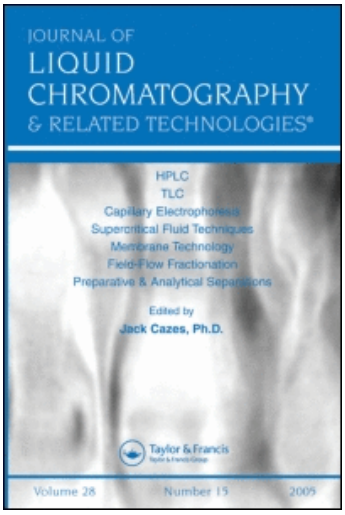

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NEURAL NETWORK CAPABILITY FOR RETENTION MODELING IN MICELLAR LIQUID CHROMATOGRAPHY WITH HYBRID ELUENTS

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ABSTRACT

Until date no papers have been reported about modeling studies in Micellar Liquid Chromatography by means of neural networks, only classical statistical methods have been used. In this work an overview into the capabilities of neural networks for modeling retention data in Micellar Liquid Chromatography is presented. To solve the problem of capacity factor modeling some parameters have been evaluated: type of activation function, number of neurons in the hidden layer and the use of some input and/or output data transformations. These studies have been carried out with the retention data for twenty-three compounds (benzene derivatives and polycyclic aromatic compounds) in an octyl silica column using micellar mobile phases containing CTAB (hexadecyltrimethylammonium bromide) as the surfactant and modified with n-propanol.

From the results obtained some considerations can be drawn. The selection of the activation function is very important to get good results and the best ones have been obtained when a linear activation function, a recurrent network and a logarithm transformation (logarithm of the capacity factor) have been used.

INTRODUCTION

Micellar Liquid Chromatography (MLC) with hybrid eluents is an attractive separation technique due to the versatility that surfactants confer to the chromatographic system and the possibilities of controlling selectivity and analysis time modifying both, the surfactant and/or the alcohol concentration in the mobile phase (alcohols are generally used as the organic modifier to avoid the efficiency lost obtained in its absence).

Moreover, some advantages can be cited when this technique is compared to conventional Reversed Phase Liquid Chromatography (RPLC): low cost and non-toxicity of surfactants *versus* expensive and flammable solvents of chromatographic grade,[1-4] unique selectivity,[4-9] compatibility of mobile phases with salts and water-insoluble compounds,[7] shorter equilibration times for gradient elution,[10] and detection enhancement.[11-15]

Until now, modeling of retention data has been performed by means of classical statistical methods such as multiple regression. Several equations that relate capacity factors with total surfactant and alcohol concentration have been evaluated. Thus, Torres Lapasió *et al.*[16] reported that for the catecholamines studied for them in mobile phases containing SDS (sodium dodecylsulphate) and propanol the best equation was as follows:

$$1 / k' = A\mu + B\varphi + C\mu\varphi + D \qquad (1)$$

where k' is the solute capacity factor, μ the total surfactant concentration, φ the alcohol volume fraction and A, B, C and D the equation parameters. Later, our investigation group[17] studied the capacity of retention prediction of some empirical equations when mobile phases containing CTAB or SDS as the surfactant and modified with n-propanol or n-butanol were used. Our results suggested that the following equation

$$1 / k' = A\mu + B\varphi^2 + C\varphi + D\mu\varphi + E \qquad (2)$$

was of more general applicability that the former (eq. 1) at least for the compounds studied for us (benzene derivatives and polycyclic aromatic compounds).

Although artificial neural networks have been developing for nearly 50 years[18] they were not implemented until now. These artificial neural networks can be applied to the resolution of a great variety of problems,[18] such as classification, modeling, association and mapping, as well as classical statistical methods or pattern-recognition methods (regression analysis, clustering methods, principal component methods, etc.); the main advantages are that the relationship between input and output data need not be specified in mathematical form and they are capable of modeling even nonlinear relationships. Moreover, some nets can associate; this means that they can recognize information although it is partial or distorted.

