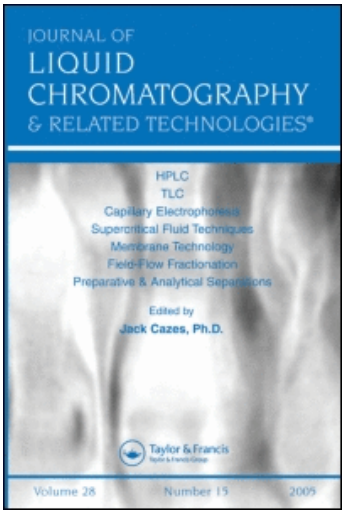


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Influence of Alcohol Organic Modifiers Upon the Association Constants and Retention Mechanism for Aromatic Compounds in Micellar Liquid Chromatography

M. Angeles García[a]; M. Luisa Marina[a]
[a] Departamento de Química Analitica Facultad de Ciencias, Universidad de Alcalá de Henares, (Madrid), Spain

To cite this Article García, M. Angeles and Marina, M. Luisa(1996) 'Influence of Alcohol Organic Modifiers Upon the Association Constants and Retention Mechanism for Aromatic Compounds in Micellar Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 19: 11, 1757 — 1776
To link to this Article: DOI: 10.1080/10826079608014003
URL: http://dx.doi.org/10.1080/10826079608014003

J. LIQ. CHROM. & REL. TECHNOL., 19(11), 1757–1776 (1996)

INFLUENCE OF ALCOHOL ORGANIC MODIFIERS UPON THE ASSOCIATION CONSTANTS AND RETENTION MECHANISM FOR AROMATIC COMPOUNDS IN MICELLAR LIQUID CHROMATOGRAPHY

Mª Angeles García, Mª Luisa Marina*

Departamento de Química Analítica
Facultad de Ciencias
Universidad de Alcalá de Henares
28871 Alcalá de Henares (Madrid), Spain.

ABSTRACT

Solute-micelle association constants and partition coefficients between stationary, aqueous, and micellar phases have been determined for a group of benzene derivatives and polycyclic aromatic hydrocarbons with sodium dodecyl sulphate and hexadecyltrimethylammonium bromide by Micellar Liquid Chromatography (MLC) with an octylsilica column using micellar mobile phases in absence and in the presence of organic modifiers (methanol, n-propanol, and n-butanol). The retention mechanism of these compounds in the chromatographic system has been studied by comparing experimental capacity factors and selectivity coefficients with those theoretically calculated assuming a direct transfer mechanism. When the surfactant concentration in the mobile phase is increased, a tendency to a change from a three-partition equilibrium mechanism to a direct transfer of solutes from micellar to stationary phase is observed for both surfactants. This change was favored when: (1) the hydrophobic character of the solute increased, (2) CTAB was used as surfactant, and (3) the

polarity of the aqueous mobile phase was increased. For highly hydrophobic compounds experiencing a direct transfer mechanism, selectivity coefficients for a pair of solutes can be predicted from the ratio of two stationary-micellarpartition coefficients.

INTRODUCTION

One application of Micellar Liquid Chromatography (MLC), has been the determination of solute-micelle association constants of great interest in chemistry and other disciplines.[1] This technique has been useful to determine these association constants for numerous organic compounds with different purely and modified micellar systems being salts and alcohols the most used modifiers.[2-12]

Solute-micelle association constants can be used to facilitate the systematic optimization in MLC.[10] In fact, the separation possibilities for a group of compounds can be forseen if their solute-micelle association constants are known. This aspect is very important, due to the unique selectivities obtained in MLC. Several articles have been published on the selectivity control in MLC through modification of the mobile phase composition. The effects, after addition of organic modifiers to micellar eluents, on solute retention, solvent strength, and selectivity have been studied.[13-18]

Gradient elution in MLC has been discussed recently.[19,20] Organic modifiers can improve separation selectivity but also increase efficiency, which is generally minor with micellar than with hydro-organic mobile phases, due to poor wetting of the stationary phase and restricted mass transfer.[21,22]

It was shown that the addition of a short- or medium-chain alcohol causes surfactant desorption from the stationary phase and improves efficiency.[23] Surfactant adsorption on the stationary phase not only has a great impact on the efficiency,[24,25] but also on the selectivity obtained in MLC. In fact, some studies have been recently made concerning the stationary phase effects on retention behavior and selectivity in MLC,[26,27] as well as on the effects of surfactant adsorption in MLC.[28]

In some works, solute-micelle association constants and partition coefficients have been used to better understand the differences in selectivity for various micellar systems,[27] or to study the retention mechanism in MLC and separation selectivity implications.[29]

Table 1

Experimental Conditions in which the Capacity Factors for the 23 Compounds have been Studied

Surfactant	Conc'n (M)	Alcohol	%	Solutes	C.M.C. (M) (ref. 34)
SDS	0.035; 0.050; 0.067 0.080; 0.100; 0.120	none	none	1-15	$8.00*10^{-3}$
SDS	0.035; 0.050; 0.067 0.080; 0.100; 0.120	methanol	10%	1-23	$8.00*10^{-3}$
SDS	0.050; 0.067; 0.080 0.100; 0.120; 0.140	n-propanol	3%	1-23	$8.00*10^{-3}$
SDS	0.050; 0.067; 0.080 0.100; 0.120; 0.140	n-propanol	5%	1-23	$7.00*10^{-3}$
SDS	0.035; 0.050; 0.067 0.080; 0.100; 0.120	n-propanol	10%	1-23	$3.50*10^{-3}$
SDS	0.050; 0.067; 0.080 0.100; 0.120; 0.140	n-butanol	3%	1-23	$5.00*10^{-3}$
SDS	0.050; 0.067; 0.080 0.100; 0.120; 0.140	n-butanol	5%	1-23	$3.50*10^{-3}$
SDS	0.050; 0.067; 0.080 0.100; 0.120; 0.140	n-butanol	10%	1-23	$1.25*10^{-2}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	none	none	1-15	$9.50*10^{-4}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	n-propanol	3%	1-23	$9.00*10^{-4}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	n-propanol	5%	1-23	$7.00*10^{-4}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	n-propanol	10%	1-23	$3.50*10^{-4}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	n-butanol	3%	1-23	$5.00*10^{-4}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	n-butanol	5%	1-23	$2.25*10^{-4}$
CTAB	0.050; 0.067; 0.080 0.100; 0.120	n-butanol	10%	1-23	$8.45*10^{-3}$

In this work, the retention mechanism and separation selectivity have been studied for a group of benzene derivatives and polycyclic aromatic hydrocarbons in an MLC system in which sodium dodecyl sulphate (SDS) and hexadecyltrimethylammoniumbromide (CTAB) were used as surfactants. Solute-micelle association constants and partition coefficients were previously determined and used to study the retention mechanism.

