the interaction of the alcohol with the micelle is of little importance with respect to the others.

Table 5

Calculated Parameter Values for Compounds in Systems Containing CTAB and n-Propanol and the Best Equation Used. Data Between Parentheses are the Parameter Standard Error

Compound	A*	B**	C***	Equation
1	0.034 (0.043)	0.724 (0.056)		(7)
2	0.161 (0.067)	0.866 (0.084)		(7)
3	0.169 (0.054)	1.095 (0.068)		(7)
4	0.00 (0.12)	1.45 (0.16)		(7)
5	0.139 (0.060)	1.014 (0.075)		(7)
6	0.091 (0.041)	0.764 (0.053)		(7)
7	0.000 (0.048)	0.847 (0.063)		(7)
8	0.048 (0.041)	0.674 (0.052)		(7)
9	0.152 (0.036)	0.708 (0.045)		(7)
10	0.169 (0.029)	0.709 (0.037)		(7)
11	0.095(0.063)	1.032 (0.081)		(7)
12	0.075 (0.057)	0.942 (0.073)		(7)
13	0.102 (0.053)	0.931 (0.068)		(7)
14	0.163 (0.041)	0.771 (0.051)		(7)
15	0.024 (0.022)	0.567 (0.029)		(7)
16	0.099 (0.066)	1.110 (0.085)		(7)
17	0.099 (0.066)	1.106 (0.085)		(7)
18	0.108 (0.040)	0.768 (0.051)		(7)
19	552 (215)	241 (96)	2.71 (0.45)	(5)
20	0.000 (0.069)	1.372 (0.091)		(7)
21	0.084 (0.034)	0.604 (0.043)		(7)
22	0.079 (0.055)	0.782 (0.070)		(7)
23	0.117 (0.039)	0.721 (0.050)		(7)
24	161 (16)	99 (11)	1.55 (0.12)	(5)
25	0.107 (0.053)	1.053 (0.068)		(7)
26	0.117 (0.061)	0.857 (0.077)		(7)
27	0.095 (0.039)	0.825 (0.049)		(7)

---

* A means k_2/a or a when equation (7) or (5) is considered, respectively.

** B means k_2k_3/a or k_2 when equation (7) or (5) is considered, respectively

*** C means k_3 when equation (5) is considered

When we consider mobile phases containing SDS as the surfactant again, the constant k_4 is low and the equation that best explains the experimental capacity factors is, in general, the equation (5). The k_3 values shown in Tables 7 and 8 are

Table 6

Calculated Parameter Values for Compounds in Systems Containing CTAB & n-Butanol. Data Between Parentheses are the Parameter Standard Error

Compound	A*	B**	C***	Equation
1	0.34 (0.13)	1.60 (0.29)		(7)
2	0.59 (0.20)	1.88 (0.42)		(7)
3	0.53 (0.16)	2.48 (0.36)		(7)
4	0.42 (0.26)	3.78 (0.62)		(7)
5	0.54 (0.17)	2.26 (0.36)		(7)
6	0.38 (0.12)	1.71 (0.26)		(7)
7	0.36 (0.14)	1.87 (0.32)		(7)
8	0.34 (0.11)	1.45 (0.24)		(7)
9	0.40 (0.12)	1.67 (0.27)		(7)
10	0.36 (0.11)	1.70 (0.23)		(7)
11	0.53 (0.16)	2.25 (0.34)		(7)
12	0.44 (0.14)	2.14 (0.31)		(7)
13	0.45 (0.13)	2.04 (0.29)		(7)
14	0.46 (0.13)	1.78 (0.28)		(7)
15	0.27 (0.10)	1.26 (0.22)		(7)
16	0.53 (0.16)	2.55 (0.36)		(7)
17	0.54 (0.17)	2.54 (0.37)		(7)
18	0.41 (0.12)	1.70 (0.27)		(7)
19	64 (15)	43 (11)	3.33 (0.62)	(5)
20	0.45 (0.23)	3.32 (0.52)		(7)
21	0.34 (0.10)	1.31 (0.22)		(7)
22	0.79 (0.14)	1.75 (0.28)		(7)
23	0.37 (0.11)	1.63 (0.24)		(7)
24	0.96 (0.22)	2.91 (0.47)		(7)
25	0.47 (0.16)	2.32 (0.36)		(7)
26	0.54 (0.17)	1.90 (0.36)		(7)
27	0.40(0.14)	1.85 (0.31)		(7)

---

* A means k_2/a or a when equation (7) or (5) is considered, respectively.

** B means k_2k_3/a or k_2 when equation (7) or (5) is considered, respectively.

*** C means k_3 when equation (5) is considered.

low, but we can observe that they are greater in the case that butanol is the organic modifier in the mobile phase. That is, the interaction alcohol/stationary phase is greater when butanol is considered. This fact is in agreement with Borgerding *et al.*,[12] who reported that the amount of surfactant desorbed by such additives

Table 7

Calculated Parameter Values for Compounds in Systems Containing SDS and n-Propanol and the Best Equation Used. Data Between Parentheses are the Parameter Standard Error

