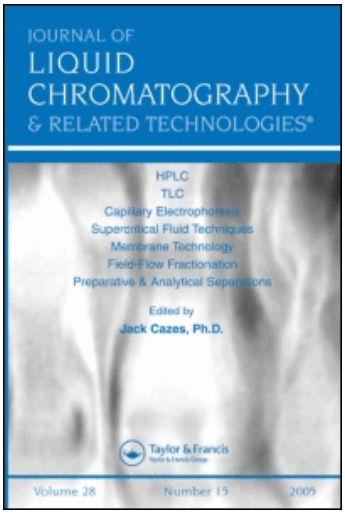

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EVALUATION OF THE ELUTION STRENGTH OF THE SURFACTANT AND ORGANIC SOLVENT IN HYBRID MICELLAR MOBILE PHASES

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ABSTRACT

The global ability of a mixed mobile phase (with two or more modifiers) to elute a solute is often measured without distinguishing between the elution strength of each modifier. An algorithm is proposed to evaluate the elution strength of the modifiers in hybrid micellar mobile phases containing a surfactant and an organic solvent. The algorithm is based on a mechanistic retention model that takes into account the competing equilibria of solutes among aqueous-organic phase, micelle, and stationary phase. The change in the elution strength of surfactant and organic solvent with respect to the concentration of both modifiers is also examined.

The results are discussed according to the values of the partition constants of the solutes, and show the complex behaviour of the elution strength in the hybrid mobile phases, which depends on the relative concentration of the different modifiers. The elu-

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tion strengths of the surfactant sodium dodecyl sulphate and three alcohols, 1-propanol, 1-butanol, and 1-pentanol, are studied, using the retention data of six probe compounds (acebutolol, amiloride, carteolol, orciprenaline, triamterene, and trimethoprim).

INTRODUCTION

Micellar mobile phases composed of only surfactant are usually weak and suffer from poor efficiency. Although the analysis time can be decreased in most instances by increasing the concentration of micelles, the chromatographic efficiencies often deteriorate. However, the addition of a small amount of an organic solvent to the micellar mobile phase often yields adequate retentions and improves the efficiencies.(1-4) This facilitates the resolution of complex mixtures.

In micellar liquid chromatography, the retention and selectivity are controlled by three competing equilibria: the association of solutes with the micelles, the partitioning of the solutes from bulk aqueous solvent to the stationary phase, and the direct transfer from the micelles to the stationary phase.(5) The retention can be described by:

$$k = \frac{K_{AS}}{1 + K_{AM}[M]} \qquad (1)$$

where k is the retention factor, $[M]$ the concentration of surfactant forming micelles, K_{AM} measures the distribution of the solute between micelle and water, and K_{AS} is the product ϕP_{AS} ,ϕ being the phase ratio and P_{AS} the partition coefficient of the solute into the stationary phase.(6)

The addition of an organic solvent to a micellar mobile phase alters, significantly, the partitioning equilibria, which are displaced away from the micelle and stationary phase towards the aqueous phase that becomes more non-polar. Both constants, K_{AM} and K_{AS}, are decreased as a result of the addition of the organic solvent, especially for highly hydrophobic solutes.(7) However, the ratio K_{AM}/K_{AS} increases, and therefore, the elution strength of the mobile phase is greater. The rate of change in solute retention varies with its charge and hydrophobicity, as well as with the nature of the surfactant and organic solvent in the mobile phase.

Khaledi et al.(2,3) studied the elution strength of several alcohols used as modifiers in micellar mobile phases, and suggested that the relationship between the retention factor and volume fraction of organic solvent, φ, is similar to that valid in conventional reversed-phase liquid chromatography (RPLC) with binary aqueous-organic mixtures:(8)

$$\log k = \log k_0 - S_{hyb}\,\varphi \qquad (2)$$

where S_{hyb} is the elution strength parameter of the organic solvent in the hybrid micellar system and k_0 the retention factor in pure aqueous micellar mobile phases (without organic solvent). Eq. (1) can also be written in the logarithmic form:

$$\log k = \log K_{AS} - \log (1 + K_{AM}\,[M]) \qquad (3)$$

Considering linear relationships between both $\log K_{AS}$ and $\log(1 + K_{AM}[M])$ with φ,[3] the following results:

$$\log K_{AS} = \log K_{AS0} - S_s\,\varphi \qquad (4)$$

$$\log (1 + K_{AM}\,[M]) = \log (1 + K_{AM0}\,[M]) - S_m\,\varphi \qquad (5)$$

where K_{AS0} and K_{AM0} are the constants for pure aqueous micellar eluents. Eq. (1) can finally be expressed as:

$$k = \frac{K_{AS0}}{1 + K_{AM0}\,[M]}\, e^{-(S_s - S_m)\,\varphi} \qquad (6)$$

The parameters S_s and S_m represent the sensitivity of the change in solute partitioning from bulk solvent into the stationary phase and into the micelles, respectively, with changes in φ. From Eqs. (1) and (3)-(6), S_{hyb} is derived to be dependent on S_s and S_m according to:

$$S_{hyb} = S_s - S_m \qquad (7)$$

The negative sign in Eq. (7) reflects the competing nature of the two partitioning equilibria (into the stationary phase and micelles). In the absence of micelles, $S_m = 0$ and $S_{hyb} = S_s$, which is the elution strength parameter in conventional RPLC. This equation shows, also, that the elution strength in hybrid micellar systems will be usually smaller than in aqueous-organic mobile phases.

