Determination of Solute–Aggregate Binding Constants of Some Polycyclic Aromatic Hydrocarbons by High-Performance Liquid Chromatography in the Presence of CTAB–Alcohol–Water Systems with High Percentages of Alcohol

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Abstract

This work presents the chromatographic study of the association between 5 polycyclic aromatic hydrocarbons and the aggregates formed by a cationic surfactant in the presence of a high percentage of two different alcohols, *n*-propanol (20–50%, v/v) and ethanol (50–75%, v/v). A generalization of the classical equations for micellar liquid chromatography can be used in order to determine the solute–aggregates binding constants. Also, by means of a multiple regression, it is possible to obtain an equation that relates the chromatographic retention (expressed as the inverse of the retention factor) and the surfactant and alcohol concentrations. This equation allows one to carry out an estimate of the association constants for any quantity of alcohol.

Introduction

Ternary systems formed by surfactant–alcohol–water mixtures form different structures in function of the percentages of each component in the sample (1–4). Solutions without alcohol, or with a low percentage of alcohol, present above the solution's critical micelle concentration (CMC) direct micelles with the hydrophobic chains at the interior of the aggregate. In the presence of very high percentages of alcohol, reverse micelles can be present, and in the presence of intermediate percentages, the structures greatly depend on the alcohol long chain for aliphatic alcohols, as can be seen in phase diagrams (5–12). For most short chain alcohols (methanol, ethanol, and *n*-propanol), the phase diagram presents a great area of isotropic solutions that begin with direct micelles and finish with reverse micelles through transitions by bicontinuous structures, which present interesting properties. These phases are used in this work to carry out the chromatographic retention study of the polycyclic aromatic hydrocarbons (PAHs).

Micellar liquid chromatography (MLC) has been widely used to determine the solute-association constants of the micelles of many different solutes by means of three models proposing to describe the retention of solutes at various surfactant concentrations: the three-phase model of Armstrong and Nome (13), the equilibrium approach of Arunyanart and Cline-Love (14), and Foley's model (15) that considers the interactions with the micellar medium as a secondary equilibrium. All of these models lead to similar equations that relate the chromatographic retention (such as retention factor) with the micelle concentration in the mobile phase. A recent work reviewed the data of these constants determined using mobile phases with direct surfactant micelles formed in water or water–alcohol mixtures with a low percentage of alcohol (16). For PAHs, several studies (17–20) have given the values of solute-binding constants in different micellar systems formed by hexadecyltrimethylammonium bromide (CTAB) and sodium dodecylsulphate (SDS) in the absence and presence of some alcohols (such as methanol, *n*-propanol, and *n*-buthanol) at low percentages.

The use of high percentages of an organic modifier in a mobile phase produces a great decrease in retention times in comparison with those obtained with none or low percentages, and the influence of the alcohol in the retention of the solutes modifies the separation selectivity of the organic and inorganic compounds. However, there are a few bibliographic references with these media (21–24).

This work presents the retention behavior of some polycyclic aromatic hydrocarbons in a cationic surfactant (CTAB) in the presence of *n*-propanol and ethanol at high percentages as mobile phases. The solute–aggregate binding constants were calculated by means of a generalization of Arunyanart and Cline-Love's equation (14) to consider the alcohol so that it permits

