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Influence of the stationary and mobile phase composition in ideal chromatographic systems on the log *k* values in column chromatography. I. ODS/methanol–water system

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On the basis of the literature data it was established that in the case of ODS column chromatography with methanol as modifier the value log x_s/x_1 (where x_s and x_1 denote methanol mole fractions in the stationary and the mobile phase, respecitvely) is a linear function of the corresponding Bosch's P_m^N parameter as well as of the log *k* value of the investigated substances. It was also found that the phase equilibrium in the system ODS/methanol-water is in accordance with the Everett's equation for ideal systems (K = 10.88). Finally, a linear relationship between the log x_s/x_1 values and the volume fraction of methanol (φ) was found in the range of 0.5–1.0, which corresponds to the linear part of the function log k = f(φ), established experimentally by other authors.

Keywords: C_{18} liquid chromatography, stationary phase composition, mobile phase composition, capacity factors, P_m^N parameter, log *k* pair linearity rule, proportionality rule, RPP scale.

INTRODUCTION

In studying the behaviour of a great number of different compounds by column chromatography on ODS with methanol and acetonitrile as modifiers, Bosch *et al.*[1] concluded that these compounds have a common P_m^N scale for each modifier, *i.e.,* that the log *k* values of the examined compounds are a linear function of the corresponding P_m^N values. The complete physicochemical meaning of this parameter is according to the authors difficult to establish. It is partially related to the E_T (30) polarity parameter (20–100 % v/v of methanol), and partially to the log *k* values of the investigated substances.

On the other hand, applying the R_M (or log *k*) pair linearity rule and the Proportionality rule[2–4] to the log *k* values obtained in the described systems for several groups of compounds, we established the existence of a common RPP scale with re-

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spect to which the log k values, with few exceptions, are a good linear function.[5] The RPP scale is related to the average log k values obtained for a group of the investigated substances. In both cases the individual properties of the substances affect only the slope and intercept of the straight lines obtained in such a way.

Finally, in a recently published paper, Nasuto *et al.*[6] claimed that the change in the mobile phase composition leads to a change in the column packing. To show how such a change affects the log k values of the examined aromatic hydrocarbons they determined, *inter alia,* the functional dependence of methanol mole fraction in the surface phase (x_s) *vs.* its mole fraction in the mobile phase (x_1) on silica gel Si 100 ODS. Thereby it was found that the log k values were not a linear function of either the x_s or x_1 values, although in the last case two linear regions with different slopes were observed.

On the basis of the above, we assumed that the x_s and x_1 values are essential characteristics of the stationary and mobile phase, respectively, and therefore log x_s/x_1 could be a linear function of the log k values, that can be defined as log $k = m_s/m_1$ (where m_s and m_1 designate the mass of the substance being separated in the stationary and mobile phase, respectively).[7] If such a hypothesis were to be correct and to have a broad significance in the investigated system, a linear dependence between log x_s/x_1 and P_m^N should be expected. The verification of this is the subject of this paper.

RESULTS AND DISCUSSION

As the first step, for each x_1 value the corresponding log x_s/x_1 and P_m^N values were calculated (the log x_s/x_1 values were calculated on the basis of the x_s and x_1 values given in the Nasuto's *et al.* diagram[6] and the P_m^N values were calculated by means of Eq. (13) given in the Bosch's *et al.* paper,[1] with preliminary conversion of the x_1 values into volume fractions). The results of these calculations are given in Table I.

TABLE I. Comparative review of the x_1, log x_s/x_1 and P_m^N values

x_1	0.025	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
log x_s/x_1	0.938	0.865	0.727	0.554	0.435	0.340	0.259	0.192	0.136	0.0859	0.0436
P_m^N	0.929	0.866	0.757	0.590	0.469	0.377	0.305	0.247	0.200	0.159	0.125

It was established using linear regression analysis that the log x_s/x_1 values over the whole region examined ($x_1 = 0.025 – 0.9$) represent a very good linear function of the P_m^N values (Fig. 1), proved by the regression data obtained:

$$\log x_s/x_1 = 1.0912\ P_m^N - 0.0824 \qquad (1)$$

$$(n = 11,\ r = 0.9996,\ s = 8.93\times10^{-3}).$$

Since tle log k values obtained in ODS column chromatography are linear function of the P_m^N parameter, which has been confirmed by a great number of

