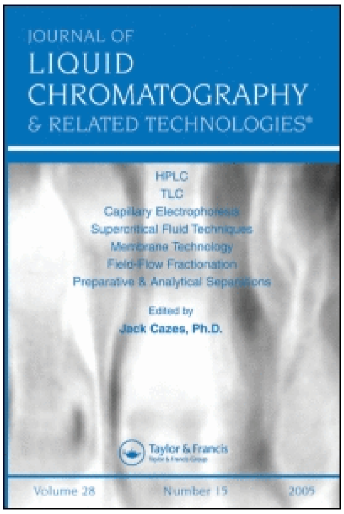

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Effect of the Chain Length and Concentration of the Alcohol Used in the Mobile Phase in Micellar Liquid Chromatography with a C_1 Column

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EFFECT OF THE CHAIN LENGTH AND CONCENTRATION OF THE ALCOHOL USED IN THE MOBILE PHASE IN MICELLAR LIQUID CHROMATOGRAPHY WITH A C_1 COLUMN

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ABSTRACT

The chromatographic behavior of a group of polycyclic aromatic hydrocarbons in micellar liquid chromatography with a C_1 column and hexadecyltrimethylammonium bromide and n-propanol or n-butanol as hybrid mobile phases is studied. Four equations, proposed in the literature, correlating the retention parameter (e.g., Log k' or 1/k'), surfactant concentration, and alcohol percentage were checked.

INTRODUCTION

In Micellar Liquid Chromatography (MLC) the solute retention is determined by its partitioning between (i) the micellar and the aqueous phase, (ii) the aqueous and the stationary phase, and (iii) the micellar and the stationary phase. Two equations are proposed to correlate solute retention and the constants of these equilibria[1,2]:

$$\frac{1}{k'} = \frac{K_{mw}}{\phi K_{sw}[L]} C_M + \frac{1}{\phi K_{sw}[L]} \tag{1}$$

$$\frac{V_s}{V_e - V_m} = \frac{v(P_{mw} - 1)}{P_{sw}} C_M + \frac{1}{P_{sw}} \tag{2}$$

K_{sw} and K_{mw} are the stationary and the micellar phase association constants of solutes, respectively. ϕ is the phase ratio. [L] is the concentration of the hydrocarbon chains in the stationary phase. C_M is the micellized surfactant concentration (total surfactant concentration minus the critical micellar concentration). V_s, V_m, V_e and v are the stationary and mobile phase volumes, the solute eluting volume, and the surfactant molar volume, respectively. P_{mw} and P_{sw} are the micellar/water and the stationary/water partition coefficients of solutes, respectively.

The use of micellar systems in the mobile phase was presented as an alternative to the hydro-organic phases. However, small amounts of an alcohol must be introduced in order to improve the poor efficiency of purely micellar mobile phases[3]. Nevertheless, not only efficiency is modified but also solute retention and selectivity.

Equations 1 and 2 were checked for different types of solutes and surfactants, and the effect of organic additives upon retention and selectivity coefficients was also studied using C_8 and C_{18} stationary phases.[4,5,6,7,8,9,10,11,12] The chromatographic behavior of a group of polycyclic aromatic hydrocarbons (PAHs) on a C_1 column using a micellar mobile phase of hexadecyltrimethylammonium bromide (CTAB) and n-propanol or n-butanol as organic modifiers, is studied in this work.

MATERIAL AND METHODS

Apparatus

The HPLC system consisted of a Model 510 pump, U6K injector, Model 440 UV-Vis detector (all from Waters) and a Model PM 8271 XYt recorder (Philips). The analytical column was a Spherisorb C_1, 15 cm × 4.6 mm I.D., d_p = 5 μm, (Teknokroma).

Reagents

CTAB, n-propanol and n-butanol (all from Merck) were used as received. PAHs were as follows: (1) pyrene, (2) phenantrene, (3) 2,3-benzofluorene, (4) fluorene, (5) fluoranthene, (6) acenaphtylene, (7) acenaphthene, (8) anthracene, (9) naphthalene, (10) 1-naphtol, (11) 2-naphtol, and (12) 1-naphthylamine.