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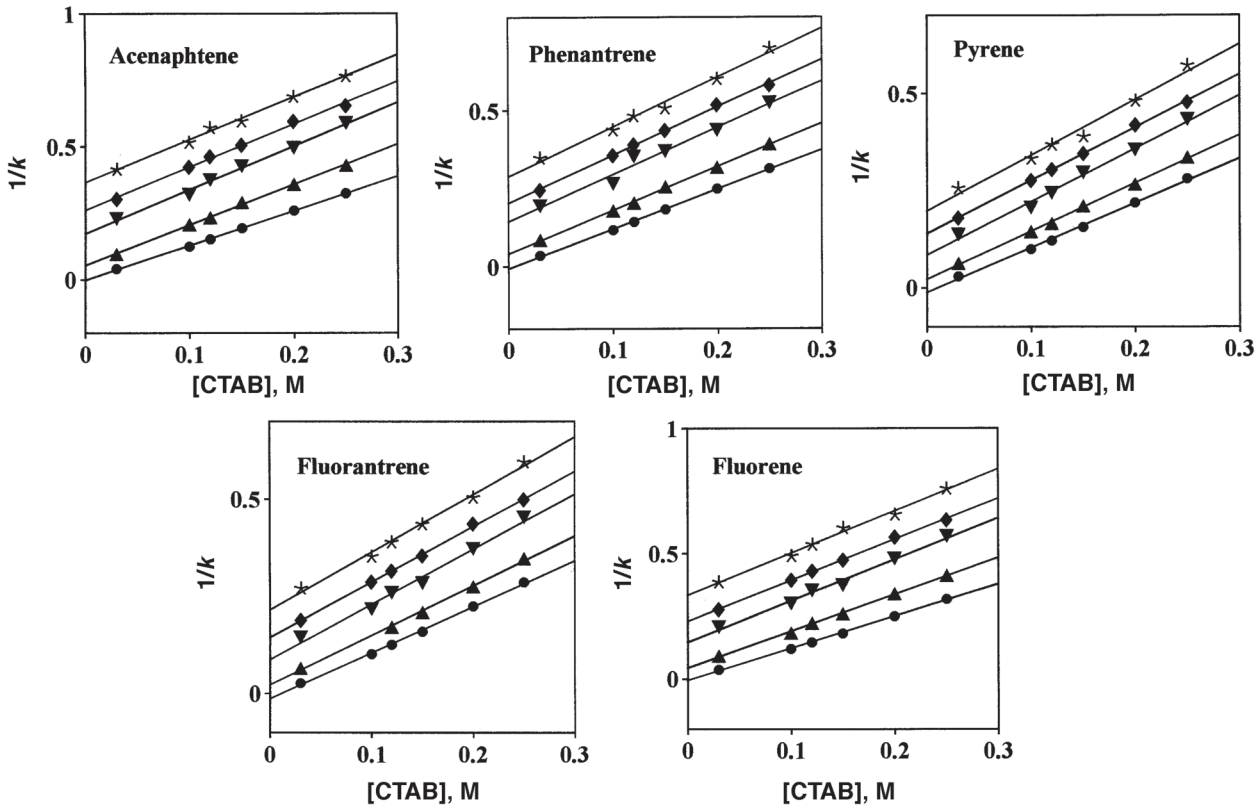

Figure 1. Variation of 1/*k* as a function of CTAB concentration at different percentages of *n*-propanol: 1, 20; s, 30; t, 40; u, 45; Q, 50.