EXPERIMENTAL

Benzene derivatives and polycyclic aromatic hydrocarbons were (1) benzene, (2) benzyl 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.

Experimental chromatographic data used in this work were previously determined in ref. 30 in the case of fifteen benzene and naphthalene derivatives and in ref. 31 in the case of polycyclic aromatic hydrocarbons.

Table 1 groups the experimental conditions in which the capacity factors for the 23 compounds were determined. Column void volumes of 1.09 mL for SDS and 0.97 mL for CTAB were used for all capacity factor calculations. Capacity factor values employed were averages of at least three determinations. Relative errors in determining the association constants were ascertained from the statistical parameters of the least-squares fitting and from error propagation.[32]

For the determination of solute-micelle association constants the following equation[2] was used:

$$Vs / (Ve-Vm) = v (Pmw-1) C_m / Psw + 1 / Psw \qquad (1)$$

where Vs, Ve, and Vm are the stationary phase volume, the solute elution volume, and the void volume of the columm respectively; Pmw is the solute partition coefficient between the micellar and aqueous phases, Psw is the partition coefficient of the solute between the stationary and aqueous phases, v is the surfactant molar volume, and C_m is the micellized surfactant concentration in the mobile phase (C_m = C - c.m.c., C being the total surfactant concentration in solution and c.m.c. the critical micelle concentration of the surfactant).

Table 2

Association Constants (and relative errors in %) Calculated from Eq. (1) for the 23 Compounds Studied and SDS Mobile Phases in Absence and in the Presence of Alcohols

No	SDS	SDS 10% MeOH	SDS 3% n-PrOH	SDS 5% n-PrOH	SDS 10% n-PrOH	SDS 3% n-BuOH	SDS 5% n-BuOH	SDS 10% n-BuOH
1	**23.52**	**17.43**	**19.10**	**15.86**	**16.88**	**16.49**	**13.28**	**10.94**
	(5.34)	(5.04)	(1.28)	(3.07)	(1.99)	(5.44)	(10.33)	(6.06)
2	**11.84**	**12.97**	**8.16**	**7.24**	**6.51**	**5.53**	**3.44**	**4.77**
	(5.06)	(8.17)	(4.01)	(18.99)	(4.59)	4.44)	(14.19)	(3.34)
3	**12.28**	**13.55**	**7.58**	**3.63**	**4.62**	**4.63**	**2.15**	**4.21**
	(6.37)	(7.39)	(5.74)	(6.08)	(7.77)	(7.20)	(49.62)	4.10)
4	**76.12**	**45.11**	**54.86**	**54.71**	**43.86**	**44.20**	**38.78**	**16.53**
	(14.00)	(4.94)	(3.86)	(12.99)	(8.94)	(10.61)	(4.93)	(7.82)
5	**20.39**	**20.21**	**14.16**	**11.07**	**10.59**	**8.99**	**6.41**	**7.23**
	(4.23)	(7.56)	(1.55)	(3.18)	(4.55)	(8.86)	(4.43)	(4.74)
6	**25.97**	**21.97**	**18.23**	**15.85**	**13.86**	**12.64**	**7.30**	**7.70**
	(6.29)	(3.18)	(2.59)	(8.57)	(4.07)	(6.64)	(6.66)	(6.66)
7	**10.47**	**12.14**	**9.41**	**7.61**	**8.83**	**6.60**	**5.94**	**6.43**
	(7.51)	(6.36)	(3.45)	(18.35)	(3.58)	(7.64)	(2.98)	(3.74)
8	**20.78**	**22.86**	**14.64**	**11.97**	**11.40**	**19.12**	**4.78**	**6.84**
	(3.17)	(8.71)	(2.31)	(12.50)	(4.42)	(9.22)	(2.30)	(1.80)
9	**105.36**	**59.97**	**72.48**	**62.05**	**55.51**	**50.60**	**28.41**	**17.54**
	(17.64)	(5.62)	(5.50)	(6.46)	(9.90)	(9.70)	(6.29)	(8.57)
10	**30.73**	**33.96**	**21.14**	**14.42**	**14.47**	**12.40**	**6.64**	**7.53**
	(4.99)	(6.71)	(3.56)	(9.54)	(4.69)	(10.18)	(2.33)	(4.38)
11	**57.91**	**66.86**	**40.21**	**24.65**	**32.05**	**24.73**	**14.40**	**12.93**
	(13.57)	(3.40)	(2.82)	(17.99)	(5.03)	(10.11)	(13.85)	(6.75)
12	**217.10**	**465.93**	**226.71**	**207.22**	**117.75**	**96.87**	**24.04**	**21.23**
	(79.77)	(38.99)	(12.47)	(23.54)	(13.73)	(16.27)	(9.23)	(9.62)
13	**189.54**	**123.98**	**79.79**	**51.98**	**62.09**	**44.74**	**25.28**	**17.60**
	(47.10)	(8.50)	(5.24)	(25.10)	(11.53)	(11.28)	(14.54)	(11.56)
14	**167.97**	**146.34**	**73.23**	**60.64**	**55.41**	**41.79**	**29.29**	**16.34**
	(40.11)	(20.01)	(5.40)	(15.07)	(10.67)	(11.74)	(13.98)	(9.37)
15	**248.00**	--	**62.19**	**44.57**	**35.26**	**31.95**	**18.38**	**12.90**
	(74.65)		(3.73)	(19.74)	(7.32)	(8.29)	(8.63)	(12.44)
16	--	--	--	**414.63**	--	**196.86**	**67.62**	**22.95**
				(97.98)		(47.97)	(13.72)	(13.97)
17	--	--	**63.33**	**161.60**	--	**173.98**	**75.23**	**22.15**
			(35.60)	(43.24)		(40.26)	(25.23)	(13.34)
18	--	--	--	--	--	**458.01**	**93.25**	**26.37**
						(106.54)	(17.70)	(14.210
19	--	--	**1326.44**	**529.75**	--	**179.27**	**61.76**	**22.34**
			(320.53)	(62.78)		(34.25)	(23.63)	(11.91)
20	--	--	--	**376.37**	--	**229.17**	**77.94**	**25.02**
				(122.40)		(41.68)	(17.75)	(13.02)
21	--	--	**496.08**	**195.90**	--	**129.28**	**56.36**	**22.06**
			(26.44)	(21.49)		(21.14)	(16.26)	(11.86)
22	--	--	**380.90**	**190.14**	--	**249.30**	**71.40**	**23.07**
			(100.28)	(42.55)		(46.33)	(13.70)	(11.39)
23	--	--	--	**330.99**	--	**229.37**	**91.76**	**26.01**
				(70.14)		(38.51)	(24.05)	(11.27)