The measurement of relative elution strength has also been proposed for hybrid micellar systems according to:

$$\log \frac{k}{k_r} = a\,(S_r - S) \qquad (8)$$

where k and k_r are the retention factors of a solute eluted with the considered mobile phase and with a mobile phase taken as reference, respectively; S and

S_r are the corresponding elution strengths, and a is a parameter that depends on the molecular size of the solute.(9) If a null value is assigned to the elution strength of the reference mobile phase:

$$\log \frac{k_r}{k} = a\ S^o . \qquad (9)$$

The parameter S^o measures the global ability of the mobile phase to elute a solute. It does not distinguish between the elution strength of each modifier (e.g., surfactant or organic solvent), being a combination of both strengths. It is, also, not expected to be a linear property, since surfactant and organic solvent may interact each other.

Recently, a model was reported to describe the retention at varying concentration of surfactant and organic solvent in hybrid mobile phases:(10)

$$k = \frac{K_{AS}\dfrac{1+K_{SD}\varphi}{1+K_{AD}\varphi}}{1+K_{AM}\dfrac{1+K_{MD}\varphi}{1+K_{AD}\varphi}[M]} = \frac{K'_{AS}}{1+K'_{AM}[M]} . \qquad (10)$$

The constants K_{AD}, K_{MD}, and K_{SD} measure the displacement of solute-micelle and solute-stationary phase equilibria due to the presence of organic solvent, and K'_{AM} and K'_{AS} are conditional partition constants with respect to this modifier.

Eqs. (2) and (9) are too simple to measure, appropriately, the elution strength in hybrid micellar mobile phases. In this work, an algorithm that describes the elution strength of surfactant and organic solvent in these mobile phases is proposed, which is based on the retention model given by Eq. (10). The algorithm does not use a reference mobile phase. The results are discussed according to the values of the partition constants of the solutes, and show the complex behaviour of the elution strength in hybrid mobile phases, which depends on the relative concentration of the different modifiers.

The chromatographic data previously reported for a set of six compounds (acebutolol, amiloride, carteolol, orciprenaline, triamterene, and trimethoprim) eluted with mobile phases of sodium dodecyl sulphate, and either 1-propanol, 1-butanol, or 1-pentanol were used to validate the proposed equations.(11) The concentration ranges of the modifiers in the mobile phases were 0.075-0.125 M for SDS, 0-12% (v/v) for 1-propanol, 0-6% (v/v) for 1 -butanol, and 0-3% (v/v) for 1-pentanol.

RESULTS AND DISCUSSION

Meaning of the Model Parameters K_{AD}, K_{MD}, and K_{SD}

In a previous work, the retention behaviour of six probe compounds (acebutolol, amiloride, carteolol, orciprenaline, triamterene, and trimethoprim) was shown to be accurately modelled according to Eq. 10, and the model parameters for each compound were obtained.(11) As expected, the values of K_{AM} and K_{AS} for each compound were similar for the three organic solvents. In contrast, K_{AD}, K_{MD}, and K_{SD} depended on the organic solvent and increased with the elution strength in the order: 1-propanol < 1-butanol < 1-pentanol. These three constants quantify the effect of the addition of organic solvent on the concentration of solute in each phase: aqueous, micellar, and stationary, respectively. Thus, for example, when a given amount of organic solvent is added to the aqueous phase, the concentration of solute in this phase will be given by:

$$[A'] = [A] + \Delta A = [A](1 + K_{AD}\,\varphi) \tag{11}$$

K_{AD} is thus the relative change in the concentration of solute in the aqueous phase, with respect to its concentration in the absence of organic solvent, per unity of added solvent:

$$K_{AD} = \frac{\Delta A}{[A]}\frac{1}{\varphi}. \tag{12}$$

On the other hand, for the equilibrium between stationary phase and water, and neglecting K_{SD}:

$$K_{A'S} = \frac{K_{AS}}{1 + K_{AD}\,\varphi} \tag{13}$$

from which:

$$K_{AD} = \left(\frac{K_{AS} - K_{A'S}}{K_{A'S}}\right)\frac{1}{\varphi}. \tag{14}$$

Therefore, K_{AD} is the factor in which the solute-stationary phase partition constant is reduced per unity of organic solvent. The detailed examination of the values of the model parameters (K_{AM}, K_{AS}, K_{AD}, K_{MD}, and K_{SD}) for the probe com-

pounds is needed in this work to discuss the behaviour of the solutes with respect to their elution strength. For this reason, although these values were reported previously,(11) they are given again in Table 1.

A General Equation to Evaluate the Elution Strength

The elution strength of a modifier in a mobile phase for a given solute is the sensitivity of the retention of the solute to the concentration of the modifier. This parameter can be expressed as the relative change in the retention of the solute, when an infinitesimal addition of the modifier is made to the mobile phase:

$$S = -\frac{1}{dC}\left(\frac{dk}{k}\right) = -\frac{1}{k}\left(\frac{dk}{dC}\right) \qquad (15)$$

where C is the concentration of modifier. Eq. (15) can be applied to any modelled retention behaviour. If the logarithmic model given by Eq. (2) is followed, the elution strength will not depend on the concentration of modifier:

$$S = -\frac{1}{k}\left(\frac{dk}{d\varphi}\right) = S_{hyb} \qquad (16)$$

which agrees with the conventional definition of elution strength in conventional RPLC with mobile phases comprising only one modifier. Also, Eq. (7) can be obtained by applying Eq. (15) to Eq. (6) with $C = \varphi$.