In this work, we are interested in investigating the capability of neural networks to model retention data in micellar liquid chromatography as a function of surfactant and alcohol concentrations, as a preliminary step to study their capacity of prediction and to compare with the statistical methods implemented earlier.

Our purposes in this paper are to study the influence of the architecture of the net (that is the way the individual neurons are connected), in particular, the node activation function, the layers number, and of some data transformations on the retention of twenty-three compounds (benzene derivatives and polycyclic aromatic compounds) in a C_8 column with micellar mobile phases containing CTAB as the surfactant and modified with n-propanol.

EXPERIMENTAL SECTION

Chromatographic Data

In this work retention data for twenty-three compounds obtained earlier,[17,19] in a C_8 column have been used. The solute capacity factors were determined in micellar mobile phases containing CTAB as the surfactant and modified with n-propanol. The mobile phases composition to obtain the experimental retention data used have been summarized in Figure 1.

Benzene derivatives and polycyclic aromatic hydrocarbons were as follows: (1) benzene, (2) benzylic 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) acenaphtylene, (22) acenaphthene, and (23) anthracene.

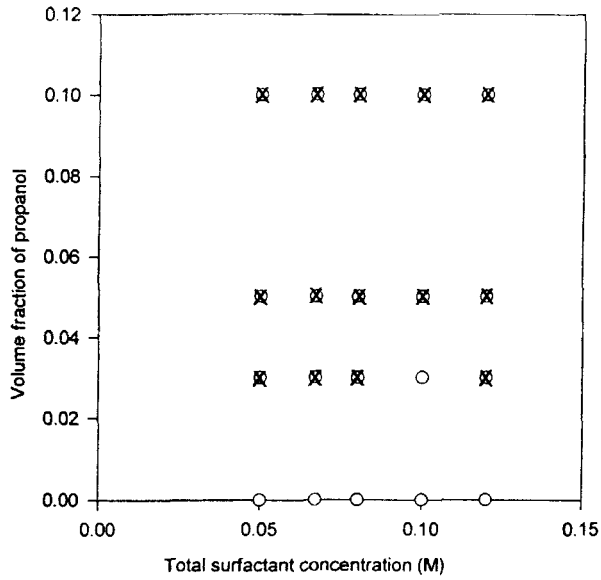

Figure 1. Mobile phase compositions for compounds 1 to 15 (○) and 16 to 23 (X).

Data Manipulation

Data manipulation was carried out by means of Microsoft Excel[20] and Neural Network Development Tool[21] software.

To study the capability of neural networks to model solute retention data in micellar liquid chromatography with hybrid eluents some parameters have been evaluated: (a) activation functions in the nodes of the hidden layer, (b) number of neurons in the hidden layer (one to three) and comparison with a recurrent link, and (c) data transformations (inverse and logarithm of capacity factors and the use of micellized surfactant concentration as input variable instead of total surfactant concentration).

Input data and output data files were created or transformed by means of Microsoft Excel and the neural network analysis was replicated five times because in nonlinear optimization studies often multiple minima can be found. The maximum number of iterations was fixed in 10000. Comparisons are always made by calculating the mean over capacity factor relative error (in absolute value) for all the mobile phases considered.

RESULTS AND DISCUSSION

The results will be presented in three different sections, although we must keep in mind that the results of the previous studies condition the latter. That is, in a first step some activation functions have been evaluated, so in the second section we have used the best function and then we have studied the influence of the number of neurons in the hidden layer and the use of a recurrent link. The third step comprises the studies achieved with data transformations, both output data transformations (k', 1/k', log k') and input data transformation (micellized surfactant concentration instead of total surfactant concentration).

A. Studies on the Activation Function in the Nodes of the Hidden Layer.

The activation functions in the nodes of the hidden layer that have been evaluated are the following:

$$y = \frac{1}{1+e^{-x}} \tag{3}$$

$$y = \frac{x}{|x|}\ln(1+|x|) \tag{4}$$

$$y = x \tag{5}$$

$$y = -1+\frac{2}{1+e^{-x}} \tag{6}$$

where y means the node output signal and x the total node input signals. These functions will be identified as 1, 2, 3, and 4, respectively, in the discussion of the results obtained. In these studies, the linear function (eq.(5)) has been the activation function in the input and the output layer.