A plot of Vs / (Ve-Vm) versus C_m should be linear and the solute-micelle binding constant per surfactant monomer, K_2 = v(Pmw -1) (33) can be calculated from the slope:intercept ratio of the straight line. Psw can be obtained from the intercept and, if the surfactant molar volume v is known, Pmw can also be calculated. As molar volumes for SDS and CTAB, values of 0.246 and 0.364 L mol^{-1} have been taken respectively.[1]

RESULTS AND DISCUSSION

Solute-Micelle Association Constants

Capacity factors for the twenty three solutes studied were determined for eighty three different mobile phases corresponding to the experimental conditions detailed at Table 1. Capacity factors for the polycyclic aromatic hydrocarbons could not be measured in absence of alcohols due to the high retention that these compounds experienced in the stationary phase in these conditions. However, when an alcohol was added to the micellar mobile phase, the capacity factors for the twenty three compounds studied were measured.

From the variation of the volume term in Eq. (1) as a function of the micellized surfactant concentration in the mobile phase (total surfactant concentration minus c.m.c. value given at Table 1) it was possible to determine the values of K_2, Pmw, and Psw from the parameters of the straight line obtained for this variation except for those cases where a negative intercept was obtained. Psm was calculated as the ratio between Psw and Pmw.

Tables 2 and 3 group the values of the association constants with SDS (Table 2) and CTAB (Table 3) for those solutes for which a positive intercept is obtained (Eq. (1)). These Tables give the values for the association constants and the relative errors obtained in absence of additives, in the presence of alcohols.

The variation of the volume term with C_m (Figures not shown) allows to obtain a straight line with a good correlation coefficient (in all cases it was higher than 0.99). Negative intercepts have already been obtained by other authors[9,35] and attributed to the error in the determination of K_2 for very hydrophobic compounds experiencing a high retention in the system and for which intercepts close to zero are obtained. Tables 4 and 5 group the values obtained for Psw for the solutes studied when SDS (Table 4) and CTAB (Table 5) mobile phases are used in absence of additives and in the presence of alcohols.

Table 3

Association Constants (and relative errors in %) Calculated from Eq. (1) for the 23 Compounds Studied and CTAB Mobile Phases in Absence and in the Presence of Alcohols

No	CTAB	CTAB 3% n-PrOH	CTAB 5% n-PrOH	CTAB 10% n-PrOH	CTAB 3% n-BuOH	CTAB 5% n-BuOH	CTAB 10% n-BuOH
1	**47.20**	**47.29**	**45.64**	**37.39**	**36.91**	**23.11**	**17.34**
	(2.10)	(2.07)	(7.20)	(3.23)	(4.36)	(4.37)	(1.350
2	**17.31**	**14.18**	**11.55**	**9.00**	**9.18**	**7.77**	**5.17**
	(3.08)	(4.60)	(3.55)	(2.82)	(7.92)	(1.44)	(8.40)
3	**12.43**	**10.05**	**7.66**	**6.95**	**8.23**	**5.53**	**3.04**
	(5.28)	(6.62)	(4.80)	(3.20)	(6.47)	(2.09)	(3.34)
4	**203.88**	**281.18**	**203.33**	**126.78**	**104.09**	**45.49**	**25.29**
	(9.41)	(30.89)	(18.20)	(8.75)	(15.46)	(5.39)	(4.07)
5	**27.17**	**24.70**	**19.19**	**16.85**	**20.72**	**8.83**	**9.00**
	(4.20)	(4.93)	(7.18)	(1.41)	(5.86)	(1.80)	(3.84)
6	**54.71**	**43.19**	**37.03**	**30.43**	**29.41**	**15.84**	**12.39**
	(3.48)	(2.90)	(12.47)	(2.34)	(3.18)	(3.15)	(2.97)
7	**79.53**	**60.48**	**37.68**	**26.78**	**22.88**	**8.91**	**11.63**
	(13.27)	(2.00)	(19.55)	(6.18)	(3.63)	(6.98)	(1.340
8	**30.02**	**23.36**	**19.18**	**15.09**	**16.75**	**9.01**	**7.97**
	(3.13)	(6.36)	(5.41)	(3.04)	(2.85)	(4.30)	(3.27)
9	**547.93**	**1434.12**	**431.94**	**234.09**	**132.94**	**54.45**	**28.16**
	(11.39)	(128.18)	(36.51)	(16.49)	(14.89)	(6.28)	(3.89)
10	**51.14**	**43.28**	**31.68**	**24.45**	**27.37**	**13.07**	**9.53**
	(5.48)	(3.30)	(12.70)	(3.42)	(7.86)	(5.43)	(3.60)
11	--	--	**225.94**	**161.01**	**69.39**	**24.06**	**25.77**
			(60.23)	(5.98)	(1.56)	(9.60)	(4.02)
12	--	--	--	--	**256.52**	**70.06**	**39.59**
					(23.83)	(13.46)	(6.71)
13	--	--	--	**779.81**	**120.05**	**33.20**	**62.06**
				(5.64)	(7.91)	(8.12)	915.54)
14	--	--	--	**597.85**	**104.54**	**30.62**	**45.33**
				(26.92)	(9.38)	(13.14)	(6.36)
15	--	--	**663.12**	**195.11**	**88.59**	**37.16**	**26.25**
			(89.31)	914.83)	(6.49)	(3.50)	(0.49)
16	--	--	--	--	**1173.87**	**98.35**	**67.40**
					(68.27)	(6.76)	(15.97)
17	--	--	--	--	**663.55**	**103.80**	**59.83**
					(39.46)	(4.10)	(13.98)
18	--	--	--	--	--	**100.24**	**69.62**
						(11.11)	(15.50)
19	--	--	--	--	**838.22**	**98.59**	**48.27**
					(82.53)	(13.58)	(9.88)
20	--	--	--	--	**970.01**	**98.39**	**71.42**
					(139.04)	(21.72)	(15.01)
21	--	--	--	--	**384.98**	**79.12**	**46.86**
					(37.91)	(16.88)	(8.87)
22	--	--	--	--	**828.42**	**59.20**	**43.31**
					(101.97)	(19.36)	(7.15)
23	--	--	--	--	**841.86**	**89.42**	**60.96**
					(63.88)	(18.13)	(11.21)