Compound	a	k_2	k_3	Equation
1	1603 (278)	240 (45)	1.917 (0.098)	(5)
2	883 (337)	267 (111)	1.33 (0.13)	(5)
3	475 (117)	192 (53)	1.36 (0.12)	(5)
4	276 (52)	120 (26)	1.96 (0.20)	(5)
5	568 (140)	208 (57)	1.32 (0.10)	(5)
6	1369 (249)	256 (51)	1.616 (0.079)	(5)
7	1030 (241)	224 (57)	1.57 (0.11)	(5)
8	2626 (1308)	369 (195)	1.65 (0.16)	(5)
9	1572 (314)	262 (57)	1.88 (0.10)	(5)
10	4117 (2011)	574 (292)	2.22 (0.15)	(5)
11	843 (191)	217 (54)	1.57 (0.11)	(5)
12	800 (109)	158 (24)	1.99 (0.12)	(5)
13	923 (254)	253 (76)	1.50 (0.11)	(5)
14	1707 (675)	387 (162)	1.44 (0.10)	(5)
15	2543 (698)	255 (76)	1.79 (0.13)	(5)
16	811 (156)	217 (46)	1.99 (0.12)	(5)
17	679 (102)	181 (30)	1.94 (0.11)	(5)
18	1044 (149)	219 (34)	1.385 (0.060)	(5)
19	201 (46)	145 (38)	1.98 (0.21)	(5)
20	583 (138)	189 (49)	2.58 (0.24)	(5)
21	2011 (507)	294 (80)	1.261 (0.074)	(5)
22	2688 (1117)	329 (146)	2.43 (0.24)	(5)
23	2332 (365)	327 (55)	1.92 (0.067)	(5)
24	124 (21)	83 (17)	0.93 (0.11)	(5)
25	437 (89)	180 (41)	1.059 (0.078)	(5)
26	524 (146)	204 (63)	1.060 (0.096)	(5)
27	621 (91)	176 (29)	1.143 (0.062)	(5)

increases as the hydrophobicity of the alcohol increases. If we compare the a and k_2 values shown in Tables 7 and 8, we can observe that solute/stationary phase and solute/micelle interactions decrease when the hydrophobicity of the alcohol increases. This means that butanol can compete in a greater extent with the stationary phase and the surfactant in the micelle, which has been reported earlier by Borgerding *et al.*[12] and by Khaledi *et al.*[17]

Table 8

Calculated Parameter Values for Compounds in Systems Containing SDS and n-Butanol and the Best Equation Used. Data Between Parentheses are the Parameter Standard Error

Compound	a	k_2	k_3	Equation
1	1717 (375)	98 (12)	18.7 (4.3)	(5)
2	355 (50)	77 (11)	6.10 (0.86)	(5)
3	237 (28)	62.7 (7.1)	6.30 (0.81)	(5)
4	203 (42)	48.9 (6.3)	11.2 (2.6)	(5)
5	275 (32)	67.2 (7.6)	6.11 (0.74)	(5)
6	941 (134)	92 (10)	10.9 (1.6)	(5)
7	631 (99)	87 (12)	8.6 (1.4)	(5)
8	211 (44)	108 (14)	17.3 (3.8)	(5)
9	1429 (251)	96 (10)	16.4 (3.1)	(5)
10*	3439 (485)	192 (64)	18.5 (7.4)	(6)
11	473 (60)	75.8 (8.3)	8.4 (1.1)	(5)
12	773 (133)	79.3 (9.2)	12.9 (2.4)	(5)
13	431 (49)	78.2 (8.5)	7.09 (0.83)	(5)
14	646 (73)	86.2 (9.0)	7.80 (0.88)	(5)
15	5580 (1923)	102 (11)	39 (14)	(5)
16	337 (41)	71.8 (7.9)	7.53 (0.97)	(5)
17	343 (44)	71.8 (8.2)	7.7 (1.0)	(5)
18	764 (100)	94 (11)	8.4 (1.1)	(5)
19	122 (20)	53 (6.4)	9.5 (1.8)	(5)
20	468 (133)	61.0 (7.5)	19.7 (6.2)	(5)
21	2160 (345)	135 (18)	12.0 (1.8)	(5)
22	1736 (452)	81.7 (9.7)	21.8 (6.1)	(5)
23	2460 (466)	111 (11)	21.6 (4.3)	(5)
24	84.6 (7.4)	38.6 (3.8)	3.63 (0.39)	(5)
25	239 (24)	67.6 (7.1)	4.75 (0.48)	(5)
26	240 (38)	105 (20)	2.88 (3.34)	(5)
27	442 (47)	84.7 (9.3)	5.64 (0.56)	(5)

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* k_4 = 1.9 (1.4)

In order to show the adequacy of the theoretical model and the equations from it derived in Figure 6, the mean relative errors (in absolute value) obtained with the best equation for every compound studied is plotted. The errors obtained were generally low and ranged from 3.04 to 6.88 (CTAB-propanol), from 10.06 to

15.70 (CTAB-butanol), from 1.06 to 3.74 (SDS-propanol) and from 2.11 to 4.23 (SDS-butanol). In the case of hybrid eluents containing CTAB and butanol, the errors are not good enough, probably due to that at high alcohol concentrations a change in the mechanism can be produced. It is important to note that in the assays with CTAB-butanol systems the alcohol concentration ranged from 3% to 10% and with eluents containing SDS and butanol it ranged from 3% to 7.5%.

CONCLUSIONS

From the results obtained in this work and for the group of dihydropyridines studied, the following statements can be established:

* Equation (2) is of more general applicability than equation (1) to predict solute capacity factors and significatively better than equation (3)

* In general, capacity factors can be related to micellized surfactant and alcohol concentrations in the mobile phase by means of only two or three equilibrium constants or related parameters and the best equation depends on the system considered.

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