Elution Strength of Organic Solvent and Surfactant in Micellar Mobile Phases

The elution strength of the organic solvent can be obtained from the derivative of Eq. (10) with respect to the concentration of organic solvent (Eq. (15)):

$$S_\varphi = -\frac{1}{k}\left(\frac{\partial k}{\partial \varphi}\right) = -\frac{1+K_{A'M}[M]}{K_{A'S}}\left(\frac{\frac{\partial K_{A'S}}{\partial \varphi}(1+K_{A'M}[M]) - \frac{\partial K_{A'M}}{\partial \varphi}[M]\,K_{A'S}}{(1+K_{A'M}[M])^2}\right) \qquad (17)$$

Table 1. Constants for the Equilibria Established in Hybrid Micellar Chromatographic Systems of SDS and Alcohol (Eq. (10)) for Several Probe Compounds[a]

Compound	K_{AS}	K_{AM}	K_{AD}	K_{MD}	K_{SD}
			1-Propanol		
Acebutolol	378	46.2	139	60.1	2.18
Amiloride	357	167	95.7	54.6	15.7
Carteolol	446	87.2	182	81.6	5.58
Orciprenaline	38.7	21.2	10.4	61.6	7.06
Triamterene	233	46.6	16.7	51.2	2.79
Trimethoprim	343	57.1	103	69.8	3.65
			1-Butanol		
Acebutolol	448	57.0	547	266	25.1
Amiloride	330	154	326	187	43.9
Carteolol	542	108	667	272	19.1
Orciprenaline	41.7	23.8	42.1	215	34.4
Triamterene	214	42.0	65.7	179	11.4
Trimethoprim	339	56.3	226	244	15.5
			1-Pentanol		
Acebutolol	377	46.1	1625	344	31.7
Amiloride	325	151	1875	452	111
Carteolol	440	85.8	3390	535	57.5
Orciprenaline	38.0	20.5	377	759	150
Triamterene	226	44.8	1030	543	74.1
Trimethoprim	339	56.3	1600	524	57.7

[a]From ref. 11.

which can be rewritten as a function of the effect of the organic solvent on the partitioning of the solute between the aqueous and stationary phases ($S_{KAS'}$, that is, the change in K'_{AS} produced by the organic solvent), and on the equilibrium between the solute and micelle ($S_{KAM'}$, that is, the change in K'_{AM}):

$$S_\varphi = S_{K'AS} - S_{K'AM} \frac{K_{A'M}\,[M]}{1 + K_{A'M}\,[M]} \tag{18}$$

$S_{KAS'}$ and $S_{KAM'}$ are given by the relative change in the conditional partition constants, K'_{AS} and K'_{AM}, respectively, at increasing concentration of organic solvent. From the terms K'_{AS} and K'_{AM} in Eq. (10):

$$S_{K'AS} = -\frac{1}{K_{A'S}}\frac{\partial K_{A'S}}{\partial \varphi} = \frac{K_{AD}}{1+K_{AD}\,\varphi} - \frac{K_{SD}}{1+K_{SD}\,\varphi} \qquad (19)$$

$$S_{K'AM} = -\frac{1}{K_{A'M}}\frac{\partial K_{A'M}}{\partial \varphi} = \frac{K_{AD}}{1+K_{AD}\,\varphi} - \frac{K_{MD}}{1+K_{MD}\,\varphi}. \qquad (20)$$

The meaning of $S_{KAS'}$ and $S_{KAM'}$ is similar to S_s and S_m (Eq. (6)). The difference between $S_{KAS'}/S_{KAM'}$ and S_s/S_m is the model which describes the parameters (Eqs. (10) and (6), respectively). Finally, from Eqs. (18)-(20) the following is obtained:

$$S_\varphi = \frac{K_{AD}+K_{MD}\,K_{AM}\,[M]}{1+K_{AD}\,\varphi+(1+K_{MD}\,\varphi)\,K_{AM}\,[M]} - \frac{K_{SD}}{1+K_{SD}\,\varphi}. \qquad (21)$$

According to Eqs. (19) and (20), K'_{AS} will decrease with the concentration of modifier ($S_{KAS'} > 0$) if $K_{AD} > K_{SD}$ (the most usual behaviour, see Table 1). Also, K'_{AM} will decrease ($S_{KAM'} > 0$) if $K_{AD} > K_{MD}$. It should be noted, that a decrease in K'_{AS} indicates the displacement of the partitioning equilibrium from the stationary phase towards the aqueous-organic phase, which will lower the retention. Also, a decrease in K'_{AM} indicates the displacement of the equilibrium from the micellar pseudophase towards the aqueous-organic phase, but this will increase the retention if a parallel decrease in K'_{AS} does not exist.