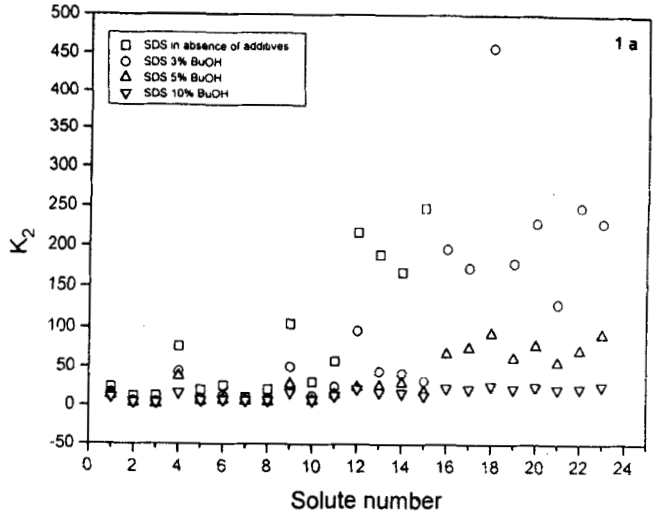
From Tables 2 and 3, the influence of the surfactant nature, and the nature and concentration of the alcohol added to the mobile phase on the association constants can be studied.

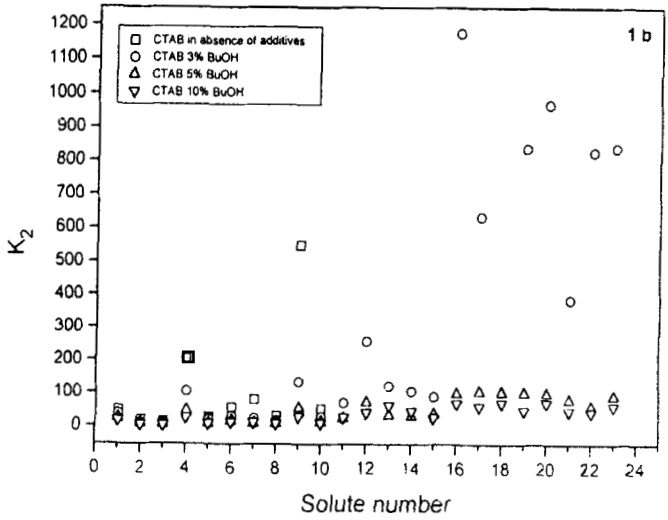
In regards to the surfactant nature, the association constants of the solutes are generally higher with CTAB than with SDS. This is due to the electrostatic interaction between the positively charged CTAB micelles and the unlocated charge of the solutes aromatic rings.

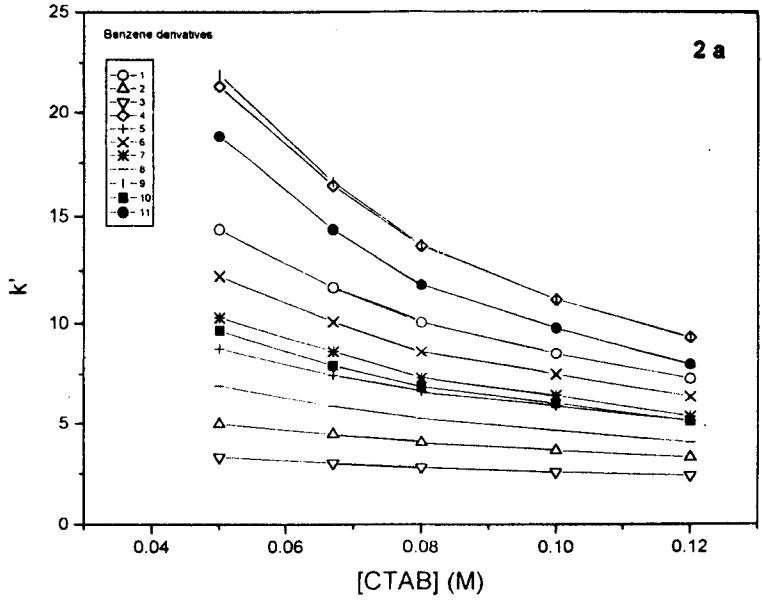
The addition of an alcohol generally decreases the solute-micelle association constant regardless of the surfactant nature. In fact, the presence of an alcohol in the mobile phase decreases the adsorption of the surfactant in the stationary phase[23] and the polarity of the aqueous nonmicellar phase, allowing to increase the affinity of the solute for the aqueous nonmicellar phase and decreasing its association with the micelle. This result is illustrated in Figure 1 which shows the association constants for the fifteen benzene and naphthalene derivatives with SDS (Figure 1a) and CTAB (Figure 1b) with and without butanol and for the polycyclic aromatic hydrocarbons in the presence of butanol.

For the compounds for which the comparison is possible, that is, for the fifteen benzene and naphthalene derivatives, it can be observed that the addition of butanol to the mobile phase decreases the solutes association constants with CTAB as well as with SDS. The same result is observed when adding n-propanol but in this case (as can be observed in Tables 2 and 3) there are more instances where the intercept of the straight line obtained for the variation of the retention term as a function of the micellized surfactant concentration is negative. The decrease in the association constant observed due to the addition of an alcohol to the mobile phase is higher for most hydrophobic compounds. Figures 1a and 1b also allow to study the influence of the alcohol percentage on the association constant values. These constants decrease when the alcohol percentage in the mobile phase increases. This also occurs with n-propanol. Such effect is also more obvious for compounds of a higher hydrophobic character. This makes it possible to ascertain solute-micelle association constants for some compounds for which such determination would be not possible in other conditions (in absence of alcohol or in the presence of small amounts of alcohol). The only instance in which this effect is not well appreciated is for SDS-n-propanol but this could be because the errors in the association constants for polycyclic aromatic hydrocarbons are the highest in this case.

Figure 1 (right). Solute-micelle association constants for the compounds studied with SDS and CTAB in absence of additives and in presence of 3%, 5%, and 10% n-butanol. a) SDS. b) CTAB.