The input data for the network are the total surfactant concentration in the mobile phase (M) and the volume fraction of n-propanol in the mobile phase and the output data in this section is the capacity factor (k'). The network in this step of the study consisted of an input layer, a hidden layer (with one neuron) and an output layer.

In Figure 2 the mean relative error (in absolute value)(calculated as $((k'_{cal}-k'_{exp})/k'_{exp})*100$) is plotted for every compound and for the four activation functions. As can be observed the lowest errors have been obtained with the activation function

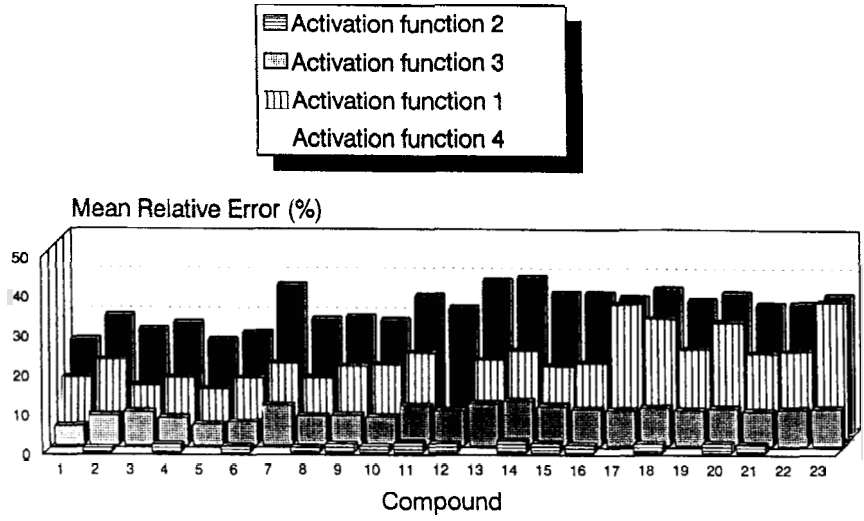

Figure 2. Mean relative errors (in absolute value) for every compound using different activation functions in the nodes of the hidden layer.

2 but it has not been considered the best function because for many compounds the parameter convergence has not been produced after 10000 iterations. The compounds for which there was not a solution are 1, 3, 5, 7, 13, 17, 19, 22 and 23.

The activation function that has been considered as the best is the linear function (y = x) because although greater errors than with function 2 have been obtained it is always possible to find a solution (parameter convergence). For the other functions (1 and 4) the errors are very important and at the same time of the five assays with the network and the same data, the solutions obtained are different. For example, it can be cited that for the compound number 4 and the activation function 1, the mean relative errors (in absolute values) are respectively 19.66 %, 24.61 %, 17.52 %, 15.38 % and 19.22 %. These data have been obtained after 5, 4, 10, 7 and 5 iterations respectively.

B. Number of Neurons in the Hidden Layer

In Figure 3 the different networks that have been evaluated are represented. It can be observed that the input and the output layers are the same and the differences between them consist in the number of neurons in the hidden layer (Figures 3a, 3b and 3c) and the use of a recurrent link in Figure 3d.

