



**RELATIONSHIP BETWEEN MICELLAR LIQUID
CHROMATOGRAPHY RETENTION OF SULFONAMIDES
AND THE pH AND CONCENTRATION OF SURFACTANTS
AND ORGANIC MODIFIERS IN THE MOBILE PHASE**

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ABSTRACT

The paper presents an attempt to adapt a retention model suggested and verified by classic RP LC in micellar liquid chromatography, MLC. Instead of hydrophobic interactions with ODS groups and electrostatic interactions with silanol residues in C-18 packing, hydrophobic interactions with alkyl groups and ionic interactions with anionic moieties of the SDS-modified stationary phase were considered. Due to the different characteristics of the stationary phase in the MLC depending on the pH of the mobile phase, the equation used to determine the contribution of electrostatic interactions to retention was modified. Theoretical curves for the relationship between retention and SDS micelle concentration in the mobile phase, organic modifier concentration and eluent pH were determined. For comparison, curves based on data obtained in basic sulfonamide studies were plotted in the same coordinate systems and units. A complete qualitative similarity was noted between the theoretical curves predicting retention changes with changing micellar mobile phase parameters and the curves determined based on experimental results for the sulfonamides. The qualitative similarity involves a similar shape of the respective curves and identical tendencies. In general, a larger reduction of sulfonamide retention with respect to the predicted value is noted. The deviation results from changes in the sulfonamide property with changing pH of the mobile phase.

Keywords: micellar liquid chromatography, retention mechanism, sulfonamides

INTRODUCTION

Neue-Carr model

In the model, Neue and Carr [1] discussed the contribution of hydrophobic and electrostatic interactions to the retention of a cationic analyte with silica-bound alkyl chains and silanol residues in C-18 packing. The nature of hydrophobic interactions was studied as a function of the organic modifier fraction volume in the mobile phase, while electrostatic interactions were studied depending on changes in the pH of the mobile phase. The authors assumed in the classic model that hydrophobic and electrostatic interactions add up, and the model is given by Eq. (1):

$$k = k_{rp} + k_{ex} \quad (1)$$

where k is the retention coefficient, k_{rp} is the contribution of hydrophobic interactions and k_{ex} is the contribution of ionic interactions.

This approach is synonymous to the assumption that two types of sites exist in which analyte retention occurs; thus, the contributions of the interactions to retention are independent [2].

A more recent version of the model (combined model) assumes the simultaneous occurrence of “pure” hydrophobic interactions and combined interactions, suggested by Yang [3], described by a product of hydrophobic and ionic interactions given by Eq. (2):

$$k = k_{rp} + k_{rp} k_{ex} \quad (2)$$

Stronger ionic interactions lead to an increase in the component responsible for combined interactions; if so, ion-exchange interactions prevail. When there are no electrostatic interactions, hydrophobic interactions alone occur. However, when hydrophobic interactions weaken, retention disappears. Therefore, a different solution had to be found.

As it is obvious that sites responsible for “pure” hydrophobic and ionic interactions and also sites where both interactions are combined occur on the packing surface, the authors suggested Eq. (3) (multiplicative model):

$$k = k_{rp} + k_{rp}^* k_{ex}^* + k_{ex} \quad (3)$$

It is obvious that the retention coefficients marked with an asterisk differ from the other coefficients; however, to simplify the model they are considered identical. Considering various RP LC packings (different bound ODS and silanol ratios), three distinct models resulting from Eqs. (1-3) were studied.

The authors of the proposed approaches used respective mathematical equations to describe relationships between k_{rp} and organic modifier fraction volume in the mobile phase (x) and k_{ex} as a function of the pH of the phase used, for predicting the analyte retention changes. For hydrophobic interactions, contribution to the retention coefficient was calculated using Eq. (4):

$$k_{rp} = 30e^{-30x/(1+3x)} \quad (4)$$

The contribution of ion-exchange interactions to retention was determined by Eq. (5):

$$k_{\text{ex}} = (1 + 10^{-\text{pH} + 8.9})^{-1} \quad (5)$$

The correctness of our assumptions was practically verified and confirmed by comparing theoretical curves calculated for the respective models with experimental curves for various packings. Based on the suitability of various models suggested by Neue and Carr, they were used for studying retention in a micellar system.

EXPERIMENTAL

Apparatus

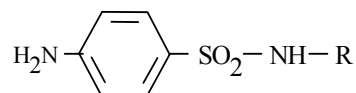
A Hewlett Packard Liquid Chromatograph, model HP 1050 (Waldbronn, Germany) with a quaternary pump with a variable-wavelength UV detector operating at 260 nm and a Rheodyne model 7125 injection valve with a 20 μL sample loop was used. Separation was performed on a Nucleosil C-18 (5 μm , 250 mm x 4.6 mm I.D.) stainless steel column. Analyses were carried out isocratically at $40 \pm 1^\circ\text{C}$ with a micellar mobile phase. Before use, the mobile phase was vacuum-filtered through a 0.45 μm cellulose filter and degassed with helium.

Reagents and standards

The sulfonamides (Table 1) were obtained from Aldrich (Germany). Stock sulfonamide solutions (1 g L^{-1}) were prepared by dissolving standard compounds in methanol (analytical reagent grade) and diluting to the desired mg L^{-1} levels with water. Additional reagents were: monobasic potassium phosphate, dibasic sodium phosphate, phosphoric(V) acid, sodium hydroxide, propanol-2 (all from POCh, Poland). Other reagents and solvents were of analytical reagent grade.