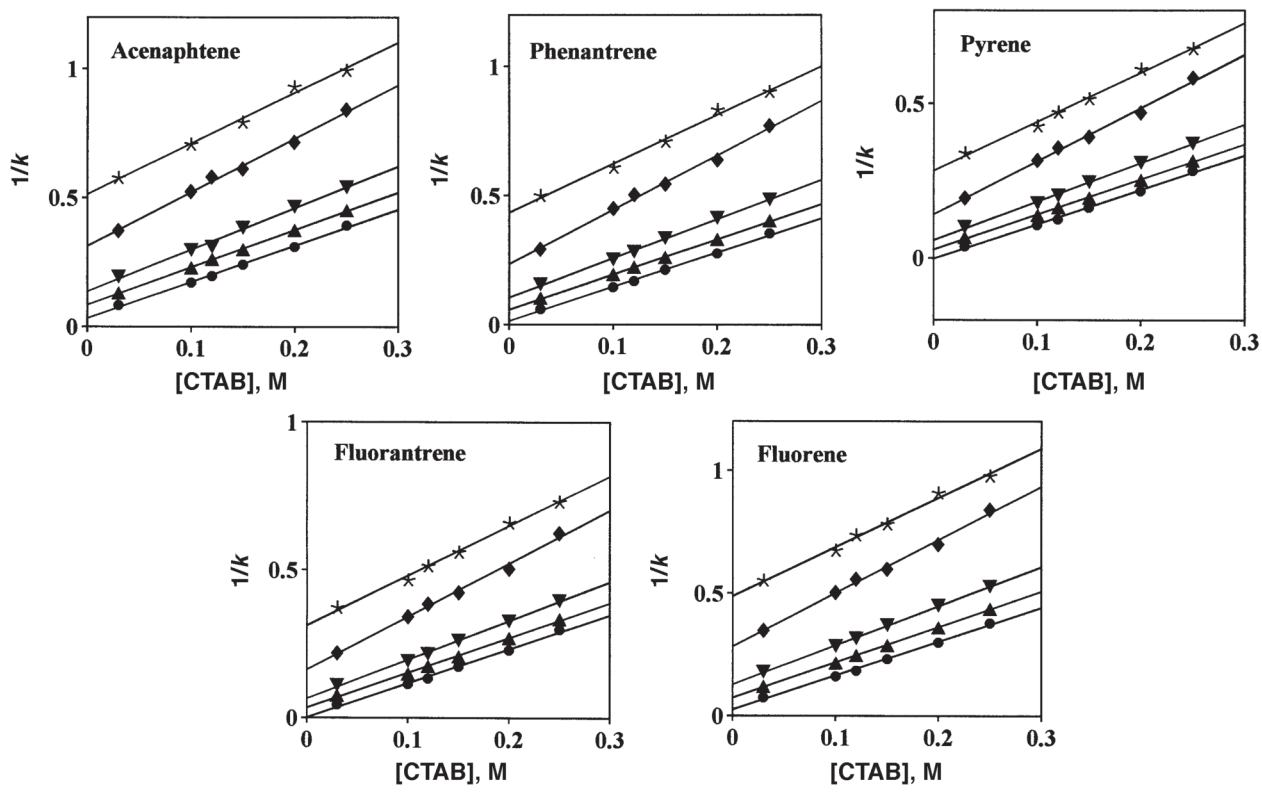

Figure 2. Variation of 1/*k* as a function of CTAB concentration at different percentages of ethanol: 1, 50; s, 55; t, 60; u, 70; Q, 75.

one to take into account the modifications upon the stationary phase and the surfactant structures. Finally, the retention data have been studied by a multiple regression analysis with surfactant and alcohol concentration as independent variables. The best relationship has also been used to calculate the binding constants.

Experimental

Apparatus

The chromatographic system consisted of a Perkin-Elmer (Norwalk, CT) model 250 pump, an ultraviolet–visible (UV–vis) detector model 785A from Applied Biosystems (Norwalk, CT), a Perkin-Elmer Turbochrom 4 software for data collection, and a Rheodyne injection valve with an injection volume of 20 µL.

The separation column was a Lichrosorb RP-18 (150 × 3.9 mm, 10-µm particle size) from Sugelabor (Madrid, Spain).

Table I. Regression Parameters and Binding Constant Values for the PAHs with CTAB at Different Percentages of PrOH Using Equation 3