Similarly, the elution strength of the surfactant will be given by:

$$S_\mu = \frac{(1+K_{MD}\,\varphi)\,K_{AM}}{1+K_{AD}\,\varphi+(1+K_{MD}\,\varphi)\,K_{AM}\,[M]} = \frac{K_{A'M}}{1+K_{A'M}\,[M]}. \qquad (22)$$

The dependence (increase or decrease) in the elution strength of organic solvent (S_φ) and surfactant (S_μ), with respect to the concentration of both components (organic solvent and surfactant) was also examined. From Eqs. (21) and (22):

$$\frac{\partial S_\varphi}{\partial [M]} = \frac{\partial S_\mu}{\partial \varphi} = \frac{(K_{MD}-K_{AD})\,K_{AM}}{(1+K_{AD}\,\varphi+(1+K_{MD}\,\varphi)\,K_{AM}\,[M])^2} \qquad (23)$$

which indicates that S_φ will increase with the concentration of surfactant if $K_{MD} > K_{AD}$. From Eq. (10), it can be seen that K'_{AM} will also increase at increasing concentration of organic solvent. This means that the effect of the organic solvent on the retention will be greater at higher concentration of the surfactant when the organic solvent increases the value of K'_{AM}, that is, when it favours the displacement of the equilibrium towards the micelles. This behaviour is observed for orciprenaline and triamterene (Table 1). However, more frequently (acebutolol, amiloride, carteolol, and trimethoprim), the elution strength of the organic solvent decreases at higher concentrations of surfactant ($K_{MD} < K_{AD}$).

On the other hand, S_φ always decreases with the concentration of organic solvent, owing to the small value of K_{SD} (Table 1):

$$\frac{\partial S_\varphi}{\partial \varphi} = \frac{K_{SD}^2}{(1+K_{SD}[M])^2} - \frac{(K_{AD}+K_{MD}\ \mathrm{KsubAM}\ [M])^2}{(1+K_{AD}\ \varphi+(1+K_{MD}\ \varphi)\ K_{AM}[M])^2} \quad (24)$$

Eq. (23) also describes the dependence of the elution strength of the surfactant on the concentration of the organic solvent ($\partial S_\mu/\partial\varphi$), whereas the dependence on the concentration of surfactant is given by:

$$\frac{\partial S_\mu}{\partial [M]} = -(S_\mu)^2 \quad (25)$$

This means that the elution strength of the surfactant always decreases at increasing concentration of surfactant.

Elution Strength for the Probe Compounds

Figures 1 and 2 show the effect of the concentration of organic solvent and surfactant on S_φ for acebutolol and orciprenaline, respectively, whereas Figures 3 and 4 correspond to S_μ. In the figures, the values of S_φ and S_μ obtained with Eqs. (21) and (22) have been multiplied by 100. Also, owing to the wide range of S_φ values, the logarithm of S_φ is plotted in Figure 1 to show the differences among the solvents. The concentrations of surfactant and alcohols are given as weight/volume to make them comparable.

It may be observed, that the elution strength of the organic solvent decreases when its concentration increases. At low solvent concentration, S_φ follows the order:

1-pentanol > 1-butanol > 1-propanol

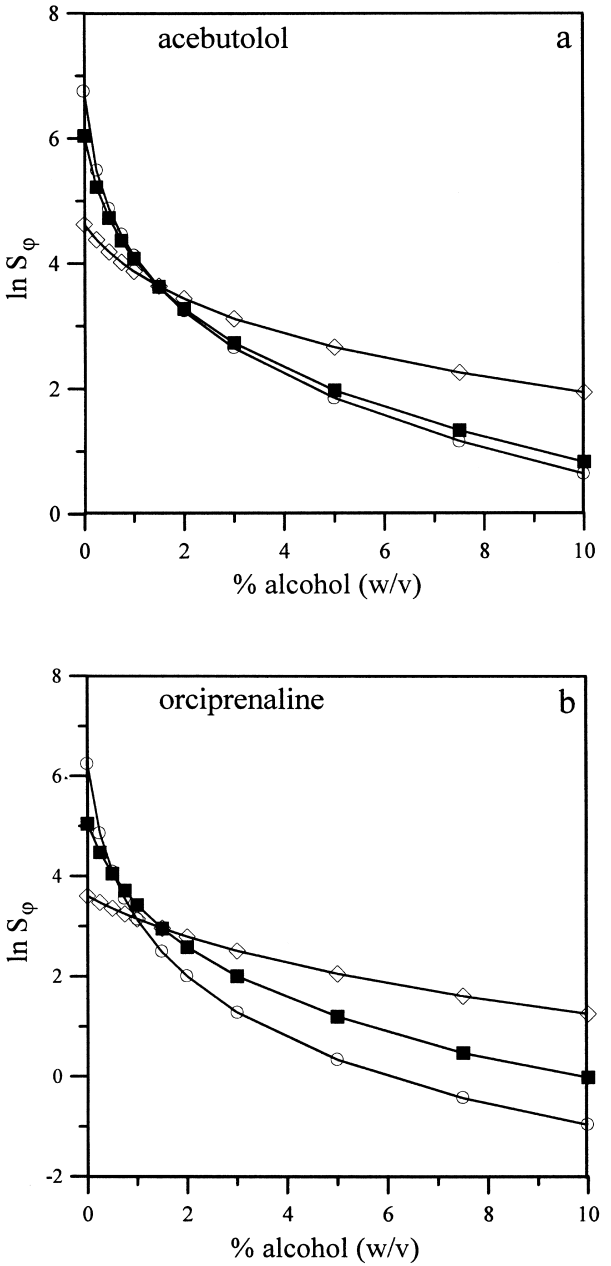
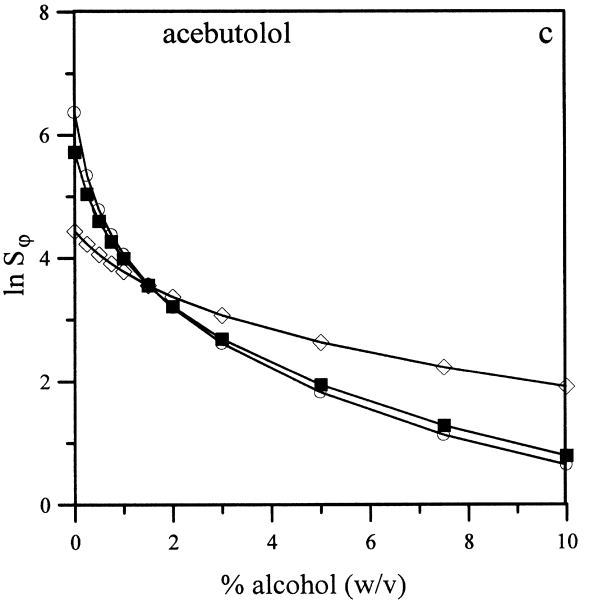