The micellar mobile phase was prepared by mixing a suitable amount of 0.2 mol L^{-1} sodium dodecylsulfate (SDS) (Aldrich, Germany), 20 mL of 2-propanol, 2 mL of 5.0 mol L^{-1} phosphoric(V) acid in 950 mL of water. The desired pH was adjusted with sodium hydroxide. The final volume was made to 1000 mL using water, purified with a Milli-Q system (Millipore, Bedford, USA).

Table 1. Structure and characteristics of sulfonamides.



Sulfonamide	R	pK _{a1} ^(*)	pK _{a2} ^(*)	log P _{ow}	λ _{max}
1. Sulfaproxiline		1.7	4.9	1.37	262
2. Sulfachloropyridazine		1.9	5.1	0.07	266
3. Sulfacetamide		1.8	6.1	-0.33	260
4. Sulfadimethoxine		1.8	6.2	0.97	252
5. Sulfadiazine		2.0	6.4	-0.18	218
6. Sulfamerazine		2.2	7.0	0.06	261
7. Sulfathiazole		2.1	7.1	0.06	285
8. Sulfamethazine		2.1	7.4	0.32	268
9. Sulfamethoxazole		1.7	5.6	0.91	270
10. Sulfafurazole (sulfisoxazole)		4,6	5,1		253
11. Sulfanilamide	H	2.4	10.4		260
12. Sulfamethizole		1.98	5.4	0.59	275

(*) [4]

RESULTS AND DISCUSSION

Both in anionic MLC and classic RP LC, hydrophobic and electrostatic interactions also occur, and are responsible for the retention mechanism. ODS chains of C-18 packing which are responsible for hydrophobic interactions and $-\text{OSO}_3^-$ moieties of the stationary phase dynamically modified with an anionic surfactant which are responsible for ionic interactions are sites capable of interacting with the analyte. Figure 1 shows a scheme of the C-18 packing surface modification with SDS molecules.

Hydrophobicity may be investigated as a function of micelle concentration or as a function of changes in the organic modifier's concentration in the micellar mobile phase at a constant SDS concentration. Similarly to Neue and Carr, the nature of electrostatic interactions was considered as a function of the eluent's pH. However, major differences, not found in the model developed for RP LC, were encountered for electrostatic interactions.

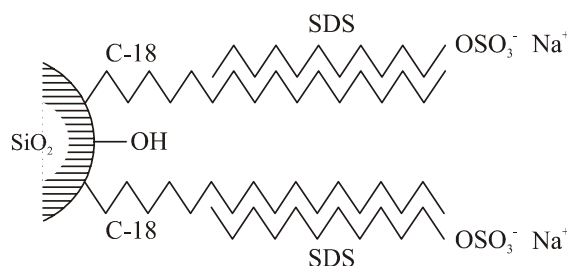


Fig. 1. Modification of C-18 packing surface with SDS molecules.

First, for classic RP LC, interactions with unreacted silanols on the silica surface with which the analyte interacts were considered. The relationship between pH and silanol proton dissociation constant ($\text{pK}_a = 8.9$) is known [5]. Due to the attraction of the positive analyte and dissociated silanols, an increased retention for higher pH values was noted for the curves illustrating the relationship between retention and pH.

This assumption is incorrect for micellar systems in which the SDS-coated stationary phase has constant properties irrespective of changes in the pH of the mobile phase. For the purposes of anionic MLC, Eq. (5) for the calculation of electrostatic interaction magnitude k_{ex} was modified:

$$k_{\text{ex}} = (1 + 10^{\text{pH}})^{-1} \quad (6)$$

Second (most important), betrylium tosylate was used by the authors of the model. The betrylium cation is a simple, quaternary amine with an aromatic ring. The charge of the ion does not depend on pH. It may be involved in hydrophobic interactions through the phenyl ring and ionic interactions owing to the positive charge on the amine nitrogen. The MLC system is only seemingly similar in this respect. In that case, retention involves zwitterionic sulfonamides.

No clearly defined analyte is present. The form of sulfonamides changes with changing pH: from cationic (or zwitterionic) through zwitterionic particles with zero net charge to ionic, depending on sulfonamide pK_{a1} .

The paper presents results obtained based on Eq. (3) which combines the advantages of the classic model which better describes retention at higher pH values and the combined model which better accounts for retention differences between low and high pH values with strong hydrophobic interactions. Figure 2 shows the predicted shape of sulfonamide retention curves for the relationship between $k = k_{rp} + k_{rp} k_{ex} + k_{ex}$ and (a) SDS micelle concentration, (b) organic modifier concentration, (c) and (d) mobile phase pH at k_{rp} calculated for SDS and organic modifier concentration, respectively.

It follows from the curves in Figure 2(a) and (b) that reduced retention is predicted with increased SDS and organic modifier concentrations. A similar effect is noted for the curves in Figure 2(c) and (d), but the predicted pH effect on sulfonamide retention is much lower. The observed pH effect on the shape of the curves in Figure 2(a) is minor. The resulting lines are parallel, they correspond to different pH values and overlap, except for the curve at pH 3.0. Specific is the shape of the curves for the relationship between retention and organic modifier concentration (Figure 2(c)). A constant though decreasing retention reduction is seen for higher concentrations. With an increasing modifier concentration, the variation in retention depending on pH increases. The shape of the curves in Figure 2(c) and (d) is more gentle. Retention values in all the curves decrease. A distinct drop is seen only at pH = 3.0. The curves in Figure 2(c), corresponding to successive SDS concentrations, are parallel and maintain the same initial retention reduction. This proves that electrostatic interactions do not change with increased hydrophobic interactions. A major difference is seen in Figure 2(d). With increasing hydrophobic interactions (reduced organic modifier concentration), the initial retention reduction, seen for low pH values, is reduced. It is negligible in the curve corresponding to 0.5% organic modifier concentration and imperceptible in the figure.