	CTAB–PrOH–water				
PAH	PrOH (%, v/v)	Intercept	Slope	*r*	K_2,M^{-1}
Acenaphthene					
	20	$-2\cdot10^{-3} \pm 2\cdot10^{-3}$	$1.30 \pm 2\cdot10^{-2}$	0.9996	—
	30	$5.4\cdot10^{-2} \pm 4\cdot10^{-3}$	$1.52 \pm 3\cdot10^{-2}$	0.9992	28 ± 2
	40	$0.181 \pm 5\cdot10^{-3}$	$1.61 \pm 3\cdot10^{-2}$	0.9993	8.8 ± 0.4
	45	$0.252 \pm 3\cdot10^{-3}$	$1.71 \pm 2\cdot10^{-2}$	0.9996	6.7 ± 0.2
	50	$0.372 \pm 7\cdot10^{-3}$	$1.58 \pm 4\cdot10^{-2}$	0.9992	4.2 ± 0.2
Phenanthrene					
	20	$-7\cdot10^{-3} \pm 3\cdot10^{-3}$	$1.27 \pm 2\cdot10^{-2}$	0.9995	—
	30	$4.1\cdot10^{-2} \pm 4\cdot10^{-3}$	$1.39 \pm 2\cdot10^{-2}$	0.9994	34 ± 3
	40	$0.147 \pm 7\cdot10^{-3}$	$1.48 \pm 4\cdot10^{-2}$	0.9992	8.8 ± 0.6
	45	$0.197 \pm 1\cdot10^{-3}$	$1.599 \pm 8\cdot10^{-3}$	0.9999	$8.11 \pm 8\cdot10^{-2}$
	50	$0.3049 \pm 4\cdot10^{-4}$	$1.486 \pm 3\cdot10^{-3}$	0.9999	$4.87 \pm 1\cdot10^{-2}$
Pyrene					
	20	$-2.3\cdot10^{-2} \pm 2\cdot10^{-3}$	$1.21 \pm 1\cdot10^{-2}$	0.9998	—
	30	$2.4\cdot10^{-2} \pm 4\cdot10^{-3}$	$1.23 \pm 2\cdot10^{-2}$	0.9994	[52 ± 9]
	40	$9.6\cdot10^{-2} \pm 6\cdot10^{-3}$	$1.33 \pm 3\cdot10^{-2}$	0.9993	14 ± 1
	45	$0.140 \pm 3\cdot10^{-3}$	$1.36 \pm 2\cdot10^{-2}$	0.9996	9.7 ± 0.3
	50	$0.18 \pm 1\cdot10^{-2}$	$1.56 \pm 6\cdot10^{-2}$	0.9985	8.7 ± 0.8
Fluoranthene					
	20	$-2.1\cdot10^{-2} \pm 2\cdot10^{-3}$	$1.23 \pm 1\cdot10^{-2}$	0.9998	—
	30	$2.7\cdot10^{-2} \pm 4\cdot10^{-3}$	$1.23 \pm 3\cdot10^{-2}$	0.9995	[45 ± 7]
	40	$6.9\cdot10^{-2} \pm 9\cdot10^{-3}$	$1.53 \pm 5\cdot10^{-2}$	0.9988	22 ± 2
	45	$0.145 \pm 3\cdot10^{-3}$	$1.42 \pm 2\cdot10^{-2}$	0.9995	9.8 ± 0.4
	50	$0.195 \pm 3\cdot10^{-3}$	$1.61 \pm 2\cdot10^{-2}$	0.9998	8.2 ± 0.2
Fluorene					
	20	$-5\cdot10^{-3} \pm 3\cdot10^{-3}$	$1.28 \pm 2\cdot10^{-2}$	0.9995	—
	30	$4.4\cdot10^{-2} \pm 4\cdot10^{-3}$	$1.47 \pm 3\cdot10^{-2}$	0.9992	[33 ± 4]
	40	$0.157 \pm 4\cdot10^{-3}$	$1.63 \pm 2\cdot10^{-2}$	0.9997	10.3 ± 0.4
	45	$0.231 \pm 5\cdot10^{-3}$	$1.63 \pm 3\cdot10^{-2}$	0.9993	7.1 ± 0.3
	50	$0.338 \pm 7\cdot10^{-3}$	$1.69 \pm 5\cdot10^{-2}$	0.9991	5.0 ± 0.2

Reagents

All reagents were of analytical grade. The surfactant (CTAB) and *n*-propanol (PrOH) from Merck (Darmstadt, Germany) and ethanol (EtOH) from Panreac (Barcelona, Spain) were used as received. The PAHs were acenaphthene, phenanthrene, pyrene, fluoranthene, and fluorene from Merck.

Procedure

The mobile phases used in this work were prepared with the organic modifier (PrOH or EtOH) and the cationic surfactant (CTAB) in an appropriate concentration in order to have percentages that allowed low retention times. These percentages were higher in the presence of EtOH than in presence of PrOH.

These mobile phases were prepared by weighing the necessary quantities of surfactant (at concentrations between 0.03 and 0.25M) and dissolving them in a mixture of PrOH or ethanol and Milli-Q (Millipore, Milford, MA) water, with the percentage of alcohol varying from 20 to 50% (v/v) with PrOH and from 50 to 75% (v/v) with EtOH. All the mobile phases were filtered through a 0.45-µm nylon membrane filter and placed in an ultrasound bath for 20 min for degasification before introduction into the chromatographic system.

The PAHs were prepared directly in the mobile phase, and these solutions were then injected into the chromatographic system. The detection was carried out by UV spectrophotometry at a wavelength of 254 nm. The variation of the retention times of the PAHs as a function of the concentration of CTAB in the mobile phase with different percentages of PrOH and EtOH (as organic modifiers) was determined. The retention factors were calculated as the average of 3 independent determinations for each solute.