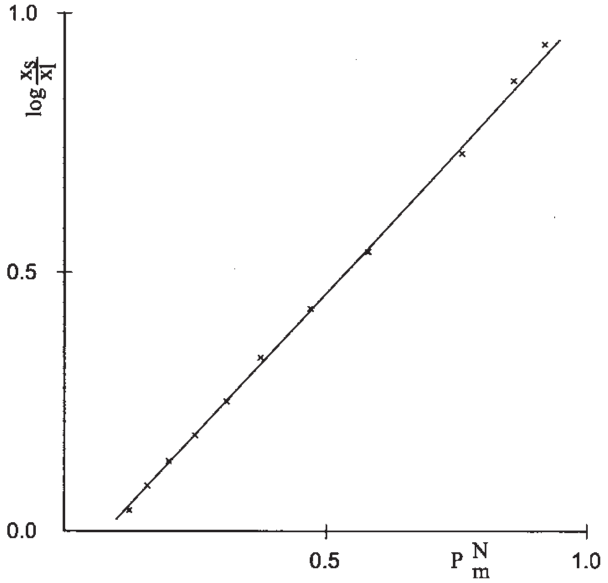

Fig. 1. Graphical presentation of the linear function $\log x_s/x_l = f(P_m^N)$.

compounds over the entire concentration range of methanol in the mobile phase (0–100 % v/v),[1] it should be expected that our parameter $\log x_s/x_l$ (named system parameter, *SP*, because it contains the mole fractions of methanol in both phases) is also in linear correlation with the $\log k$ values of the examined substances. In order to confirm this we chose the $\log k$ values determined for some aromatic hydrocarbons by Nasuto *et al.,*[6] as well as those for phenol and some of its derivatives and nitrobenzene obtained by Bosch *et al.*[1] The results obtained are given in Table II and Figs. 2 and 3. They confirm a good linear dependence of the function: $\log k = f(\log x_s/x_l)$ for all the examined compounds, over a wide range of $\log x_s/x_l$ values (from 0.044 till 0.864). The only exception is the point $x_l = 0.1$ for benzene which is considerably lower than the expected regression value.

On the basis of the above, it can be concluded that the *SP* values for a series of x_l, as given in Table I, actually represent a system scale with respect to which the $\log k$ values of the examined substances are a linear function.

The obtained scale is evidently the consequence of the found dependence $x_s = f(x_l)$, which is in full accordance with the corresponding ideal phase system equilibrium:

$$(\text{methanol})_l + (\text{water})_s = (\text{methanol})_s + (\text{water})_l$$

For such an equilibrium, the following Everett equation[8] can be applied:

$$x_s/x_l = K/x_l(K-1) + 1 \qquad (2)$$

(K denotes the equilibrium constant). By rearrangement of this equation the following relationship is obtained:

$$(x_l)^{-1} = K(x_s)^{-1} + 1-K \qquad (3)$$

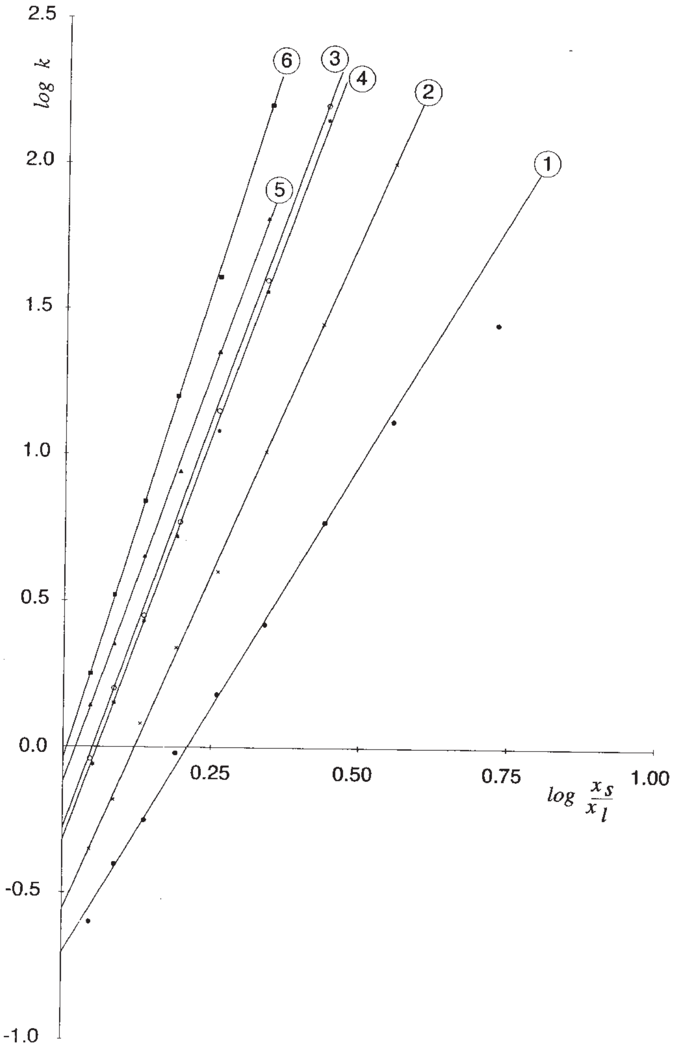

Fig. 2. Graphical presentation of the linear function log k = f(log x_s/x_l) for the compounds having the same numbers as in Table II.