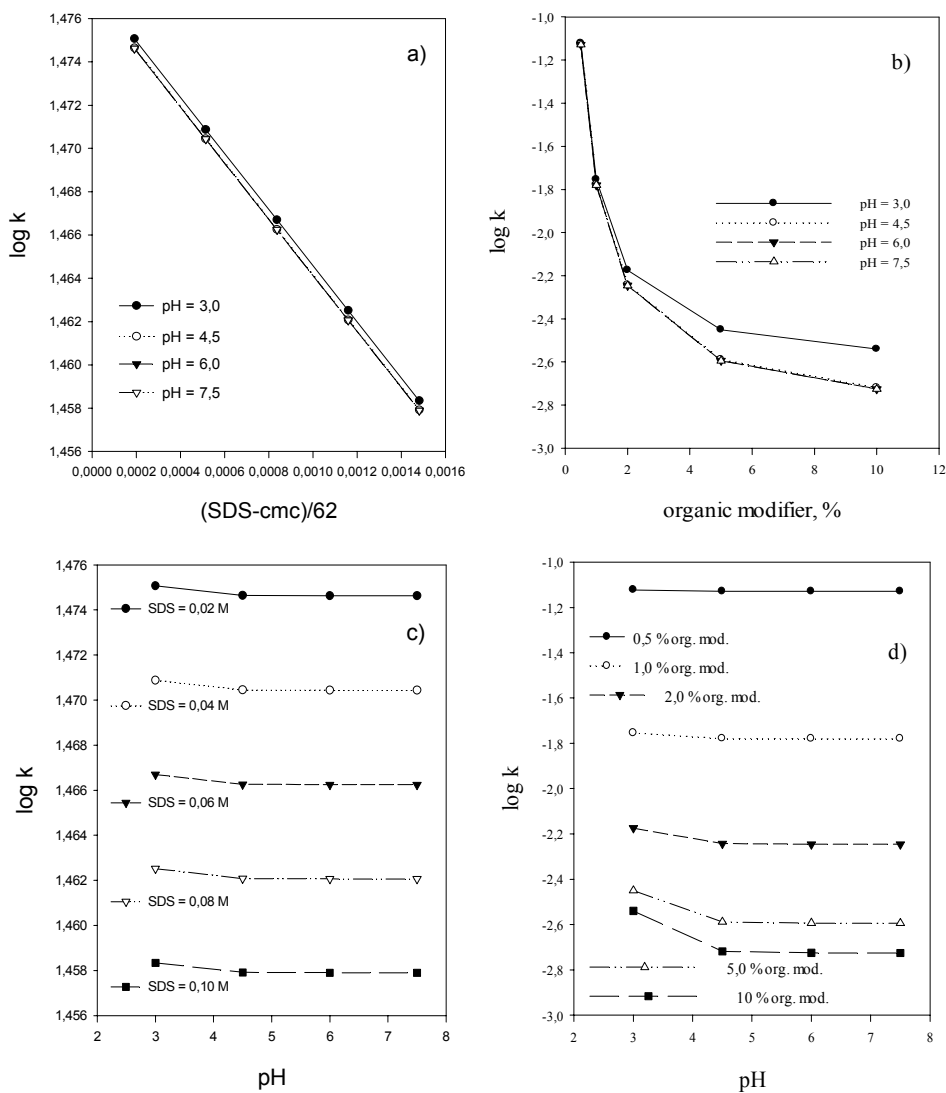


Fig. 2. Predicted shape of sulfonamide retention curves in micellar liquid chromatography as a function of: (a) $(\text{SDS-cmc})/62$ – micelle concentration at pH 3.0; 4.5; 6.0 and 7.5; (b) organic modifier concentration at SDS 0.02; 0.04; 0.06; 0.08 and 0.10 M; (c) pH at k_{rp} determined for various SDS concentrations; (d) pH at k_{rp} determined for various organic modifier concentrations.