Figure 1. Change in elution strength of the organic solvent with its concentration, at two concentrations (w/v) of SDS: (a,b) 1.45% (0.05 M), and (c,d) 4.3% (0.15 M). Organic solvent: 1-propanol (◊), 1-butanol (■), and 1-pentanol (○).



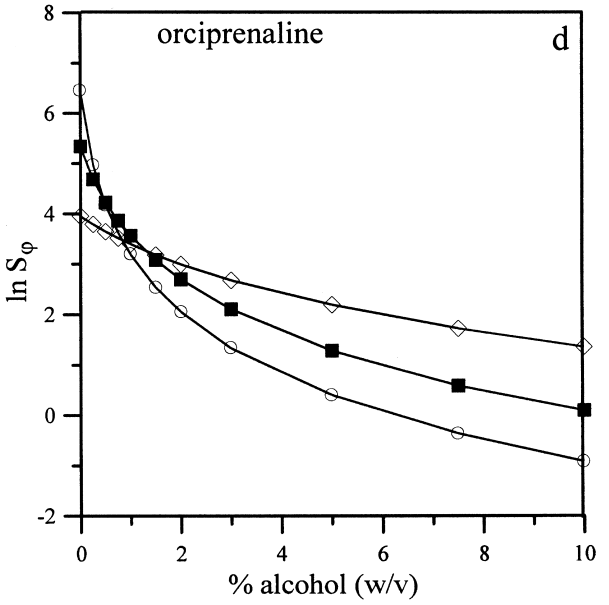


Figure 1. Continued.