Procedure

Mobile phases were prepared by dissolving the appropriate amounts of CTAB and n-propanol or n-butanol in HPLC-grade water. Surfactant and alcohol concentration ranged from 0.08 to 0.16 M and 5 to 10%, respectively. Solutions were filtrated through a 0.45-μm filter and degassed in an ultrasonic bath. Stock solutions of test solutes were prepared in the mobile phase itself and directly injected (20 μL) into the chromatographic system at a concentration adjusted to permit detection. Solutes were injected in triplicate and the mean value of retention times was used for calculations. The void volume of the column was determined from the first deviation of the baseline. The stationary phase volume was taken as the difference between the total volume of the column and the void volume.

The Statgraphics plus 1.0 (Statistical graphics Corp.) was used for data analysis.

RESULTS AND DISCUSSION

Solute Retention

A linear relationship is observed when 1/k' or $V_s/(V_e - V_m)$ is plotted versus C_M (data not shown). Table 1a-c shows the parameters for the straight lines obtained in each case. According to these results, the behavior of a C_1 column may be explained in a similar way as that of stationary phases with larger chains (e.g. C_8 or C_{18}), that is, through the three-phase partition mechanism[1].

As Figure 1 shows, if n-butanol is present in the mobile phase, k' factors are lower than for n-propanol. Therefore, the increase in the hydrophobicity of the mobile phase will likely produce an increase in solute affinity towards this phase, agreeing with the high hydrophobicity of these compounds (Table 2).

Table 1a

1/k' vs C_M Straight Line Parameters

	5% BuOH				5% PrOH		
PAH	**Slope**	**Intercept**	**R^2**	**PAH**	**Slope**	**Intercept**	**R^2**
1	1.424	0.011	0.998	1	1.401	-0.039	0.958
2	1.407	0.016	0.999	2	1.275	-0.024	0.999
3	1.346	0.011	0.997	3	1.363	-0.047	0.981
4	1.437	0.009	0.996	4	1.498	-0.047	0.966
5	1.454	0.006	0.997	5	1.520	-0.053	0.970
6	1.473	0.012	0.998	6	1.341	-0.021	0.999
7	1.407	0.007	0.999	7	1.477	-0.044	0.974
8	1.531	0.002	0.989	8	1.504	-0.047	0.976
9	1.520	0.001	0.983	9	1.301	-0.012	0.998
10	1.520	0.034	0.994	10	1.129	-0.013	0.999
11	1.540	0.003	0.999	11	1.470	-0.018	0.997
12	1.750	0.032	0.997	12	1.552	-0.009	0.999

Table 1b

1/k' vs C_M Straight Line Parameters

	7.5% BuOH				7.5% PrOH		
PAH	**Slope**	**Intercept**	**R^2**	**PAH**	**Slope**	**Intercept**	**R^2**
1	1.747	0.014	0.990	1	1.242	-0.00004	0.998
2	1.781	0.013	0.993	2	1.284	0.001	0.999
3	1.890	-0.009	0.982	3	1.190	-0.005	0.999
4	1.793	0.011	0.994	4	1.305	-0.003	0.999
5	1.757	0.013	0.997	5	1.280	-0.005	0.999
6	1.830	0.018	0.995	6	1.349	0.004	0.999
7	1.642	0.024	0.999	7	1.266	-0.0001	0.999
8	1.745	0.016	0.992	8	1.307	-0.004	0.999
9	1.952	0.014	0.985	9	1.394	0.003	0.998
10	1.957	0.039	0.970	10	1.459	0.018	0.992
11	2.102	0.019	0.993	11	1.455	0.002	0.998
12	1.900	0.074	0.986	12	1.488	0.027	0.990

Table 1c

1/k' vs C_M Straight Line Parameters

	10% BuOH				10% PrOH		
PAH	Slope	Intercept	R^2	PAH	Slope	Intercept	R^2
1	2.202	0.053	0.998	1	1.553	-0.019	0.991
2	2.345	0.045	0.981	2	1.638	-0.017	0.957
3	2.322	0.045	0.990	3	1.465	-0.023	0.999
4	2.522	0.022	0.985	4	1.249	0.014	0.958
5	2.456	0.027	0.998	5	0.746	0.060	0.480
6	2.576	0.032	0.997	6	1.590	-0.009	0.998
7	2.500	0.026	0.996	7	1.439	-0.009	0.997
8	2.558	0.012	0.997	8	1.498	-0.012	0.996
9	2.662	0.034	0.992	9	1.823	-0.025	0.907
10	2.690	0.062	0.970	10	0.807	0.115	0.508
11	2.533	0.073	0.972	11	1.975	-0.053	0.969
12	2.740	0.101	0.952	12	2.242	-0.018	0.983