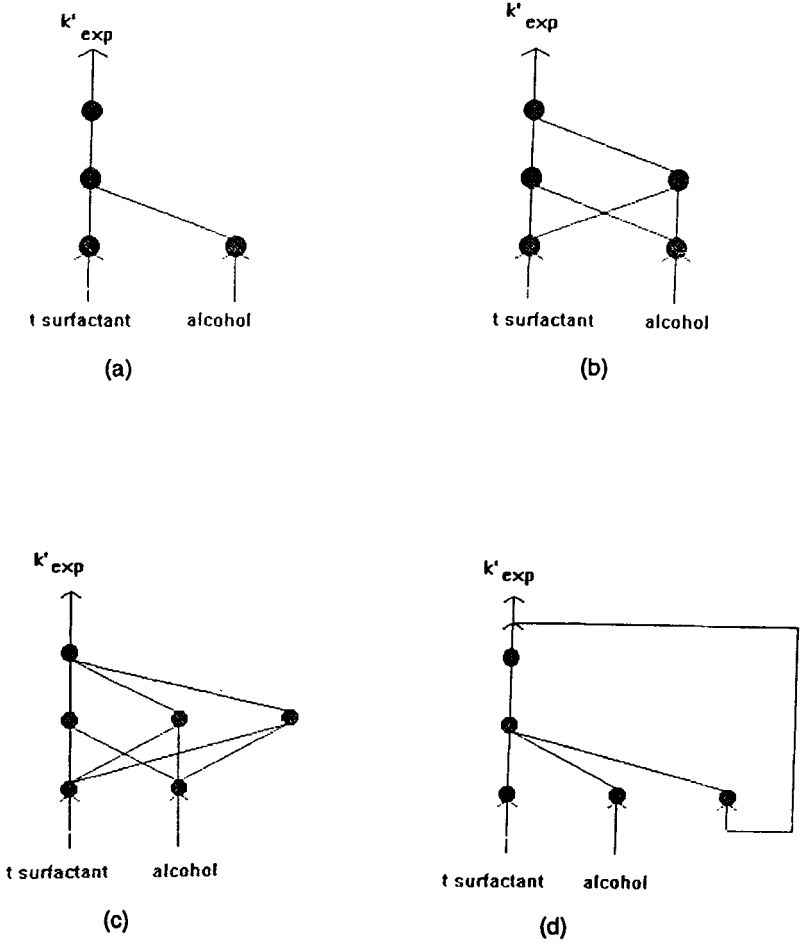

Figure 3. Architecture of the networks employed.

For all the assays a linear activation function in the different layers is used. The results of these studies are shown in Table 1. The mean relative errors for compounds are tabulated for the networks shown in Figure 3 (with one, two and three neurons in the hidden layer and with the recurrent link).

Table 1

Mean Relative Error (%) for Every Compound and for the Networks Shown in Figure 3

Compound	1 Neuron	2 Neurons	3 Neurons	Recurrent Link
1	4.96	4.96	4.96	3.22
2	7.52	7.52	7.52	4.78
3	8.54	8.54	8.54	3.64
4	7.04	7.04	7.04	4.50
5	5.39	5.39	5.39	4.00
6	5.94	5.94	5.94	4.13
7	10.12	10.12	10.12	7.74
8	7.49	7.49	7.49	5.36
9	7.68	7.68	7.68	4.82
10	7.23	7.23	7.23	5.35
11	10.16	10.16	10.16	7.74
12	8.84	8.84	8.84	5.50
13	10.70	10.70	10.70	8.25
14	11.32	11.32	11.32	8.40
15	9.96	9.96	9.96	6.86
16	9.18	9.18	9.18	5.31
17	9.02	9.02	9.02	5.19
18	9.59	9.59	9.59	5.60
19	8.99	8.99	8.99	5.14
20	9.46	9.46	9.46	5.29
21	8.76	8.76	8.76	4.95
22	9.10	9.10	9.10	5.22
23	9.38	9.38	9.38	5.38

The mean relative errors for networks with one, two and three neurons in the hidden layer are the same, so it seems that the number of neurons does not influence the errors obtained. These errors ranged from 4.96 % (for compound 1) to 11.32 % (for compound 14).

When a network with a recurrent link is used for the capacity factor modeling an important decrease in the mean relative error is obtained. Thus, the ratio between the relative errors obtained with the network with one neuron and the recurrent link ranged from 1.3 (for compound 5) to 2.35 (for compound 3).