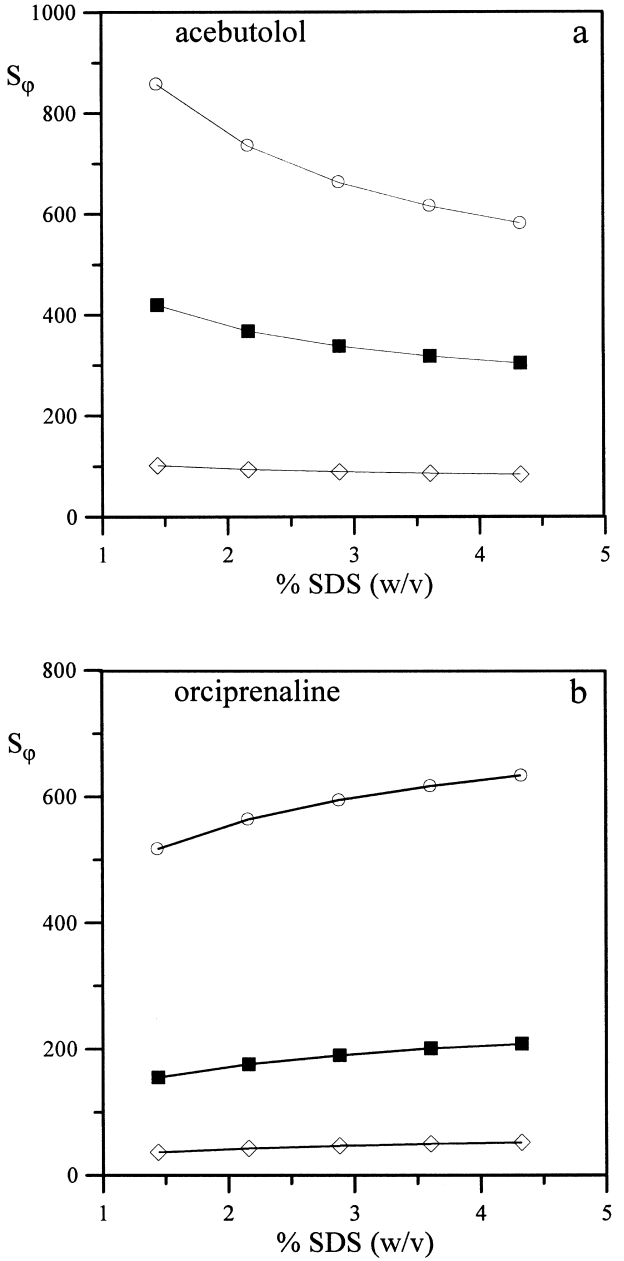
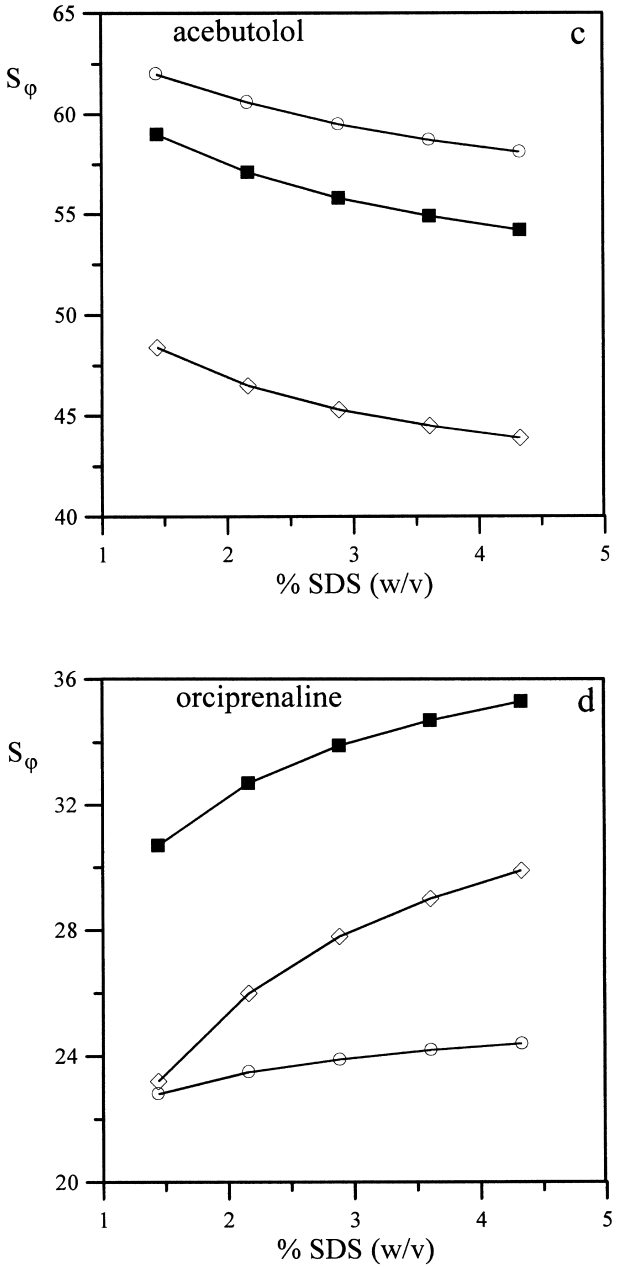


Figure 2. Change in elution strength of the organic solvent with the concentration of surfactant, at two concentrations (w/v) of organic solvent: (a,b) 0%, and (c,d) 1%. See Figure 1 for symbols.



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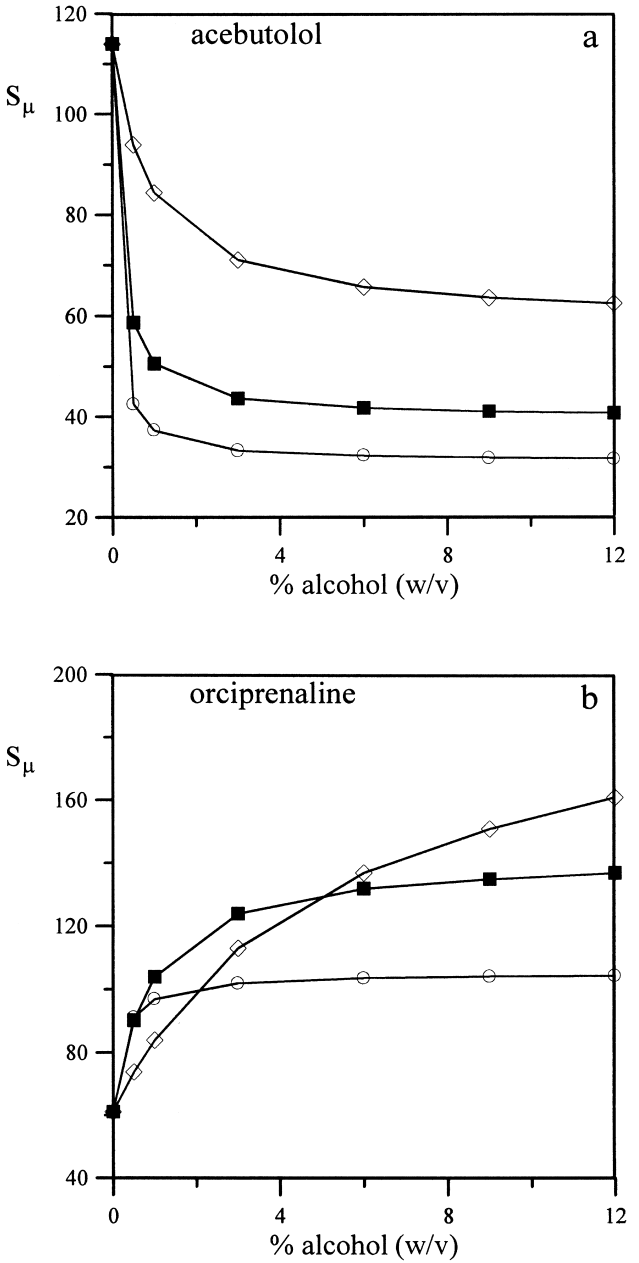

Figure 3. Change in elution strength of the surfactant with the concentration of organic solvent, at two concentrations (w/v) of SDS: (a,b) 0.25% (8.7×10^{-3} M), and (c,d) 2% (0.069 M). See Figure 1 for symbols.