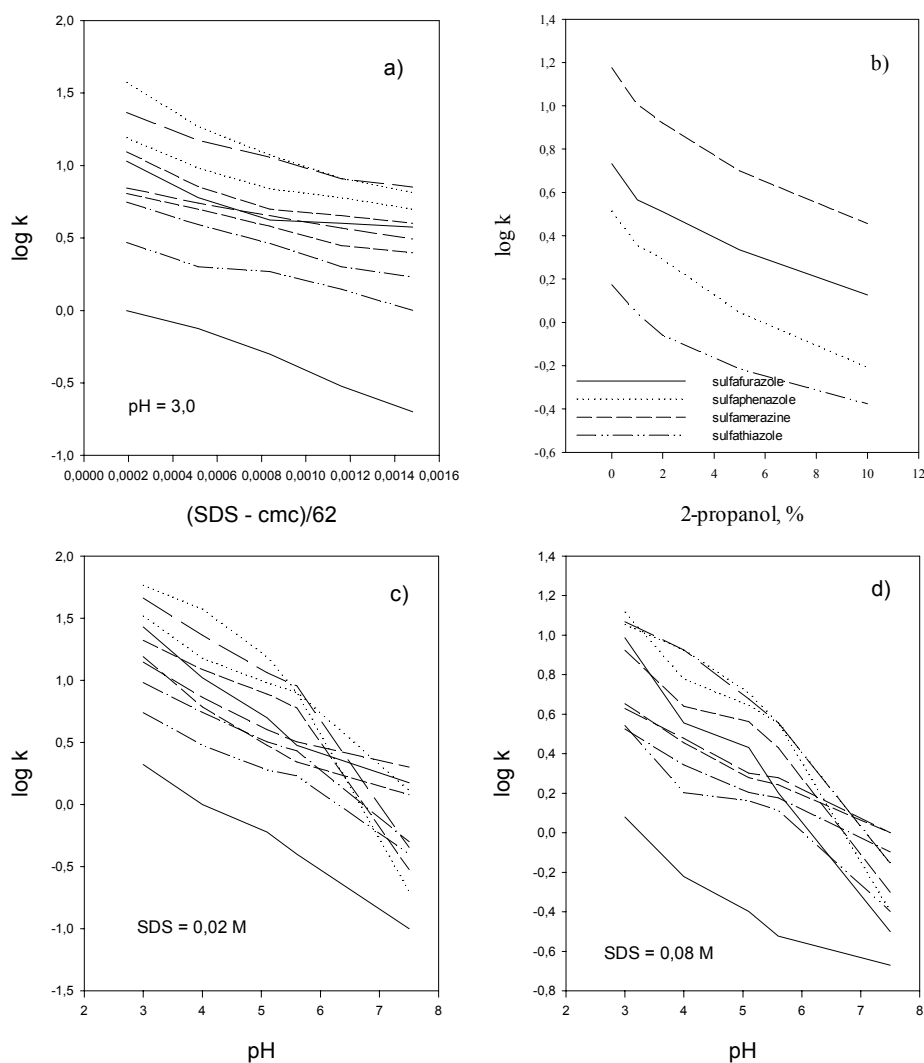


Fig. 3. Experimental curves of sulfonamide retention as a function of: (a) (SDS-cmc)/62 – micelle concentration at pH 3.0; (b) 2-propanol concentration for selected sulfonamides; (c) pH at SDS = 0.02 M; (d) pH at SDS = 0.08 M.

For comparison, Figure 3 shows the shape of curves based on experimental data. It corresponds to the predicted curves in Figure 2 to a varied degree. In general, the reduced retention and plot shape tendency is maintained. The experimental curves in Figure 3(a), corresponding to various sulfonamides, have roughly the same shapes. Albeit to a different degree, all the compounds have much larger retention reduction than expected. The conclusion made when comparing the curves as a function of the organic modifier concentration is different. A larger retention reduction was predicted than that achieved in prac-

tice. When studying pH effects, it is noted that the slopes of the experimental curves show larger variation than predicted.

In practice, the slight discrepancy noted when comparing the theoretical model with the results may be assigned to the analyte properties. The variable characteristics of the test compounds depending on pH led to no stable reference. The predicted retention change with the changed mobile phase pH did not include changes of the sulfonamide properties in Equation (3). In order to determine the correctness and suitability of the model in MLC fully and objectively, an analyte whose properties do not depend on micellar mobile phase pH should be used as the author suggests. This requires additional experimental studies, not within the field of sulfonamide investigation.

A different solution to approximate the predicted retention with experimental results is to include the analyte (sulfonamide) property changes, at least partly, as a function of changes of the pH of the micellar mobile phase. As each of the test sulfonamides has distinct pK_a values, a single general equation is not sufficient to describe retention changes for all of the sulfonamides. This requires an individual approach to each test compound when plotting the curves. In order to account for retention changes as a function of mobile phase pH changes, Eq. (5) was modified, where pK_a , corresponding to the pK_{a1} of a sulfonamide, was introduced.

The resulting equation is as follows:

$$k_{ex} = (1 + 10^{pH - pK_a})^{-1} \quad (7)$$

where:

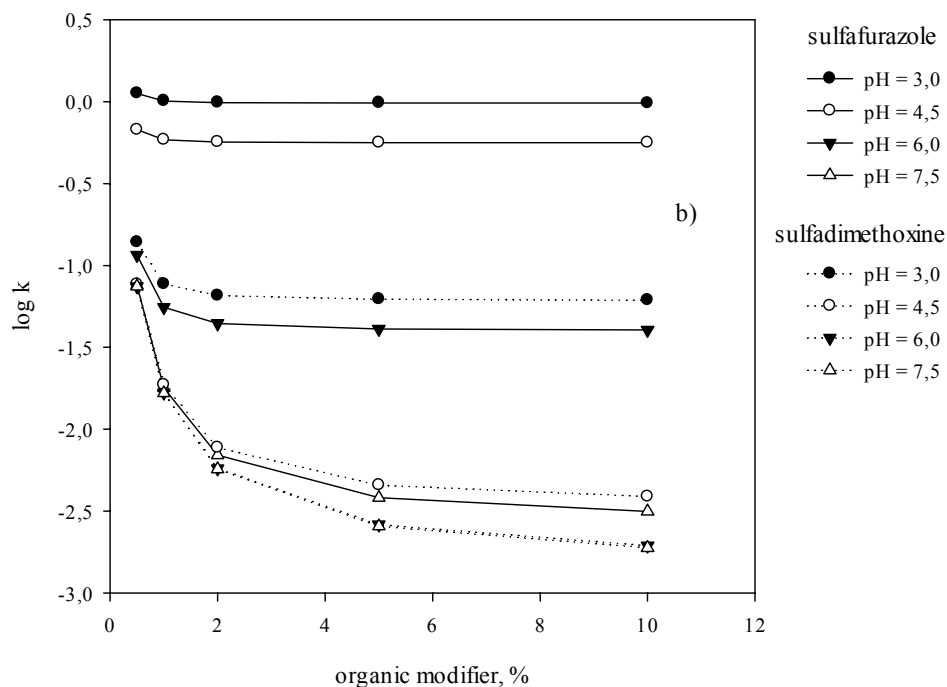
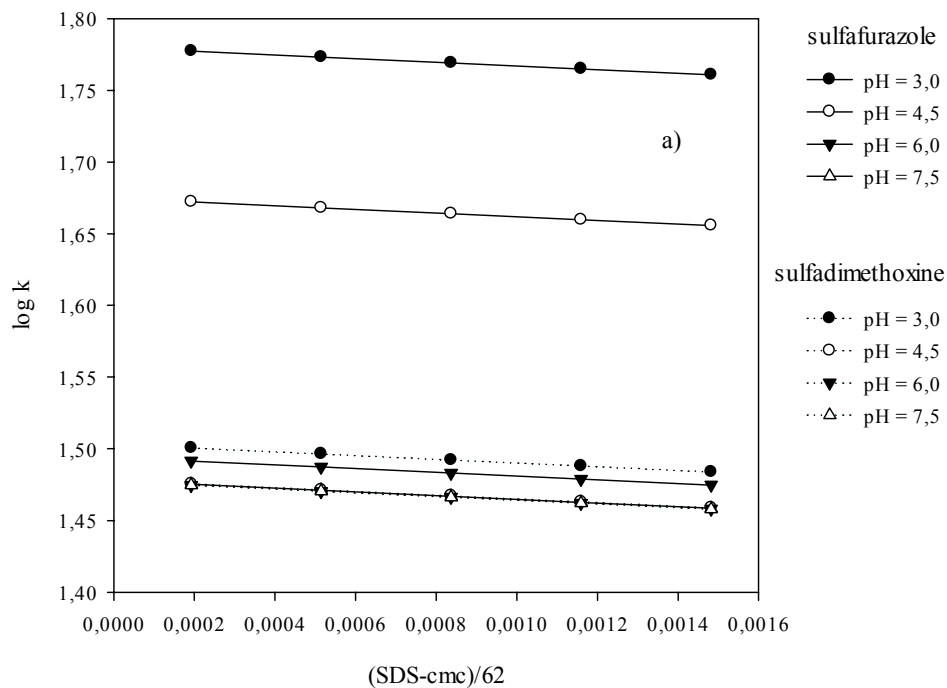
pH – pH of the micellar mobile phase,

pK_a – corresponds to dissociation constant pK_{a1} of a sulfonamide.

Figure 4 shows curves plotted using Equation (3) (combined model) and Equations (4) and (7). The curves represent two sulfonamides in all the plots: sulfafurazole (continuous line) and sulfadimethoxine (dotted line), for which the pK_{a1} values are 4.6 and 1.8, respectively.

The curves in Figure 4(a)-(d) confirm that the proposed modification is correct. Similarly to Figures 2(a)-(d), a permanent tendency for reduced sulfonamide retention is seen in all the curves, resulting from higher SDS (Figure 4(a)) and organic modifier (Figure 4(b)) concentration and higher mobile phase pH (Figures 4(c) and (d)). Figures 4(a) and (b) show a relatively minor effect of the factors on retention depending on SDS and organic modifier concentration (minor retention coefficient changes with changing surfactant and modifier concentration). However, a much higher variation for respective sulfonamides depending on the mobile phase pH is seen. The variation in both plots (Figures 4(a) and (b)) is much larger for sulfafurazole, for which pK_{a1} is much higher than for sulfadimethoxine. The curves in Figures 4(c) and (d) (relationship between retention and pH) confirm the observations. A minor variation of the curves depending on SDS concentration (Figure 4 (c)) and for low pH values as a function of modifier concentration (Figure 4 (d)) is noted. The differences increase when approaching the pH

corresponding to pK_{a2} values of both sulfonamides; the approximation, however, does not include the second dissociation constant.