Table 2

Hydrophobicity of PAHs Studied Expressed as the Logarithms of Their Octanol-Water Partition Coefficients (Log P_{ow})

PAH	Log P_{ow}
1	4.88*
2	4.46*
3	5.03**
4	4.18*
5	4.50**
6	3.48**
7	3.82**
8	4.45*
9	3.37*
10	2.98*
11	2.84*
12	2.22*

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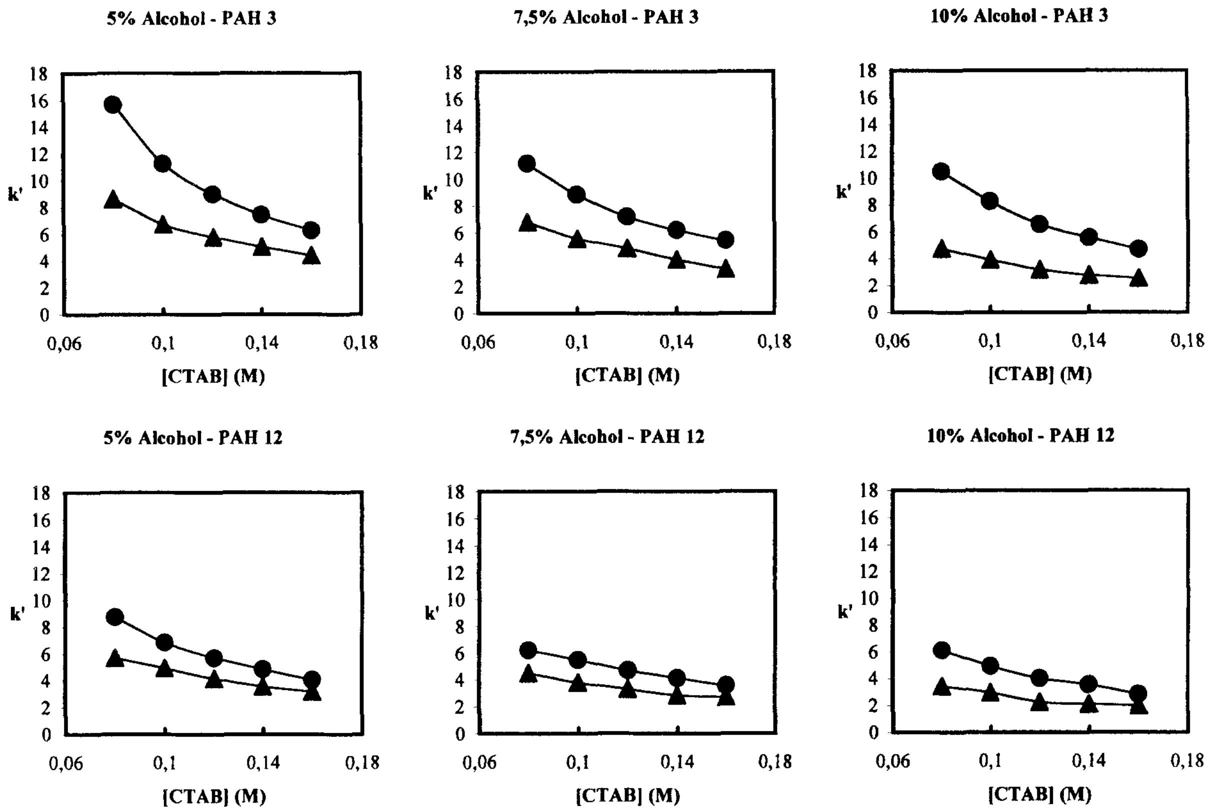
* Data from Reference 13.

** Data from Reference 14.


5% Alcohol - PAH 3
7,5% Alcohol - PAH 3
10% Alcohol - PAH 3
5% Alcohol - PAH 12
7,5% Alcohol - PAH 12
10% Alcohol - PAH 12
k'
18
16
14
12
10
8
6
4
2
0
0,06
0,1
0,14
0,18
[CTAB] (M)

Further, the alcohol can also compete against PAH molecules for binding to the stationary phase, decreasing the value of their capacity factors. Figure 1 also shows that retention follows an order determined by solute hydrophobicity. In this way, k' factors for PAH 3 (Log P_{ow}= 5.03) are larger than those obtained for PAH 12 (Log P_{ow}= 2.22) (Figure 1), that is, the larger the Log P_{ow} for a solute, the larger its retention.