Results and Discussion

Figures 1 and 2 show the experimental plots of 1/*k* versus [CTAB] in the presence of PrOH and EtOH, respectively. As can be seen, there exists a good linear correlation between the parameters in all cases. This behavior is the same found for many organic compounds in micellar media with low percentages of different alcohols or without them. Also, these linear plots of 1/*k* versus surfactant concentration have been found for some metal diethyldithiocarbamate complexes in CTAB and SDS in the presence of high percentages of *n*-propanol and ethanol (22,24).

When one observes a lineal correlation between 1/*k* and [surfactant], the Arunyanart and Cline-Love model (14) has been used on many occasions to determine (using HPLC) the binding constants of organic and inorganic

solutes to normal micelles and mixed micelles in the presence of certain organic modifiers in sufficiently small percentages. One reference (16) lists the conditions in which these constants have been determined for a great number of solutes.

According to this model, the determination of solute–aggregate binding constants can be carried out by the following equation:

$$\frac{1}{k} = \frac{K_2}{\phi[L_S]K_1} C_M + \frac{1}{\phi[L_S]K_1} \quad \text{Eq. 1}$$

where K_2 is the association or binding constant of a solute to micelles; ϕ is the phase ratio (V_S/V_M); V_S and V_M are the total stationary phase volume and the dead column volume, respectively; $[L_S]$ is the stationary phase concentration; K_1 is the binding constant for the solute between the stationary phase and the bulk solvent; and C_M is given by the total surfactant concentration minus the CMC. From the plot of experimental $1/k$ versus C_M, the binding constants can be obtained.

Equation 1 does not consider the presence of an alcohol in the mobile phase. With the objective of studying the influence of the modifier in the values of K_2, we have been developing an extension of the Arunyanart and Cline-Love model based on the interactions between the stationary phase and the alcohol. For some time, it has been known that the presence of an alcohol in the mobile phases used in MLC favors the progressive decrease in the sorbed surfactant in the stationary phase; the amount of surfactant desorbed is proportional to the alcohol concentration and increases as the hydrophobicity of the alcohol increases (25–28).

For this reason, it is possible to write the equilibrium model (14) with certain modifications in such a way as to consider the interaction of the solutes with the stationary phase modified by the surfactant (FES) and by the presence of growing quantities of the alcohol (FEOH). The complete equilibria are as follows:

$$S_W + \text{FES} \overset{K_1}{\rightleftharpoons} S_{ES}$$

$$S_W + \text{D} \overset{K_2}{\rightleftharpoons} S_M$$

$$S_W + \text{FEOH} \overset{K_3}{\rightleftharpoons} S_{EOH}$$

$$\text{ROH} + \text{FES} \overset{K_4}{\rightleftharpoons} \text{FEOH}$$

Table II. Regression Parameters and Binding Constant Values for the PAHs with CTAB at Different Percentages of EtOH Using Equation 3