which gives rise to the linear correlation $(x_l)^{-1} = f(x_s)^{-1}$. Using the x_l and x_s values obtained by Nasuto *et al.*[6] a very good correlation ($r = 0.9999$, $n = 11$) was found and the corresponding K value, obtained from the slope and intercept of the regression line, amounted to 10.88±0.05. By taking the logarithm of Eq. (2) and substituting K for 10.88, a new equation is obtained, which enables the calculation of SP on the basis of the corresponding x_l values:

$$SP = \log x_s/x_l = \log [K/x_l(K-1)+1] = \log 10.88/9.88\, x_l + 1 \qquad (4)$$

Using linear regression analysis, the following correlation between the experimental SP parameters and those calculated by means of Eq. (4) was obtained:

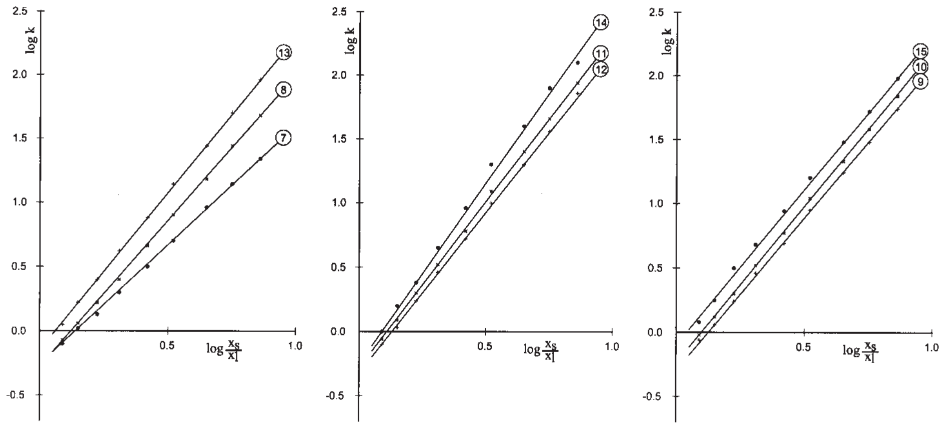

Fig. 3. Graphical presentation of the linear function log k = f(log x_s/x_l) for the compounds having the same numbers as in Table II.

$$(SP)_{calc} = 1.0032\,(SP)_{exp} + 0.0017 \qquad (5)$$

$$(n = 11,\ r = 0.9999,\ s = 4.27\times10^{-3})$$

On the basis of the regression data obtained (the slope has the value very close to 1 and the intercept very close to zero), it can be concluded that the experimental and theoretical SP parameters are in good agreement.

As is known, in RPLC on ODS with methanol-water as the mobile phase, the function log k = f(φ) is used for various investigations in the methanol volume frac-

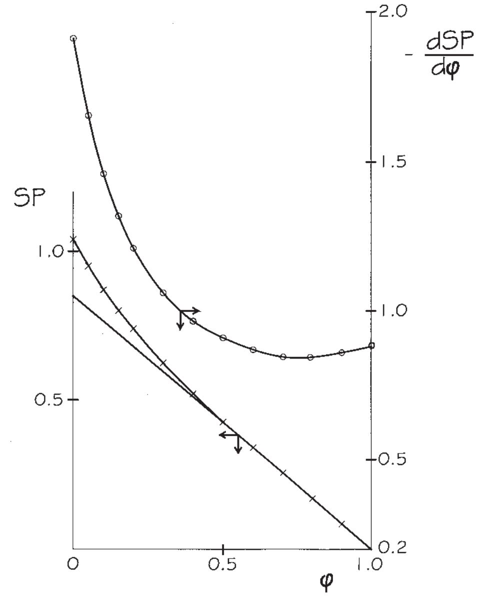

Fig. 4. Functional correlation of the SP and differential quotient d(SP)/dφ, respectively, with the methanol volume fraction (φ) in the methanol–water mixture.

tion (φ) range in which this correlation is very close to linearity.[9,10] For this reason it is of interest to consider the functional correlation $SP = \mathrm{f}(\varphi)$.