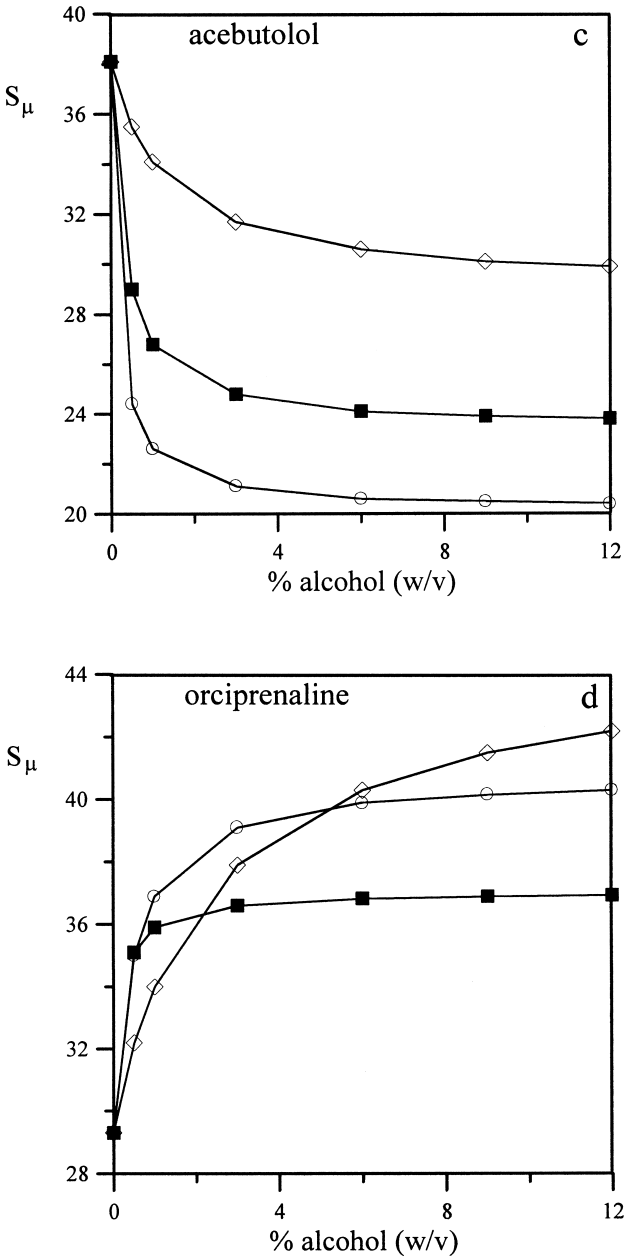

Figure 3. Continued.

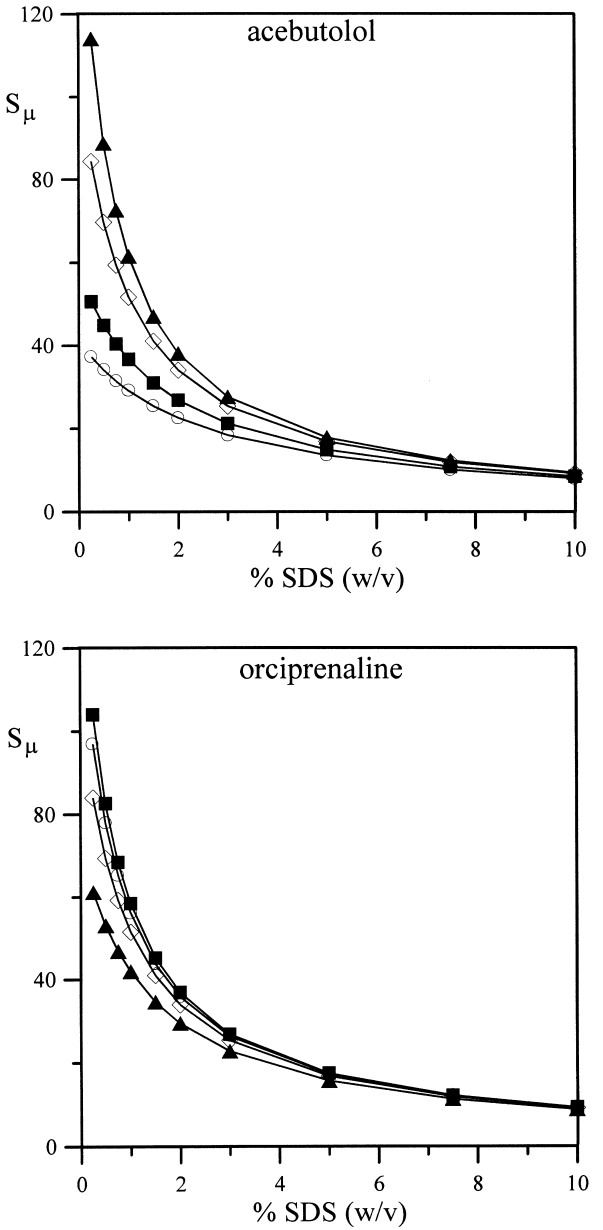

Figure 4. Change in elution strength of the surfactant with its concentration, in the absence of organic solvent (▲), and in the presence of 1% 1-propanol (◊), 1% 1-butanol (■), and 1% 1-pentanol (○).