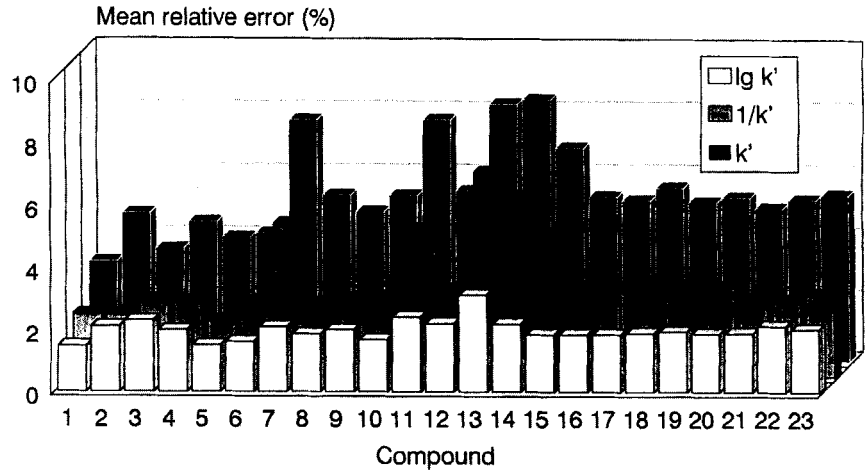

Figure 4. Mean relative errors (in absolute value) for the different compounds studied when k', 1/k' and log k' are used as the output data.

From the results presented in this section it can be concluded that by means of networks with recurrent links a great improvement in the capability of retention modeling is obtained.

C. Data Transformations.

The studies of data transformations have been carried out by using the linear activation function in the nodes of the hidden layer and the network shown in Figure 3d.

In a first step some transformations of the output data have been evaluated, that is, k', 1/k' and log k' are the output of the net. In Figure 4 the mean relative errors for compounds one to twenty-three are shown. It can be observed that both, inverse and logarithm transformations significantly improve the errors obtained with respect to that shown when k' is the output of the net. The best results were achieved when the logarithm of the capacity factors is used as the output data. Thus, it can be cited that the errors are clearly low and ranged from 1.46 % (for compound 1) to 3.13 % (for compound 13).

For the inverse transformation, errors ranged from 1.80 % to 6.58 %, that is, sometimes a ratio of more than two is found when inverse and logarithm transformation are compared.

Table 2

Comparison of Mean Relative Errors for Compounds when Total Surfactant Concentration in the Mobile Phase and Micellized Surfactant Concentration are used as the Input Data

Compound	Total Surf. Concentration (M)	Micellized Surf. Concentration (M)
1	1.46	1.47
2	2.11	2.13
3	2.30	2.31
4	1.99	1.99
5	1.49	1.51
6	1.61	1.63
7	2.09	2.10
8	1.86	1.88
9	2.00	2.00
10	1.67	1.68
11	2.42	2.44
12	2.20	2.19
13	3.13	3.14
14	2.19	2.19
15	1.84	1.85
16	1.84	1.84
17	1.84	1.85
18	1.89	1.88
19	1.94	1.95
20	1.88	1.88
21	1.89	1.90
22	2.14	2.14
23	2.03	2.04

Then, by using the logarithm of the capacity factor as the output data we have compared the results obtained when the input data are micellized surfactant concentration (total surfactant concentration *minus* the critical micellar concentration) and the alcohol volume fraction to the previous data (in which total surfactant concentration and alcohol volume fraction have been used as the input data).

Table 2 groups the mean relative errors for compounds, when total surfactant concentration in the mobile phase and micellized surfactant concentration are used as the input data. The error values show that there are not significative differences when both total surfactant concentration and micellized surfactant concentration are used as the input data. Equal or slightly greater errors are obtained when micellized surfactant concentration is used, so we propose the use of total surfactant concentration as the input data together with the n-propanol volume fraction.

From the results presented in the discussion, we propose the use of the linear activation function ($y = x$) in the nodes of the hidden layer, the network with the recurrent link and the logarithm transformation of the output data to achieve the retention modeling in micellar liquid chromatography, at least for the compounds studied, and the mobile phases considered.

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