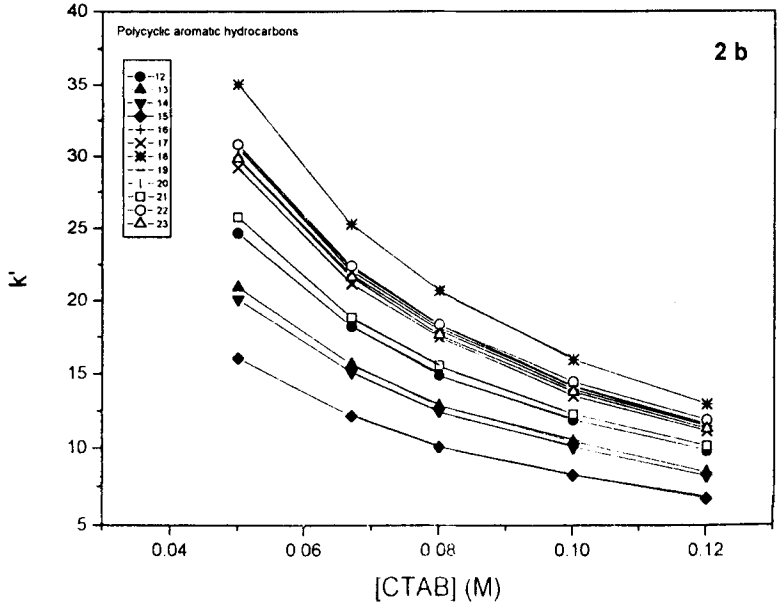


Table 4

Solute Partition Coefficients Between the Stationary and Aqueous Phases, Psw, Calculated from Eq. (1) for SDS Mobile Phases in Absence and in the Presence of Alcohols

No	SDS	SDS 10% MeOH	SDS 3% n-PrOH	SDS 5% n-PrOH	SDS 10% n-PrOH	SDS 3% n-BuOH	SDS 5% n-BuOH	SDS 10% n-BuOH
1	51.64	31.65	34.49	34.15	26.10	26.78	24.90	12.45
2	12.09	7.98	7.06	5.55	3.99	4.42	3.56	2.32
3	9.96	6.55	5.31	3.52	2.45	3.09	2.32	1.46
4	198.45	95.35	112.44	124.01	75.52	78.32	71.09	20.03
5	30.56	21.09	18.40	14.60	10.51	11.31	89.46	6.07
6	46.55	29.55	27.42	24.38	16.77	17.48	13.81	8.18
7	12.03	8.29	7.97	7.05	5.35	5.39	5.29	3.39
8	24.86	17.02	14.19	11.07	7.63	8.11	5.86	3.66
9	289.03	127.60	149.98	144.05	93.03	91.42	60.03	21.38
10	42.22	31.23	24.70	17.93	12.26	13.03	9.29	5.36
11	90.23	68.98	50.55	33.06	28.50	27.55	18.94	9.74
12	715.48	1076.50	538.08	528.12	221.81	195.53	66.04	27.64
13	349.77	161.12	109.93	74.93	61.00	53.07	34.52	14.09
14	311.44	180.87	98.35	79.02	51.19	46.73	34.89	11.88
15	434.91	--	88.05	61.86	34.51	38.20	24.08	9.64
16	--	--	--	1606.20	--	552.14	197.03	34.97
17	--	--	281.56	591.54	--	445.23	202.99	32.71
18	--	--	--	--	--	1389.81	293.51	39.93
19	--	--	4086.15	1728.89	--	438.16	167.66	32.11
20	--	--	--	1453.78	--	637.41	225.59	36.93
21	--	--	1304.58	560.53	--	282.94	137.43	29.75
22	--	--	1118.70	637.84	--	582.80	183.26	32.65
23	--	--	--	1183.80	--	591.20	246.12	36.86

As could be expected, solute-micelle association constants decrease when the carbon atom number of the alcohol chain is increased due to the fact that an increase in the chain length causes a polarity decrease. This effect was observed for CTAB and SDS with n-propanol and n-butanol when comparing the three percentages studied and for SDS when comparing methanol, n-propanol, and n-butanol at 10 %.

Retention Mechanism and Separation Selectivity

Figure 2 shows the variation of the capacity factor as a function of the surfactant concentration for the benzene derivatives (Figure 2a) and for the polycyclic aromatic hydrocarbons (Figure 2b) with a CTAB - 5% n-propanol

Figure 2 (left). Variation of the experimental capacity factor of the compounds studied as a function of the total CTAB concentration in a mobile phase modified with 5% n-propanol. a) benzene derivatives. b) polycyclic aromatic hydrocarbons.

mobile phase. Similar results were obtained with all mobile phases, showing that separation selectivity generally increased when surfactant concentration was decreased in the mobile phase, this being true for both CTAB and SDS. Some authors[27] have explained this effect by stating that selectivity is primarily due to solute-stationary phase interactions, which are more favorable at lower surfactant concentrations. According to a previous paper,[36] SDS generally enhances separation selectivity with respect to CTAB and also the addition of a medium-chain alcohol, such as n-propanol or n-butanol, at medium percentages (3 or 5%) positively influences selectivity. Separation selectivity can be theoretically calculated for a group of compounds if a direct transfer mechanism of the solute between the stationary and micellar phases is assumed.[29] In fact, Borgerding et al.[35] have proposed a limit theory for those compounds whose affinity toward the micellar phase is large enough to experience a direct transfer from this phase to the stationary phase. These solutes only undergo a partition between the micellar pseudophase and the stationary phase since the solute amount in the aqueous phase is almost negligible. The capacity factor for these compounds can be expressed as:

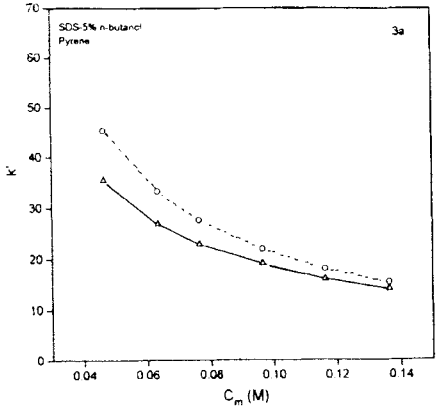
$$k' = Vs\ Psm / Vm\ v\ C_m \qquad (2)$$

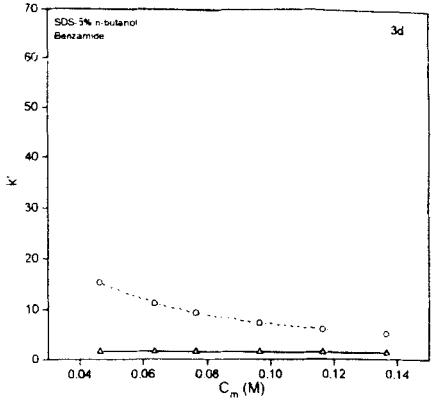
If this direct transfer mechanism is assumed for the solutes, and the surfactant concentration in the mobile phase is increased, the selectivity coefficient (I) for two compounds can be calculated from the distribution coefficients of the two solutes between the stationary and micellar phases:[29]