In the region close to a null concentration of the alcohols ($\varphi = 0$), the ratios of the elution strengths of the three modifiers (1-pentanol:1-butanol:1-propanol) were: 8.4:4.1:1 and 14:4.2:1 for acebutolol and orciprenaline, respectively. However, the reduction in S_φ with the concentration of organic solvent was greater in the same order. Therefore, at concentrations of the alcohols greater than 1-2%, the elution strengths reversed. Thus, for 5% alcohol, the ratios of the elution strengths were 1:1.1:2.2 for acebutolol and 1:2.3:5.6 for orciprenaline. Because of this behaviour, concentrations of 1-butanol and 1-pentanol above 2% did not yield a significant reduction in the retention for the probe compounds.

Figures 2 and 3 show the combined influence of organic solvent and surfactant on the elution strength, with two opposite behaviours. For acebutolol, the elution strength of the organic solvent decreased with the concentration of surfactant (Figures 2a and 2c) and the elution strength of the surfactant decreased with the concentration of organic solvent (Figures 3a and 3c), since the equilibrium between solute and micelle is negatively affected by the addition of organic solvent. The same behaviour was observed for amiloride, carteolol, and trimethoprim. For all these compounds $K_{MD} < K_{AD}$. Orciprenaline and triamterene showed the opposite behaviour: the elution strength of the organic solvent increased with the concentration of surfactant (Figures 2b and 2d), and that of the surfactant increased with the concentration of modifier (Figures 3b and 3d). In this case,

Table 2. Elution Strength of the Organic Solvent (S_φ) for the Probe Compounds

Compound	Propanol	Butanol	Pentanol
1.5% (w/v) SDS-0% alcohol			
Orciprenaline	36.7	155	517
Amiloride	53.8	240	622
Triamterene	47.4	192	759
Carteolol	118	462	1248
Trimethoprim	92.9	340	917
Acebutolol	102	420	858
1.5% (w/v) SDS-1% (w/v) alcohol			
Orciprenaline	23.2	30.7	22.8
Amiloride	26.0	35.6	30.7
Triamterene	30.4	51.2	41.9
Carteolol	49.0	61.2	51.6
Trimethoprim	45.1	57.8	50.7
Acebutolol	48.4	59.0	62.0

the equilibrium between solute and micelle was favoured by the presence of increasing amounts of organic solvent. Finally, Figure 4 shows the general behaviour given by Eq. (25) (i.e., the elution strength of the surfactant always decreases at higher concentration of the surfactant).

Tables 2 and 3 indicate some values of S_φ and S_μ for the probe compounds studied in this work. The values given in Table 2 for the elution strength of the organic solvent correspond to 0% alcohol (extrapolated value) and 1% (w/v) alcohol (in v/v unities: 1.24% for 1-propanol, and 1.23% for 1-butanol and 1-pentanol). The values given in Table 3 for the surfactant correspond to 0.25% and 2% (w/v) SDS (8.7×10^{-3} M and 0.069 M, respectively, note that micelles are formed above 8.1×10^{-3} M SDS). The high value of the extrapolated S_φ to 0% alcohol corresponds to the large variation in retention with the first additions of alcohol. This variation is largely decreased at increasing volume fraction of the alcohol, with little change in retention above 10% 1-propanol, 5% 1-butanol, and 2% 1-pentanol.(11)

As observed, both elution strengths of organic solvent and surfactant depend on the eluted solute, due to the different intermolecular forces responsible for the retention and the diverse effects of each modifier on these forces. The more hydrophobic the solute, the more intense the effect of the organic solvent on the apparent elution strength of the micellar mobile phase. It is indeed the diverse dependence of the elution strength for each solute, which gives rise to the

Table 3. Elution Strength of the Surfactant (S_μ) for the Probe Compounds

Compound	No Modifier	1% Propanol	1% Butanol	1% Pentanol
		0.25% (w/v) SDS		
Orciprenaline	61.1	84.0	104	96.9
Amiloride	230	213	130	108
Triamterene	132	137	116	72.4
Carteolol	170	131	62.7	47.6
Trimethoprim	132	117	79.8	55.7
Acebutolol	114	84.4	50.6	37.3
		2% (w/v) SDS		
Orciprenaline	29.5	34.0	36.9	35.9
Amiloride	45.9	45.1	19.7	37.3
Triamterene	38.0	40.3	38.3	31.9
Carteolol	42.8	39.7	29.9	26.0
Trimethopri	39.9	38.4	33.3	28.2
Acebutolol	38.1	34.1	26.8	22.6

particular changes in selectivity observed in micellar liquid chromatography, at varying concentration of the modifiers.

The proposed methodology succeeded in describing the elution strength observed for solutes eluted with hybrid micellar mobile phases. The theory can easily be extended to other systems where two or more modifiers are involved.

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