If the decrease in retention is mainly determined by the alcohol hydrophobicity, when that is increased (e.g., changing n-propanol by n-butanol) those PAHs with higher Log P_{ow} should show a larger decrease in their retention. In this way, the difference in k' values between n-propanol and n-butanol for PAH 3 (Log P_{ow}= 5.03) is ca. 45%, using a CTAB (0.08 M) + alcohol (5% v/v) mobile phase, and 34% for PAH 12 (Log P_{ow}= 2.22), under the same chromatographic conditions.

A linear relationship between Log k' and the percentage of alcohol in the mobile phase (θ) is described in the literature for purely hydro-organic mobile phases:

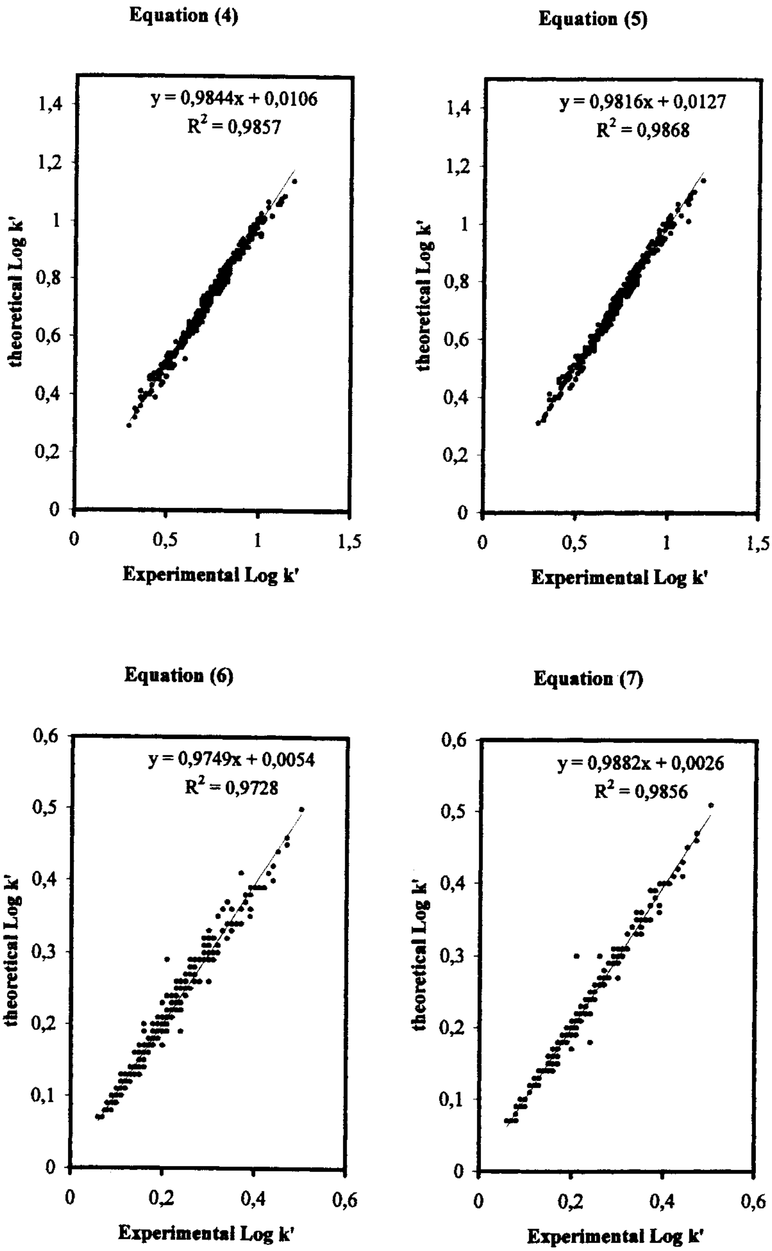
$$\text{Log } k' = -S\theta + \text{Log } k'_o \qquad (3)$$

S being a constant which defines the eleutropic capacity of the alcohol and Log k_o' the capacity factor for a purely water mobile phase. However, the linear relationship is inadequate and a quadratic expression matches better experimental data, when the percentage of alcohol is low.[15,16,17,18] For lower percentages (e.g., ca. below 10%), even the quadratic equation is inadequate to correlate retention and alcohol concentration in the mobile phase.