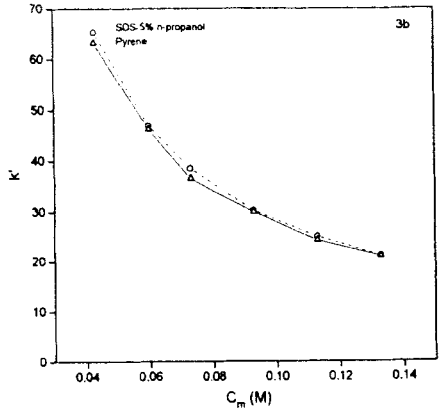
$$I = Psm_2 / Psm_1 \qquad (3)$$

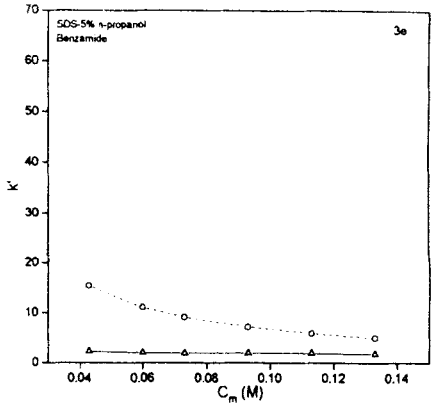
This equation shows that if this mechanism takes place, the separation selectivity will be constant and will not vary with the surfactant concentration in the mobile phase. Eqs. (2) and (3) have been used to calculate the capacity factor and selectivity coefficient for the compounds studied herein under different conditions. This has been made by using the partition coefficient, Psm, for each solute previously calculated (Psm = Psw / Pmw; Psw values are given in Tables 4 and 5; Pmw values can be calculated from K_2 values given in Tables 2 and 3 from the equation $K_2 = v\ (Pmw - 1)$ (33)). The agreement between the theoretical and experimental capacity factors and selectivity coefficients would indicate the experimental conditions in which a direct transfer mechanism for our compounds occurs.

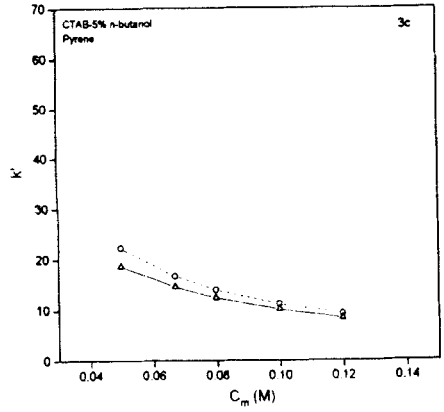
Figure 3 (right). Variation of experimental and theoretical capacity factors for pyrene and benzamide as a function of the micellized surfactant concentration in mobile phase. a) pyrene in SDS-5% n-butanol. b) pyrene in SDS-5% n-propanol. c) pyrene in CTAB-5% n-butanol. d) benzamide in SDS-5% n-butanol. e) benzamide in SDS-5% n-propanol. f) benzamide in CTAB-5% n-butanol.