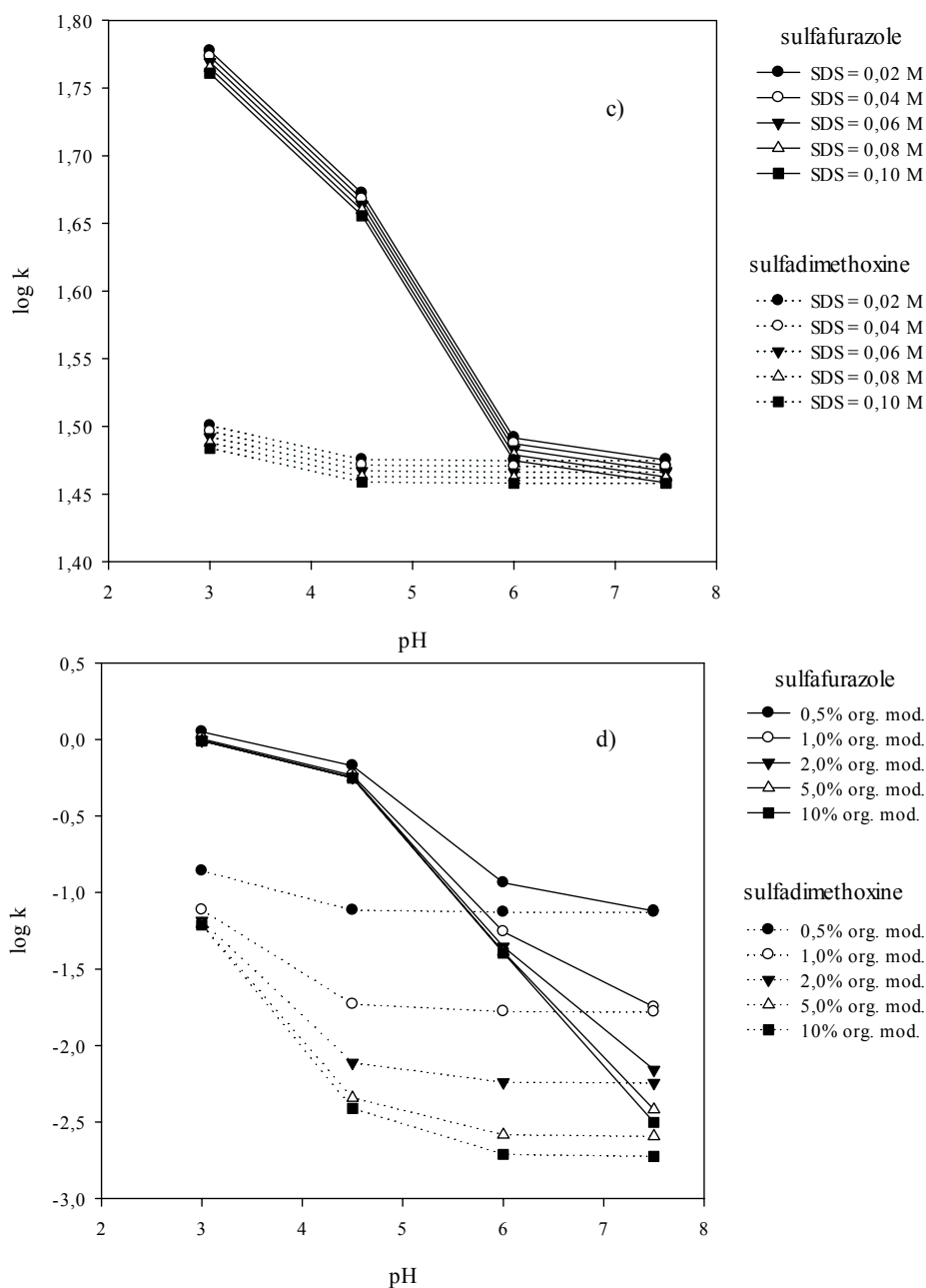


Fig. 4. Predicted shape of retention curves as function of pH for sulfonamides in MLC which include pK_{a1} of the compounds as a function of: (a) $(SDS-cmc)/62$ – micelle concentration at pH 3.0; 4.5; 6.0 and 7.5; (b) organic modifier concentration at SDS 0.02; 0.04; 0.06; 0.08 and 0.10 M; (c) pH at k_{rp} determined for various SDS concentrations; (d) pH at k_{rp} determined for various organic modifier concentrations.

When pK_a is introduced in the model equation the curves, as a function of pH, differ more, which is reflected in all the plots shown. When a respective pK_{a1} value, typical of the test sulfonamide, is introduced in the equation, the shapes of the predicted curves are more similar to the actual curves found in the chromatographic studies. The convergence is optimal for lower pH values of the mobile phase. The relationships in Figures 4(a)-(d) prove that the effects of SDS and organic modifier concentrations on retention are relatively minor. Much larger variation is seen as a function of pH changes in the same figures.

The curves of the relationship between retention and various parameters describing the micellar mobile phase confirm the conclusion that hydrophobic interactions (confirmed by the effects of SDS and organic modifier concentrations) accompany electrostatic interactions (they depend on pH changes). Ionic interactions prevail, having a major role in sulfonamide retention.

The approximation shown is appropriate for monoprotic acids and bases. With this assumption, the retention coefficient depending on analyte ionisation is given by Eq. (8) [6]:

$$k = \frac{k_0 + k_1 d}{1 + d} \quad (8)$$

where:

- k_0 – protonated form retention coefficient,
- k_1 – non-protonated form retention coefficient,
- d – degree of protonation.

If the analyte occurs in a completely protonated form, then $k = k_0$, and if in a completely non-protonated form, then $k = k_1$. The degree of protonation depends on mobile phase pH and analyte pK_a :

$$d = 10^{pH - pK_a} \quad (9)$$

An similar equation for the retention coefficient depending on the degree of analyte ionisation for analytes which may have a double charge, such as diprotic acids or bases, and also amphoteric compounds (including sulfonamides) is the following [6]:

$$k = \frac{k_0 + k_1 d_1 + k_2 d_1 d_2}{1 + d_1 + d_1 d_2} \quad (10)$$

where:

- k_0 – protonated form retention coefficient, H_2L^+ ,
- k_1 – retention coefficient of a form without one proton (also the zwitterionic form), HL^\pm ,
- k_2 – anionic form retention coefficient, L^- ,
- d_1 and d_2 – coefficients which allow for the first and second pK_a value, respectively, $d_1 = 10^{pH - pK_{a1}}$, $d_2 = 10^{pH - pK_{a2}}$.