Khaledi et al.[4] have shown a linear relationship between Log k' and θ for hybrid mobile phases, even for low percentages of alcohol. Nevertheless, these[7] and other workers[12,6,11] have also shown some exceptions to this behavior.

As an alternative to Log k' vs θ expressions other equations which correlate 1/k' and θ are proposed in the literature.[6,11]

Figure 1 (left). Effect of alcohol concentration and chain length on k' factors for two PAHs of those studied with high (a-c) and low (d-f) hydrophobicity, respectively. The same behavior is shown by all of the solutes studied in this work (data not shown). ● 1-propanol and ▲ 1-butanol, respectively.



Equation (4)

Equation (5)

Equation (6)

Equation (7)

Figure 2. Experimental vs calculated retention factors (e.g., Log k' or 1/k') for each of the equations studied.

There are mainly four equations proposed in the literature to correlate the retention parameter (e.g., Log k' or 1/k') and the concentration of surfactant (C_M) and alcohol (θ) in the mobile phase in MLC:[19]

$$\text{Log } k' = A_1 + A_2C_M + A_3\theta \qquad (4)$$

$$\text{Log } k' = A_1 + A_2C_M + A_3\theta + A_4C_M\theta \qquad (5)$$

$$\frac{1}{k'} = A_1 + A_2C_M + A_3\theta + A_4C_M\theta \qquad (6)$$

$$\frac{1}{k'} = A_1 + A_2C_M + A_3\theta + A_4C_M\theta + A_5\theta^2 \qquad (7)$$

Where A_1 to A_5 are adjustable parameters which depend on each solute and chromatographic condition. In this work, 30 different mobile phases and 12 solutes were used, that is, 360 different experimental retention data were used to verify these expressions. The A_i parameters were obtained by a multivariate correlation analysis with the statgraphics plus 1.0 software.

As shown in Figure 2, good agreement between the calculated and experimental values was found for all these equations. Figure 3 shows that the difference between the predicted and experimental values is almost the same in all instances, except for n-butanol when equation 6 is used. This means, that under the conditions used in this work, results may be predicted through any of these equations with almost the same precision.

If these equations are used to extrapolate at 0% of organic modifier in the mobile phase for the two alcohols used in this work, the same value for the retention parameter should be obtained in both instances. A difference of 3.0% (σ_{n-1} = 1.9) and 5.1% (σ_{n-1} = 4.1) for the retention parameters between both alcohols was obtained for equations 4 and 5, versus 112% (σ_{n-1} = 47) and 127% (σ_{n-1} = 53) for equations 6 and 7, respectively.

Solute-Micelle Partition Coefficients

As retention follows the three-phase partition equilibria mechanism (Table 1a-c), micelle-water (P_{mw}) (or solute-micelle association constants K_{mw}) and stationary phase-water (P_{sw}) partition coefficients may be calculated with the equations described at the introduction of this work.

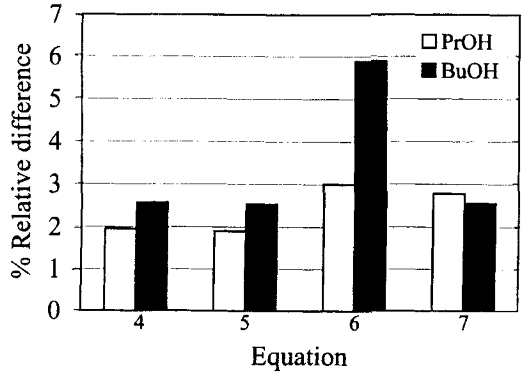


Figure 3. Difference average between the experimental and the calculated retention parameters.

Table 3 shows P_{mw} and P_{sw} coefficients of these compounds calculated from parameters of straight lines shown at Table 1a-c. Values of a negative sign are not present in Table 3 since they have no physical sense. Due to the high hydrophobic nature of these compounds and that of the stationary phase, P_{sw} coefficients have a high value, that is, intercepts of straight lines (e.g., $1/P_{sw}$) are close to zero. In this way, small uncertainties in the value for the slope may produce negative values for the intercept. The probability to get a negative sign for the intercept increases when increasing the value of the P_{sw} coefficient, that is, the solute hydrophobicity.