PAH	CTAB–EtOH–water EtOH (%, v/v)	Intercept	Slope	r	K_2, M^{-1}
Acenaphthene					
	50	$3.4 \cdot 10^{-2} \pm 6 \cdot 10^{-3}$	$1.41 \pm 4 \cdot 10^{-2}$	0.9983	[42 ± 9]
	55	$8.5 \cdot 10^{-2} \pm 3 \cdot 10^{-3}$	$1.45 \pm 2 \cdot 10^{-2}$	0.9996	16.9 ± 0.8
	60	$0.144 \pm 4 \cdot 10^{-3}$	$1.59 \pm 2 \cdot 10^{-2}$	0.9996	11.0 ± 0.5
	70	$0.31 \pm 1 \cdot 10^{-2}$	$2.07 \pm 8 \cdot 10^{-2}$	0.9970	6.6 ± 0.5
	75	$0.517 \pm 6 \cdot 10^{-3}$	$1.90 \pm 4 \cdot 10^{-2}$	0.9993	3.6 ± 0.1
Phenanthrene					
	50	$1.9 \cdot 10^{-2} \pm 4 \cdot 10^{-3}$	$1.26 \pm 3 \cdot 10^{-2}$	0.9992	[63 ± 13]
	55	$5.8 \cdot 10^{-2} \pm 3 \cdot 10^{-3}$	$1.36 \pm 2 \cdot 10^{-2}$	0.9996	23 ± 2
	60	$0.105 \pm 5 \cdot 10^{-3}$	$1.52 \pm 3 \cdot 10^{-2}$	0.9992	14.4 ± 0.9
	70	$0.231 \pm 9 \cdot 10^{-3}$	$2.16 \pm 6 \cdot 10^{-2}$	0.9987	9.3 ± 0.6
	75	$0.444 \pm 6 \cdot 10^{-3}$	$1.82 \pm 4 \cdot 10^{-2}$	0.9995	4.1 ± 0.1
Pyrene					
	50	$3 \cdot 10^{-3} \pm 3 \cdot 10^{-3}$	$1.05 \pm 3 \cdot 10^{-2}$	0.9988	[273 ± 281]
	55	$2.7 \cdot 10^{-2} \pm 3 \cdot 10^{-3}$	$1.13 \pm 2 \cdot 10^{-2}$	0.9992	[41 ± 6]
	60	$5.8 \cdot 10^{-2} \pm 4 \cdot 10^{-3}$	$1.25 \pm 2 \cdot 10^{-2}$	0.9991	21 ± 2
	70	$0.141 \pm 2 \cdot 10^{-3}$	$1.77 \pm 1 \cdot 10^{-2}$	0.9999	12.6 ± 0.3
	75	$0.285 \pm 8 \cdot 10^{-3}$	$1.56 \pm 6 \cdot 10^{-2}$	0.9980	5.5 ± 0.4
Fluoranthene					
	50	$7 \cdot 10^{-3} \pm 5 \cdot 10^{-3}$	$1.09 \pm 3 \cdot 10^{-2}$	0.9984	[162 ± 119]
	55	$3.1 \cdot 10^{-2} \pm 4 \cdot 10^{-3}$	$1.19 \pm 2 \cdot 10^{-2}$	0.9992	[38 ± 5]
	60	$6.5 \cdot 10^{-2} \pm 4 \cdot 10^{-3}$	$1.32 \pm 3 \cdot 10^{-2}$	0.9992	20 ± 2
	70	$0.173 \pm 7 \cdot 10^{-3}$	$1.68 \pm 6 \cdot 10^{-2}$	0.9982	9.7 ± 0.7
	75	$0.319 \pm 7 \cdot 10^{-3}$	$1.65 \pm 4 \cdot 10^{-2}$	0.9990	5.2 ± 0.2
Fluorene					
	50	$1.3 \cdot 10^{-2} \pm 5 \cdot 10^{-3}$	$1.45 \pm 3 \cdot 10^{-2}$	0.9993	[113 ± 48]
	55	$7.3 \cdot 10^{-2} \pm 2 \cdot 10^{-2}$	$1.44 \pm 1 \cdot 10^{-2}$	0.9998	19.6 ± 0.8
	60	$0.127 \pm 3 \cdot 10^{-3}$	$1.59 \pm 2 \cdot 10^{-2}$	0.9997	12.5 ± 0.4
	70	$0.283 \pm 5 \cdot 10^{-3}$	$2.23 \pm 3 \cdot 10^{-2}$	0.9997	7.9 ± 0.2
	75	$0.495 \pm 7 \cdot 10^{-3}$	$1.93 \pm 4 \cdot 10^{-2}$	0.9994	3.9 ± 0.1

Table III. Adjusted Equations for $1/k$ in Function of CTAB and *n*–Propanol Obtained by Multiple Regression (Confidence Level, 95%) for the 5 PAHs*