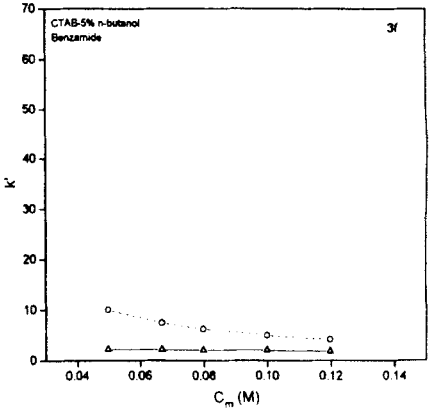




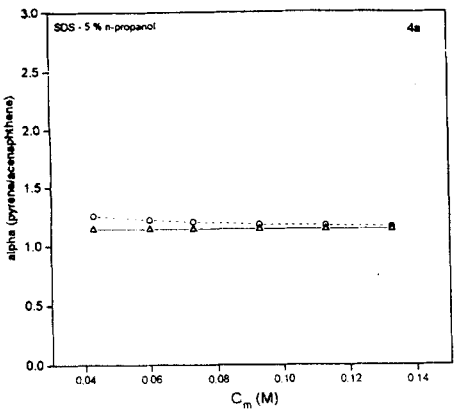


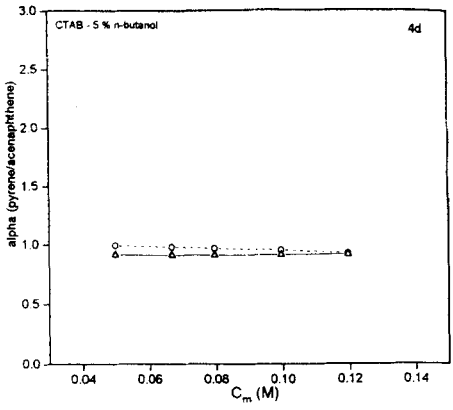


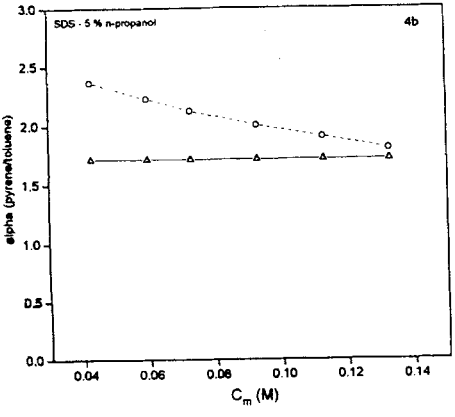


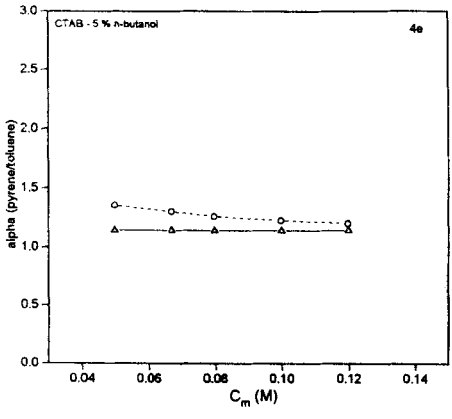


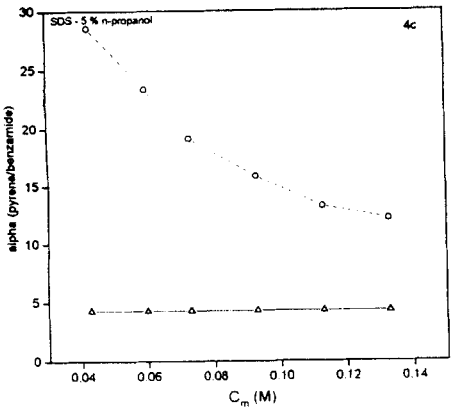
theoretical experimental

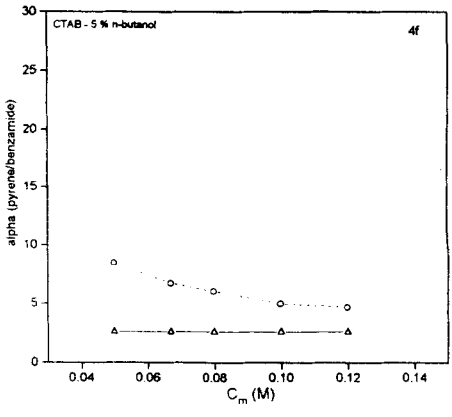












○ experimental alpha △ theoretical alpha

Figure 3 shows the variation of the theoretical and experimental capacity factor as a function of the micellized surfactant concentration for a very hydrophobic compound (pyrene) with a logarithm of the octanol-water partition coefficient, log P_{ow} = 4.88 and, for the lesser hydrophobic compound (benzamide) with log P_{ow} = 0.64. For each compound, the capacity factors are given for three mobile phases: SDS-5% n-butanol, SDS-5% n-propanol, and CTAB 5% n-butanol. This figure shows that the theoretical capacity factor is generally higher than the experimental one because the theoretical capacity factor is calculated from the partition coefficient between the stationary and the micellar phases, therefore neglecting the amount of solute in the aqueous nonmicellar phase. However, this partition between the aqueous and micellar phases is reflected in the experimental capacity factor. The difference between the theoretical and experimental capacity factors decreases when the surfactant concentration in solution for both solutes increases, allowing to obtain practically the same value for the capacity factor.

Consequently, it is possible to think that the three-partition equilibria mechanism changes to a direct transfer mechanism when the surfactant concentration is increased. The difference between the theoretical and experimental capacity factors does not depend only on the surfactant concentration, but also on the nature of the solute and the mobile phase. In fact, for the same mobile phase, this difference is less significant for pyrene than for benzamide, showing a lesser affinity of a highly hydrophobic compound for the aqueous nonmicellar phase and its higher affinity for the stationary phase. In regards to the nature of the mobile phase, when the polarity of the mobile phase is decreased by adding an alcohol, the affinity of a hydrophobic solute for the aqueous nonmicellar phase increases, subsequently increasing the difference between the theoretical and experimental capacity factors. This occurs in the case of pyrene when adding butanol to the mobile phase. The difference between the theoretical and experimental capacity factors for pyrene is minimum when using n-propanol in the mobile phase which has a higher polarity than n-butanol and also when using CTAB as surfactant. For a low hydrophobic compound such as benzamide, the nature of the alcohol does not influence, appreciably, the difference between the capacity factors, since it has a certain affinity for the aqueous nonmicellar mobile phase. However, this difference is minor for CTAB than for SDS since the higher association constant with CTAB decreases its affinity for the aqueous nonmicellar mobile phase.

Figure 4 (left). Variation of the experimental and theoretical selectivity coefficients (I) as a function of the micellized surfactant concentration for three pairs of solutes: pyrene-acenaphthene, pyrene-toluene and pyrene-benzamide. a), b), and c) SDS-5% n-propanol. d), e), and f) CTAB-5% n-butanol.

Table 5

Solute Partition Coefficients between the Stationary and Aqueous Phases, Psw, Calculated from Eq. (1) for CTAB Mobile Phases in Absence and in the Presence of Alcohols

No	CTAB	CTAB 3% n-PrOH	CTAB 5% n-PrOH	CTAB 10% n-PrOH	CTAB 3% n-BuOH	CTAB 5% n-BuOH	CTAB 10% n-BuOH
1	58.35	52.56	49.92	36.50	33.00	22.13	12.35
2	16.05	10.72	8.33	5.28	6.25	4.71	2.65
3	10.02	6.58	4.86	3.20	4.56	3.14	1.68
4	278.14	343.18	251.10	137.36	101.23	47.52	19.46
5	29.87	23.00	18.03	13.25	14.44	8.22	5.71
6	63.29	43.66	36.84	25.49	23.56	14.28	8.35
7	88.56	52.63	31.68	16.25	17.68	8.42	5.12
8	28.34	18.29	14.24	9.05	10.65	6.46	3.94
9	735.70	1720.23	520.33	243.06	129.67	55.75	21.30
10	51.71	36.35	26.17	16.42	18.09	9.80	5.40
11	--	--	242.97	124.14	61.94	23.15	12.84
12	--	--	--	--	257.80	74.46	29.01
13	--	--	--	597.84	112.14	32.04	27.54
14	--	--	--	443.43	97.70	29.69	20.57
15	--	--	580.49	130.06	69.37	28.74	12.80
16	--	--	--	--	1376.69	116.35	50.46
17	--	--	--	--	711.02	117.06	44.07
18	--	--	--	--	--	125.58	52.73
19	--	--	--	--	942.27	114.14	37.16
20	--	--	--	--	1121.99	114.75	52.02
21	--	--	--	--	395.56	85.19	33.96
22	--	--	--	--	944.61	77.18	34.87
23	--	--	--	--	944.86	103.69	44.91

From the results obtained on the capacity factors, it can be stated that a direct transfer mechanism occurs for solutes in MLC when increasing the hydrophobicity of the solute, the surfactant concentration, and when using CTAB instead of SDS and the polarity of the alcohol in the mobile phase increases. These results would explain the fact that most of the negative intercepts or the highest errors in the determination of the association constants for the highest hydrophobic compounds are obtained when CTAB is the surfactant or n-propanol is the organic modifier in mobile phase (see Tables 2 and 3).

In fact, when a direct transfer mechanism occurs, an intercept close to zero should be obtained (Eq. 2) for the variation of the inverse of the capacity factor as a function of C_m. Consequently, the calculation of the association constant in these conditions would not be adequate due to the high error associated to this calculation.