As mentioned above, n-butanol produces a decrease in retention larger than that of n-propanol (Figures 1a-f). This was attributed to the higher hydrophobicity of n-butanol, which increases the affinity of solute molecules towards the mobile phase. In this way, it is likely that using n-propanol P_{sw} coefficients show higher values than in the case of n-butanol (e.g., lower intercepts). This could be the reason for the negative values obtained for partition coefficients by using n-propanol in the mobile phase, and not so for n-butanol.

As shown in Figure 4, there is a linear relationship between P_{mw} and P_{sw} coefficients in every chromatographic condition used in this work. This may be interpreted assuming that solute-stationary and solute-micellar phase interactions are similar in nature. Due to the hydrophobic nature of the stationary phase (e.g., a C_1 column) and solute hydrophobicity (Table 2), solute-stationary phase interaction is mainly determined by hydrophobic forces.

Table 3

P Coefficients Calculated from Parameters of Equation 2

PAH	5% PrOH			7.5% PrOH			10% PrOH		
	P_{mw}	P_{sw}	P_{sm}	P_{mw}	P_{sw}	P_{sm}	P_{mw}	P_{sw}	P_{sm}
1	---	---	---	---	---	---	---	---	---
2	---	---	---	4688	1701	0.362	---	---	---
3	---	---	---	---	---	---	---	---	---
4	---	---	---	---	---	---	245	91	0.371
5	---	---	---	---	---	---	35	21	0.606
6	---	---	---	---	---	---	---	---	---
7	---	---	---	---	---	---	---	---	---
8	---	---	---	---	---	---	---	---	---
9	---	---	---	1284	429	0.334	---	---	---
10	---	---	---	222	70	0.318	20	11	0.548
11	---	---	---	232	74	0.318	---	---	---
12	---	---	---	111	34	0.310	---	---	---

PAH	5% BuOH			7.5% BuOH			10% BuOH		
	P_{mw}	P_{sw}	P_{sm}	P_{mw}	P_{sw}	P_{sm}	P_{mw}	P_{sw}	P_{sm}
1	347	113	0.326	346	92	0.266	114	23	0.209
2	249	82	0.330	389	102	0.261	143	28	0.197
3	347	120	0.345	---	---	---	141	28	0.199
4	424	137	0.324	459	119	0.259	316	58	0.184
5	649	208	0.320	372	98	0.264	247	47	0.189
6	326	103	0.315	274	69	0.253	216	39	0.180
7	548	181	0.330	189	53	0.282	268	50	0.185
8	2591	788	0.304	301	80	0.266	366	67	0.181
9	407	125	0.306	379	90	0.238	220	38	0.174
10	122	37	0.303	139	33	0.236	119	20	0.171
11	157	47	0.300	303	67	0.221	96	17	0.182
12	148	39	0.265	71	17	0.242	76	13	0.167

Consequently, the nature of the interaction between the solute and the micellar phase should also be governed by the hydrophobic effect, since P_{mw} and P_{sw} show a linear relationship between them. This conclusion also agrees with the structure of CTAB micelles, which have a polar surface with a positive charge and a non-polar core.

