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 \( \log w/x_1 \) (where \( w \) and \( x_1 \) denote methanol mole fractions in the stationary and the mobile phase, respectively) 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 \( \log w/x_1 \) values and the volume fraction of methanol \( (\varphi) \) was found in the range of 0.5–1.0, which corresponds to the linear part of the function \( \log k = f(\varphi) \), established experimentally by other authors.

Keywords: C18 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-
spect to which the log k values, with few exceptions, are a good linear function. 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. 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). 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 and the P_m^N values were calculated by means of Eq. (13) given in the Bosch's *et al.* paper, with preliminary conversion of the x_1 values into volume fractions). The results of these calculations are given in Table 1.

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

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:

\[ \log x_s/x_1 = 1.0912 P_m^N - 0.0824 \]  

\[ (n = 11, r = 0.9996, s = 8.93 \times 10^{-3}). \]

Since the 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
compounds over the entire concentration range of methanol in the mobile phase (0–100 % v/v),¹ it should be expected that our parameter \( \log x_g/x_1 \) (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: \( \log k = f(\log x_g/x_1) \) for all the examined compounds, over a wide range of \( \log x_g/x_1 \) values (from 0.044 till 0.864). The only exception is the point \( x_1 = 0.1 \) 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 \( x_1 \), 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 \( x_g = f(x_1) \), which is in full accordance with the corresponding ideal phase system equilibrium:

\[
\text{(methanol)}_1 + \text{(water)}_s = \text{(methanol)}_s + \text{(water)}_1
\]

For such an equilibrium, the following Everett equation⁸ can be applied:

\[
x_g/x_1 = K/x_1(K-1) + 1 \tag{2}
\]

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

\[
(x_1)^{-1} = K(x_g)^{-1} + 1-K \tag{3}
\]
which gives rise to the linear correlation \((x_1)^{-1} = f(x_g)^{-1}\). Using the \(x_1\) and \(x_g\) 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 \(x_1\) values:

\[
SP = \log x_g/x_1 = \log [K/x_1(K-1)+1] = \log 10.88/9.88 x_1 + 1
\]  

(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 $\log k = f(\log \chi_0/\chi)$ for the compounds having the same numbers as in Table II.

$$\left( SP \right)_{\text{calc}} = 1.0032 \left( SP \right)_{\text{exp}} + 0.0017$$

$$\left( n = 11, \quad r = 0.9999, \quad s = 4.27 \times 10^{-3} \right)$$

(5)

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 $\log k = f(\varphi)$ is used for various investigations in the methanol volume frac-
tion (φ) range in which this correlation is very close to linearity.\textsuperscript{9,10} For this reason it is of interest to consider the functional correlation $SP = f(φ)$.

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

*The log $x_c/x_1$ values for the compounds 7–15 were calculated from the corresponding $P_{\text{P}10}$ values\textsuperscript{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 $x_1$: $φ = A x_1 / x_1 (A-1) + 1$ with respect to $x_1$ and combining both derivatives, the following equation is obtained:

$$
d(\phi) d(φ) = -0.434 K' (1-x_1 + Ax_1)^2 / A (x_1 K'-1)$$

$$(K' = (K-1) = 9.88, A = 2.2457).$$

From Fig. 4 (the right scale) it is clear that the differential quotient $d(φ)$ changes when $\phi$ changes, but these changes are relatively so small over the interval 0.5–1.0 that the function $SP = f(φ)$ 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:

$$SP = -0.8552φ + 0.8546$$

$(r = -0.99998; n = 11; s = 8.96 \times 10^{-4}).$
A similar $\varphi$ range over which it is possible to apply the function $\log k = f(\varphi)$ was also found experimentally by Harnisch et al.\textsuperscript{9} and Jander.\textsuperscript{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 congenersity 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 $\varphi$ scale.\textsuperscript{9,10}

**ИЗВОД**

**УТИЦАЈ САСТАВА СТАЦИОНАРНЕ И МОБИЛНЕ ФАЗЕ У ИДЕАЛНИМ ХРОМАТОГРАФСКИМ СИСТЕМИМА НА $\log k$ ВРЕДНОСТИ У ХРОМАТОГРАФИИ НА КОЛОНИ: 1. СИСТЕМ ОДС/МЕТАНОЛ-ВОДА**

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На основу литературних података утврђено је да у случају хроматографисања на колони од октацел — силика-гела (ОСС) метанолом као модификатором вредности $\log \chi_0/\chi_1$ (где $\chi_0$ и $\chi_1$ представљају моларне фракције метанола у стационарној и мобилној фази) јесте линеарна функција одговарајућег Боновог параметра $P_n^{W}$ као и $\log k$ вредности изучаваних супстанци. Такође је нађено да је фаза равнотежа у систему ОСС/метанол-вода у складу са Евереттовом једначином за идеалне системе ($K = 10.88$).

Најзад, нађена је линеарна зависност између $\log \chi_0/\chi_1$ и запреминских фракција метанола ($\varphi$) у опсервацији 0.5–1.0, што одговара линеарном делу функције $\log k = f(\varphi)$, експериментално нађеном од стране других аутора.

(Примљено 38. јул 2000)

**REFERENCES**