The pK_a values of the sulfonamides in the micellar environment, calculated using Eq. (11), have been used for the calculation [7].

$$K_{am} = K_a \frac{1 + K_{mA^-} M}{1 + K_{mHA} M} \quad (11)$$

where:

- K_{am} – dissociation constant in micellar solution,
- K_a – dissociation constant in aqueous solution,
- K_{mA^-} and K_{mHA} – association constants of respective forms (dissociated and non-dissociated) of the sulfonamide in micellar solution,
- M – SDS concentration less the cmc value.

The values of calculated pKa in micellar solution are listed in Table 2.

Table 2. Sulfonamide dissociation constants depending on SDS concentration.

pK _{a1} / pK _{a2}	H ₂ O	SDS, M				
		0.02	0.04	0.06	0.08	0.1
sulfacetamide	1.8 6.1	2.30 6.71	2.34 6.61	2.35 6.53	2.35 6.46	2.38 6.40
sulfanilamide	2.4 10.4	3.10 10.18	3.16 9.85	3.18 9.66	3.19 9.53	3.66 9.44
sulfamerazine	2.2 7.0	2.82 7.62	2.84 7.26	2.85 7.07	2.85 6.94	2.67 6.84
sulfathiazole	2.1 7.1	2.70 7.61	2.71 7.23	2.71 7.03	2.71 6.89	2.68 6.79
sulfamethazine	2.1 7.4	2.26 8.15	2.27 7.78	2.27 7.59	2.27 7.45	2.19 7.35
sulfafurazole	4.6 5.1	6.49 6.25	6.66 5.92	6.71 5.74	6.74 5.61	5.15 5.51
sulfadiazine	2.0 6.4	2.30 6.57	2.31 6.17	2.31 5.96	2.31 5.82	2.22 5.72
sulfachloropyridazine	1.9 5.1	2.29 5.26	2.29 4.84	2.29 4.63	2.30 4.49	2.24 4.39
sulfadimethoxine	1.8 6.2	2.47 7.01	2.50 6.65	2.51 6.45	2.51 6.31	1.87 6.21
sulfaproxiline	1.7 4.9	3.07 5.99	3.11 5.65	3.12 5.46	3.13 5.33	2.27 5.23
sulfamethoxazole	1.7 5.6	2.24 5.78	2.26 5.37	2.26 5.16	2.26 5.02	2.16 4.92
sulfamethizole	1.98 5.4	2.74 5.69	2.76 5.29	2.76 5.08	2.77 4.94	2.49 4.84

Equation (10) is appropriate and proven for simple eluents with fixed composition (such as methanol/water) and no additional electrostatic interactions.

Based on the equation, retention coefficients of the test sulfonamides have been calculated. Therefore, the chromatographic data obtained were used and retention coefficient k was determined based on the retention coefficients of the respective forms of each sulfonamide and their degrees of ionisation d . Using the quantities calculated with Equation (10), curves were plotted of the relationship between sulfonamide retention and micellar mobile phase pH, as shown in Figure 5. The course, shapes and slopes of the curves are consistent with the experimental curves shown in Figure 3(c). A reduced retention of the test compounds is observed with higher pH. The magnitude of the reduction increases when the pH value corresponding to the second dissociation constant is exceeded, whereby the analyte occurs in the anionic form and with repulsion with the C-18 phase, negatively modified by the surfactant. This reduction does not apply to sulfanilamide, for which pK_{a2} is approx. 10 and much exceeds the column operating range.

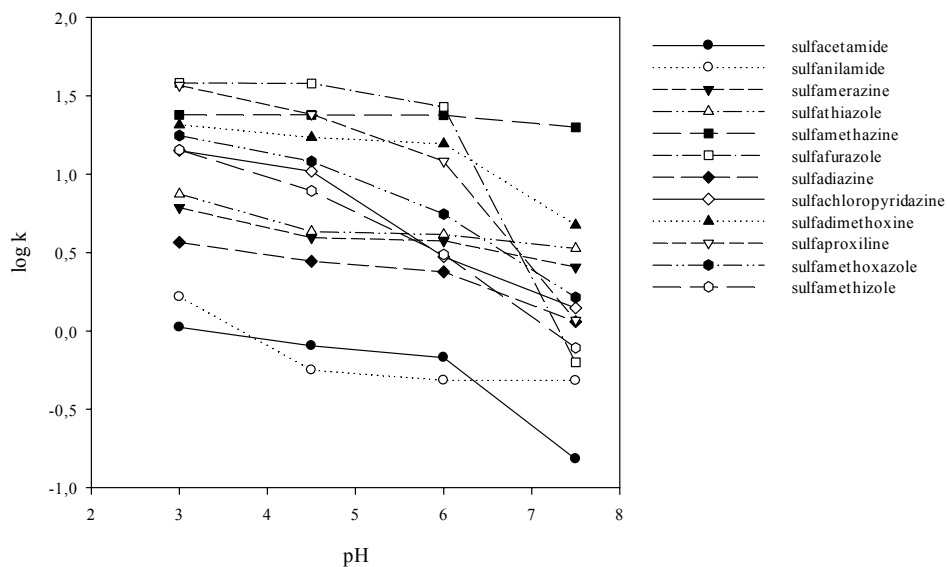


Fig. 5. Shape of sulfonamide retention curves as a function of mobile phase pH in MLC which include pK_{a1} and pK_{a2} of the test compounds. SDS concentration: 0.02 M.

Subsequently, the effect of the presence of SDS and the organic modifier on sulfonamide retention was tested. Therefore, correction for adjusting the retention coefficient was used; assuming a linear relationship between retention and SDS and organic modifier concentration, the correction is as follows [6]:

$$k = k_i 10^{-x/(1+x)} \quad (12)$$

where:

x – SDS concentration or ratio of the organic modifier and water volume.