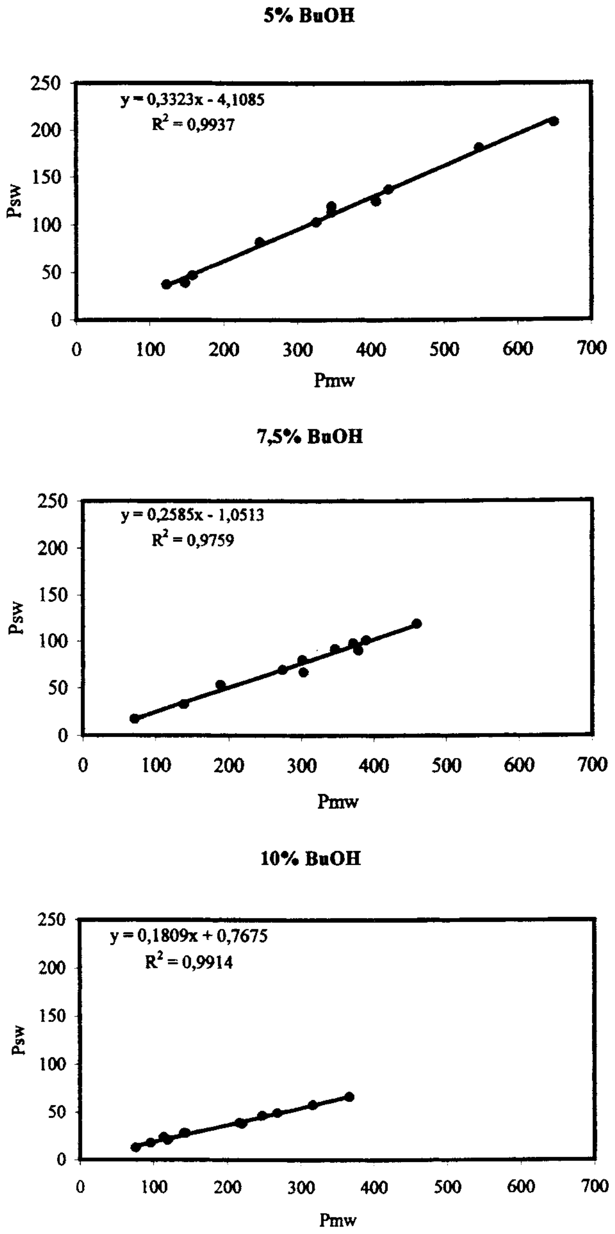


Figure 4. Variation of the P_{sw} vs P_{mw} coefficient.

In this instance, it could be concluded that PAH molecules are likely located at the highly hydrophobic core region of the micelle. It has been demonstrated in the literature for different solutes and chromatographic conditions that increasing the percentage of alcohol in the mobile phase in MLC the P_{mw} and P_{sw} coefficients show a decrease.[8,4] This result is also shown in this work for n-butanol (Table 3). Due to the reasons mentioned above, it was not possible to obtain the P coefficients for n-propanol, but a similar decrease as for n-butanol should be expected for them.

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REFERENCES

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

2. M. Arunyanart, L. J. Cline Love, Anal. Chem., **56**, 1557 (1984).

3. J. G. Dorsey, M. T. DeEchegaray, J. S. Landy, Anal. Chem., **55**, 924 (1983).

4. M. G. Khaledi, E. Peuler, J. Ngeh-Ngwainbi, Anal. Chem., **59**, 2738-2747 (1987).

5. M. G. Khaledi, Anal. Chem., **60**, 876-887 (1988).

6. M. F. Borgerding, R. L. Williams Jr, W. L. Hinze, F. H. Kina, J. Liq. Chromatogr., **12(8)**, 1367-1406 (1989).

7. M. G. Khaledi, J. K. Strasters, A.H. Rodgers, E. D. Breyer, Anal. Chem., **62**, 130-136 (1990).

8. F. P. Tomasella, J. Fett, L. J. Cline Love, Anal. Chem., **63**, 474-479 (1991).

9. A. S. Kord, M. G. Khaledi, Anal. Chem., **64**, 1894-1900 (1992).

10. A. S. Kord, M. G. Khaledi, J. Chromatogr., **631**, 125-132 (1993).

11. J. R. Torres-Lapaisó, R. M. Villanueva-Camañas, J. M. Sanchis-Mallols, M. J. Medina-Hernández, M. C. García-Alvarez-Coque, J. Chromatogr., **639**, 87-96 (1993).

12. M. A. García, S. Vera, M. Bombín, M. L. Marina, J. Chromatogr., **646**, 297-305 (1993).

13. H.Hanai, Chromatographia, **12**, 77 (1979).

14. K. Jinno, K. Kawasaki, Chromatographia, **17**, 445 (1983).

15. H. Colin, G. Guiochon, P. Jandera, Anal. Chem., **55**, 442 (1983).

16. P. J. Schoenmakers, H. A. H. Billiet, L. DeGalan, J. Chromatogr., **282**, 107 (1983).

17. L. R. Snyder, J. W. Dolan, J. R. Gant, J. Chromatogr., **165**, 3 (1979).

18. W. R. Melander, C. Horváth, in **High Performance Liquid Chromatography, Advances and Perspectives**, C. Horváth Ed., Vol. 2, p 113, 1980.

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

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