PAH	$a \pm$ CI	$b \pm$ CI	$c \pm$ CI	% Agreement	Equation
Acenaphthene	–0.36 ± 0.04	1.6 ± 0.1	0.105 ± 0.007	98.3	$1/k$ = –0.36 + 1.6[CTAB] + 0.105[PrOH]
Phenanthrene	–0.28 ± 0.04	1.4 ± 0.1	0.084 ± 0.006	98.1	$1/k$ = –0.28 + 1.4[CTAB] + 0.084[PrOH]
Pyrene	–0.21 ± 0.02	1.30 ± 0.08	0.058 ± 0.004	98.7	$1/k$ = –0.21 + 1.30[CTAB] + 0.058[PrOH]
Fluoranthene	–0.22 ± 0.04	1.3 ± 0.1	0.065 ± 0.005	97.4	$1/k$ = –0.22 + 1.3[CTAB] + 0.065[PrOH]
Fluorene	–0.31 ± 0.04	1.5 ± 0.1	0.090 ± 0.007	98.1	$1/k$ = –0.31 + 1.5[CTAB] + 0.090[PrOH]

* $1/k = a + b$[CTAB] + c [PrOH]

where the subscripts *W* and *M* denote the bulk aqueous and surfactant phases, respectively, and the subscripts ES and EOH correspond to modified stationary phase by surfactant and alcohol, respectively. The equilibrium constants that involve the direct transfer of the solute (S_M) to the stationary phase (FES and FEOH) can be calculated by the combination of the previous equilibria. Substitution of the equilibrium constants in the expression giving the retention factor leads to

$$k = \frac{[\text{FES}]\phi(K_1 + K_3K_4[\text{ROH}])}{1 + K_2[\text{D}]} \qquad \text{Eq. 2}$$

that can be rewritten as

$$1/k = \{K_2/(\phi[\text{FES}]K_1 + \phi K_3K_4[\text{FES}][\text{ROH}])\}[\text{D}] + 1/(\phi[\text{FES}]K_1 + \phi K_3K_4[\text{FES}][\text{ROH}]) \qquad \text{Eq. 3}$$

where [D] and [ROH] are the total concentration of surfactant and alcohol, respectively. With these conditions, the system surfactant–alcohol–water corresponds to a bicontinuous structure of water and alcohol separated by the surfactant layer (29). For this reason, in the previous equations, we have considered the total concentrations of surfactant and of alcohol instead of the micellized concentrations.

In accordance with the results shown in the Figures 1 and 2 and applying Equation 3, it is possible to obtain the values of the solute–aggregate's binding constants as the ratio of slope/intercept.

Tables I and II show the values of the intercept and slope with errors, the regression coefficient, and the calculated binding constants with the estimation of error for the 5 PAHs studied as a function of the *n*-propanol and ethanol percentage. In these tables, those constant values with a relative error greater than 10% are noted in brackets. In certain cases with low percentages of PrOH (20%, v/v), it has not been possible to calculate the values of K_2 for any of the studied solutes, because the intercept values are negative. In MLC, it is accepted that negative intercepts are really zero as a consequence of the experimental error. As it is observed in Tables I and II, the values of the constants diminish when increasing the percentage of alcohol, the variation being more acute for low percentages until reaching practically constant values for high quantities of alcohol. The values obtained for high percentages are almost the same independent of the nature of the alcohol (except for pyrene and fluoranthene in presence of PrOH), which makes one think that the aggregates formed with the surfactant have similar characteristics; that is, they present a similar environment in the interaction with the solutes.

Several papers have been published describing the modelization of the retention in MLC with low percentages of an organic modifier, generally a short-chain alcohol (30–34). In these papers, the equations use ln *k* or the inverse, as well as combinations of these magnitudes (such as their product, their square, etc.), as the retention parameter in a function of the micellized surfactant and alcohol concentrations. In order to find an equation that adjusts the data for the 5 PAHs in the presence of the mobile phases employed (CTAB with PrOH and EtOH at high percentages), the equations that are given in the literature were tested, finding that the best adjustment by means of a multiple regression analysis completes the equation:

$$\frac{1}{k} = a + b[\text{D}] + c[\text{ROH}] \qquad \text{Eq. 4}$$

Tables III and IV show the adjustment of experimental $1/k$ to Equation 4 for *n*-propanol and ethanol, respectively; the values of different coefficients are presented with the confidence interval ($\alpha = 0.05$).