When the correction is included, the equation for the relationship between retention and mobile phase pH and analyte pK_a for zwitterionic compounds which allows for SDS and organic modifier effects is the following:

$$k = \frac{10^{-x/(1+x)}}{1 + d_1 + d_1 d_2} (k_0 + k_1 d_1 + k_2 d_1 d_2) \quad (13)$$

Based on Equation (13), retention coefficients were calculated which include the presence of 0.02 M SDS in the mobile phase. The curves which only allow for mobile phase pH changes and analyte pK_a (according to Equation (10)) and the curves obtained using Equation (13) are shown in the same coordinate system (Figure 6).

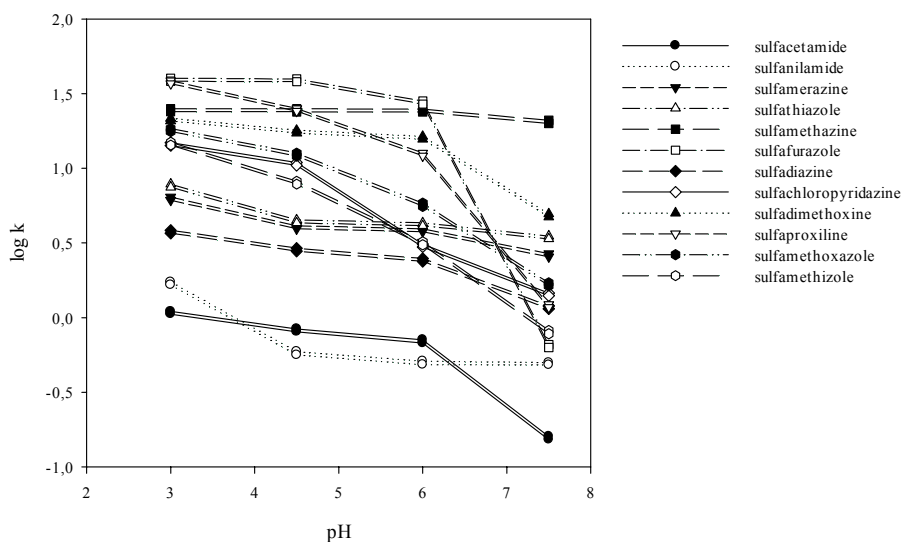


Fig. 6. Effect of 0.02 M SDS on sulfonamide retention curves as a function of mobile phase pH.

It follows from the curves in the figure that the effect of SDS concentration on retention is minor (bottom curves). The value of the correction is close to 1 and it may be omitted in the discussion. A similar conclusion can be drawn by comparing the curves in Figure 7. The effect of 2% organic modifier on retention is negligible. Changes in sulfonamide retention in the micellar mobile phase depend on the mobile phase pH changes and sulfonamide pK_a .

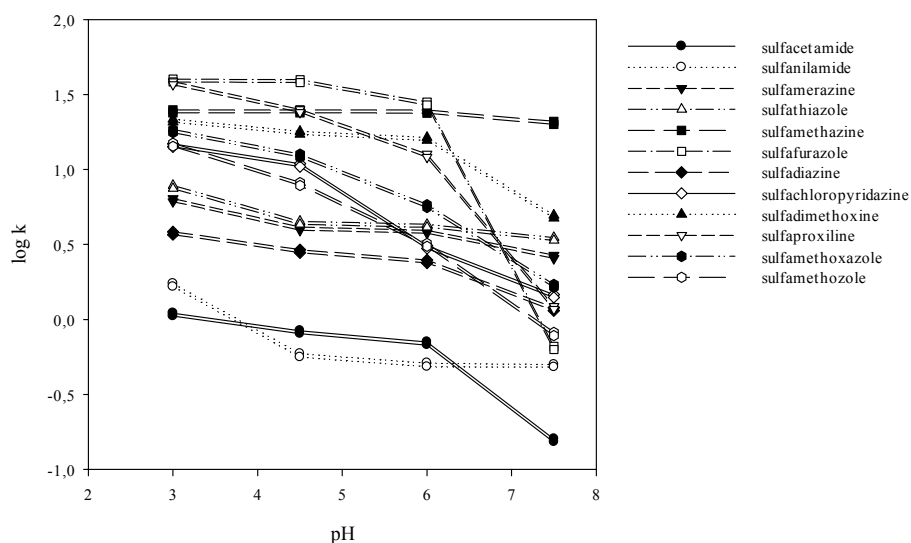


Fig. 7. Effect of 2% organic modifier on sulfonamide retention curves as a function of mobile phase pH.

CONCLUSIONS

Irrespective of the method of investigation, an analysis of the discussed sulfonamide retention mechanism in micellar liquid chromatography is sufficient for drawing the following conclusions:

- Sulfonamide retention on an anionic surfactant-modified stationary phase is based on hydrophobic and electrostatic interactions.
- The magnitude of hydrophobic interactions is maintained at a constant level. The effects of SDS and organic modifier concentration on retention are constant and they may be omitted from the discussion (Equation (13) and Figures 6 and 7).
- Ionic interactions are crucial for the retention of zwitterionic sulfonamides in MLC. This is proved by the results of retention coefficient calculations for Equations 10 and 13 and comparison of retention curves as a function of pH in Figures 5 to 7.
- The following factors are most important for retention in the test chromatographic system: micellar mobile phase pH and pK_a values which describe the analyte.

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