TABLE II. Regression data of the linear function $\log k = \mathrm{f}(\log x_s/x_1)$

No.	Compound	–Inter.	Slope	r	$s\times10^2$	n	Conc. range (log x_s/x_1 range)*
1	Benzene	0.7003	3.3401	0.9988	2.91	8	0.2–0.9 mole fr. (0.044–0.554)
2	Naphthalene	0.5632	4.5980	0.9998	1.63	8	ditto
3	Anthracene	0.3016	5.6664	0.9995	2.52	7	0.3–0.9 mole fr. (0.044–0.435)
4	Phenanthrene	0.3262	5.5941	0.9992	3.15	7	ditto
5	Pyrene	0.1212	5.6736	0.9997	1.54	6	0.4–0.09 mole fr. (0.044–0.340)
6	Chrysene	0.0424	6.5257	0.9997	2.26	6	ditto
7	Phenol	0.2892	1.8966	0.9992	2.06	9	10–90 % v/v (0.089–0.864)
8	4-Nitrophenol	0.3128	2.3125	0.9992	2.51	9	ditto
9	3-Nitrophenol	0.3084	2.3834	0.9997	1.59	9	ditto
10	2-Methylphenol	0.2574	2.4541	0.9998	1.33	9	ditto
11	2-Chlorphenol	0.3065	2.6207	0.9994	2.47	9	ditto
12	2,4-Dinitrophenol	0.3452	2.5489	0.9998	1.39	9	ditto
13	2-Nitrophenol	0.1574	2.4785	0.9998	1.35	9	ditto
14	3-Chlorphenol	0.2529	2.8219	0.9986	4.06	9	ditto
15	Nitrobenzene	0.1038	2.4382	0.9992	2.65	9	ditto

*The $\log x_s/x_1$ values for the compounds 7–15 were calculated from the corresponding P_m^N values[1] using the regression Eq. (1)

By differentiation of Eq. (4), as well as of the equation used for the calculation of the φ from x_1: $\varphi = Ax_1/x_1\,(A–1) + 1$ with respect to x_1 and combining both derivatives, the following equation is obtained:

$$d(SP)/d\varphi = -\,0.434\,K'(1-x_1+Ax_1)^2/A(x_1\,K'+1) \qquad (6)$$
$$(K' = (K-1) = 9.88,\ A = 2.2457).$$

From Fig. 4 (the right scale) it is clear that the differential quotient $d(SP)/d\varphi$ changes when φ changes, but these changes are relatively so small over the interval 0.5–1.0 that the function $SP = \mathrm{f}(\varphi)$ can be considered almost linear over this interval (Fig. 4 the left scale). By the application of linear regression analysis to this interval one obtains:

$$SP = -0.8552\varphi + 0.8546 \qquad (7)$$
$$(r = -0.99998;\ n = 11;\ s = 8.96\times10^{-4}).$$

A similar φ range over which it is possible to apply the function log $k = f(\varphi)$ was also found experimentally by Harnisch *et al.*[9] and Jandera.[10] This means that this relation can be used to determine the straight line intercept (*i.e.,* the log k value for $\varphi = 0$) when relatively great extrapolations are needed, for example during, examination of the congenerity of compounds, as well as lipophilicity determinations of examined substances. Because of this it is quite clear that the *SP* scale has an advantage over the earlier described φ scale.[9,10]

ИЗВОД

УТИЦАЈ САСТАВА СТАЦИОНАРНЕ И МОБИЛНЕ ФАЗЕ У ИДЕАЛНИМ ХРОМАТОГРАФСКИМ СИСТЕМИМА НА log *k* ВРЕДНОСТИ У ХРОМАТОГРАФИЈИ НА КОЛОНИ. I. СИСТЕМ ОДС/МЕТАНОЛ-ВОДА

ТОМИСЛАВ Ј. ЈАЊИЋ, ГОРДАНА ВУЧКОВИЋ и МИЛЕНКО Б. ЋЕЛАП

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На основу литературних података утврђено је да у случају хроматографисања на колони од октадецил – силика-гела (ОДС) метанолом као модификатором вредности log x_s/x_1 (где x_s и x_1 представљају молске фракције метанола у стационарној и мобилној фази) јесте линеарна функција одговарајућег Бошовог параметра P_m^N као и log k вредности изучаваних супстанци. Такође је нађено да је фазна равнотежа у систему ОДС/метанол–вода у складу са Еверетовом једначином за идеалне системе ($K = 10,88$). Најзад, нађена је линеарна зависност између log x_s/x_1 и запреминских фракција метанола (φ) у опсегу 0,5–1,0, што одговара линеарном делу функције log $k = f(\varphi)$, експериментално нађеном од стране других аутора.

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