In Equation 4, it is possible to define a new coefficient a':

$$a' = a + c[\text{ROH}] \qquad \text{Eq. 5}$$

so that Equation 4 can be written as follows:

$$\frac{1}{k} = a' + b[\text{D}] \qquad \text{Eq. 6}$$

In this way, the parameters *a*, *b*, and *c* of Equation 4 can be associated with some of the terms that appear in Equation 3, and the binding constants can be evaluated by $K_2 = b/a'$ at any alcohol concentration.

Table V shows the values of the binding constants for the 5 PAHs obtained by means of the multiple regression analysis from the data in Tables III and IV. It is necessary to indicate that

Table IV. Adjusted Equations for $1/k$ as a Function of CTAB and Ethanol Obtained by Multiple Regression (Confidence Level 95%) for the 5 PAHs*

PAH	*a* ± CI	*b* ± CI	*c* ± CI	% Agreement	Equation
Acenaphthene	–1.3 ± 0.1	1.6 ± 0.2	0.13 ± 0.01	96.9	$1/k$ = –1.3 + 1.6[CTAB] + 0.13[EtOH]
Phenanthrene	–1.0 ± 0.1	1.6 ± 0.2	0.11 ± 0.01	96.4	$1/k$ = –1.0 + 1.6[CTAB] + 0.11[EtOH]
Pyrene	–0.66 ± 0.07	1.2 ± 0.1	0.074 ± 0.007	97.1	$1/k$ = –0.66 + 1.2[CTAB] + 0.074[EtOH]
Fluoranthene	–0.87 ± 0.09	1.5 ± 0.2	0.093 ± 0.008	97.3	$1/k$ = –0.87 + 1.5[CTAB] + 0.093[EtOH]
Fluorene	–1.2 ± 0.1	1.7 ± 0.2	0.13 ± 0.01	97.4	$1/k$ = –1.2 + 1.7 [CTAB] + 0.13[EtOH]

* $1/k = a + b$[CTAB] + c[EtOH]

Table V. Estimated Binding Constants for the PAHs with CTAB at Different Percentages of PrOH and EtOH by Multiple Regression

	K_2, M^{-1} (PrOH)				
PrOH (%, v/v)	Acenaphthene	Phenantrene	Pyrene	Fluorantrene	Fluorene
20	—	—	—	—	—
30	27.1	25.4	60.7	33.1	30.5
40	8.1	8.4	132	10.3	8.9
45	5.8	6.2	9.3	7.4	6.4
50	4.7	5.1	7.4	6.1	5.2
	K_2, M^{-1} (EtOH)				
EtOH (%, v/v)	Acenaphthene	Phenantrene	Pyrene	Fluorantrene	Fluorene
50	—	—	—	—	—
55	—	58.4	38.5	—	—
60	11.4	13.3	12.8	19.5	13.7
70	6.5	5.2	5.4	6.4	5.0
75	4.5	3.9	4.2	4.8	3.7

the associate error in the calculation of the constants is, in all the cases, greater than 10%. Consistent with data from Table V, it has not been possible to obtain the values of K_2 for low percentages of the modifier, because they are negative. However, for percentages such as 40–50% for PrOH and 60–75% for EtOH, the values of the association constants are similar to those obtained previously by means of application of the equation.

From the results shown in this work, it is important to highlight that by means of a multiple regression analysis, it is possible to predict the solute binding constant values for the system surfactant–alcohol–water at any alcohol percentage.

Conclusions

The CTAB–alcohol–water systems with high percentages of alcohol are very suitable mobile phases in HPLC, because they reduce the retention times (especially when the solutes have a strong hydrophobic character, as with polycyclic aromatic hydrocarbons).

For high percentages of alcohol, the relationship among the inverse of the retention factor and the surfactant concentration is lineal; that is, it presents the same behavior as that in the presence of direct micelles (absence of the modifier) and mixed micelles with low percentages of the alcohol. According to this behavior, it is possible to calculate the binding constants as a function of the alcohol type and concentration. From the K_2 values, one can consider that starting from high percentages of the modifier, the environment that it offers the formed aggregates is practically the same one that would agree with a bicontinuous structure in those conditions.

Finally, it is possible to obtain the estimated binding constants by a multiple regression analysis where it has been considered in the presence of an alcohol in the mobile phase. Data derived from the multiple regression allow the possibility of predicting the solute binding constants at any alcohol percentage.

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