In those cases where the theoretical and experimental capacity factors are similar for two solutes, that is, when a direct transfer mechanism occurs, the selectivity coefficient can be forseen from the ratio between the solutes partition coefficients between the stationary and micellar phases (Eq. 3). Figure 4 shows the variation of the theoretical and experimental selectivity coefficient as a function of the surfactant concentration in a SDS-5% n-propanol (Figures 4a, 4b, and 4c) and in a CTAB-5% n-butanol mobile phase (Figures 4d, 4e, and 4f) for three pairs of solutes: pyrene- acenaphthene which are both very hydrophobic and for which a direct transfer mechanism can be assumed for any surfactant concentration in these mobile phases, pyrene-toluene in which only for pyrene a direct transfer mechanism can be assumed for all surfactant concentrations, and pyrene-benzamide in which benzamide does not experience a direct transfer mechanism except at very high surfactant concentrations. Figure 4 shows that, when both solutes experience a direct transfer mechanism, the experimental and theoretical selectivity coefficients are very similar for all surfactant concentrations in solution, being therefore possible to predict the selectivity coefficient from the partition coefficients Psm for the two solutes. When one of the two solutes does not experience a direct transfer mechanism, the theoretical and experimental selectivity are different and this difference decreases under the same conditions in which the direct transfer mechanism is favored, that is, by increasing the hydrophobicity of the solute, the surfactant concentration, the polarity of the alcohol in mobile phase, and also using CTAB as surfactant.

CONCLUSIONS

From the results obtained in this work for the twenty three benzene derivatives and polycyclic aromatic hydrocarbons studied, it can be concluded that, when the surfactant concentration in mobile phase is increased, there is a progressive tendency to change from a three-partition equilibria mechanism to a direct transfer of solutes from micelles to the stationary phase. This tendency is higher when increasing solute-micelle association constants, that is, when the hydrophobicity of the solute is increased, CTAB is used as surfactant, and the length of the alcohol chain in the mobile phase decreases. Consequently, the separation selectivity for a pair of solutes also shows a tendency to match a limit value when the surfactant concentration in solution is increased. This limit value is close to the ratio of stationary-micellar partition coefficients of two solutes and does not depend on the surfactant concentration in solution.

For very hydrophobic compounds, for which a direct transfer mechanism is observed, regardless of the surfactant concentration in the mobile phase, the selectivity coefficient can be estimated from the ratio of two stationary-micellar partition coefficients.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by DGICYT (Spain) for this work (project reference PS90-0026). We also thank C. Marina for linguistic assistance.

REFERENCES

1. W. L. Hinze, D. W. Armstrong, Eds., **Ordered Media in Chemical Separations**, ACS Symposium Series, Vol. 342. Washington, 1987.

2. D. W. Armstrong, F. Nome, Anal. Chem., **53**, 1662 (1981).

3. M. Arunyanart, L. Y. Cline Love, Anal. Chem., **56**, 1557 (1984).

4. A. Berthod, I. Girard, C. Gonnet, Anal. Chem., **58**, 1359 (1986).

5. M. L. Marina, S. Vera, A. R. Rodríguez, Chromatographia, **28**, 379 (1989).

6. P. Yarmchuk, R. Weinberger, R. F. Hirsch, L. J. Cline Love, Anal. Chem., **54**, 2233 (1982).

7. E. Pramauro, E. Pelizzetti, Anal. Chim. Acta, **154**, 153 (1983).

8. E. Pramauro, G. Saini, E. Pelizzetti, Anal. Chim. Acta, **166**, 166 (1984).

9. M. G. Khaledi, E. Peuler, J. Ngeh-Ngwainbi, Anal. Chem., **59**, 2738 (1987).

10. J. P. Foley, Anal. Chim. Acta, **231**, 237 (1990).

11. M. A. García, S. Vera, M. L. Marina, Chromatographia, **32**, 148 (1991).

12. M. L. Marina, M. A. García, J. Liq. Chromatogr., **17**, 957 (1994).

13. M. G. Khaledi, Anal. Chem., **60**, 876 (1988).

14. M. G. Khaledi, J. K. Strasters, A. H. Rodgers, E. D. Breyer, Anal. Chem., **62**, 130 (1990).

15. J. K. Strasters, E. D. Breyer, A. H. Rodgers, M. G. Khaledi, J. Chromatogr., **511**, 17 (1990).

16. J. K. Strasters, S. T. Kim, M. G. Khaledi, J. Chromatogr., **586**, 221 (1991).

17. A. S. Kord, M. G. Khaledi, Anal. Chem., **64**, 1894 (1992).

18. A. S. Kord, M. G. Khaledi, Anal. Chem., **64**, 1901 (1992).

19. L. S. Madamba-Tan, J. K. Strasters, M. G. Khaledi, J. Chromatogr. A, **683**, 321 (1994).

20. L. S. Madamba-Tan, J. K. Strasters, M. G. Khaledi, J. Chromatogr. A, **683**, 335 (1994).

21. J. G. Dorsey, M. T. De Echegaray, J. S. Landy, Anal. Chem., **55**, 924 (1983).

22. P. Yarmchuck, R. Weinberger, R. F. Hirsch, L. J. Cline Love, J. Chromatogr., **283**, 47 (1984).

23. A. Berthod, A. Roussel, J. Chromatogr., **449**, 349 (1988).

24. M. F. Borgerding, W. L. Hinze, Anal. Chem., **57**, 2183 (1985).

25. R. Bailey, R. M. Cassidy, Anal. Chem., **64**, 2277 (1992).

26. S. Yang, M. G. Khaledi, Anal. Chim. Acta, **294**, 135 (1994).

27. B. K. Lavine, S. Hendayana, J. Tetreault, Anal. Chem., **66**, 3458 (1994).

28. B. K. Lavine, W. T. Cooper, Y. He, S. Hendayana, J. H. Han, J. Tetreault, J. Colloid and Inter. Sci., **165**, 497 (1994).

29. J. M. Saz , M. L. Marina, J. Chromatogr. A, **687**, 1 (1994).

30. M. A. García, M. L. Marina, J. Chromatogr. A, **687**, 233 (1994).

31. M. A. García, O. Jiménez, M. L. Marina, J. Chromatogr. A, **675**, 1 (1994)

32. J. C. Miller, J. N. Miller, **Statistics for Analytical Chemistry**, John Wiley, New York, 1988.

33. I. V. Berezin, K. Martiner, A. K. Yatsimirskii, Russ. Chem. Rev., Engl. Transl., **42**, 787 (1973).

34. I. Benito, M. A. García, C. Monge, J. M. Saz, M. L. Marina, submitted.

35. M. F. Borgerding, F. H. Quina, W. L. Hinze, J. Bowermester, H. M. McNair, Anal. Chem., **60**, 2520 (1988).

36. M. A. García, S. Vera, M. Bombín, M. L. Marina, J. Chromatogr., **646**, 297 (1993).

Received March 21, 1995
Accepted July 12, 1995
Manuscript 5123