

Influence of the composition of the stationary and mobile phase on the retention factors and solvent strength parameters in RP chromatographic systems in which the Everett equation is valid

T. J. JANJIĆ[#], G. VUČKOVIĆ^{*#} and M. B. ČELAP[#]

Faculty of Chemistry, University of Belgrade, P. O. Box 158, YU-11001 Belgrade, Yugoslavia

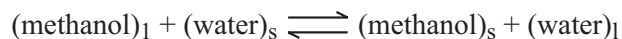
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It is shown how in RP chromatography the Everett equation for ideal phase equilibria can be used to estimate *SP* values ($SP = \log x_s/x_1$, x_s and x_1 denoting the modifier mole fractions in the stationary and mobile phases, respectively) which are in a linear dependence with the $\log k$ values. The described procedure includes the determination of the approximate phase equilibrium constant *K*. By analysis of the Everett equation it was found that in the field of x_1/K there are regions of linear dependence of the *SP* parameter or $\log k$ values and the mole fraction of modifiers or its logarithm. Consequently, only in these regions it is possible for two different chromatographic systems to have the same solvent strength scale: x_1 or $\log x_1$.

Keywords: Everett equation, RP column chromatography, capacity factor, *SP* parameter.

INTRODUCTION

In a recently published paper¹ it was demonstrated that in the case of C₁₈ column chromatography with a methanol/water mobile phase the $\log k$ values are a linear function of the system parameter (*SP*), which represents the logarithm of the quotient of the methanol mole fractions in the stationary and in the mobile phases: $\log x_s/x_1$. Therefore, the *SP* values for a series of x_1 values represent a *SP* scale. In the same paper, after considering the functional dependence $x_s = f(x_1)$, it was concluded that this is in accordance with an ideal phase equilibrium:



to which, on the basis of the Everett equation,² the phase equilibrium constant (*K*) equal to 10.88 corresponds. This led us to assume that there are some other chromatographic systems for which the theoretical system scales for different *K* values can be calculated using the Everett equation. If there is a good linear correlation between the average $\log k$ values of a compound group and a *SP* scale for some *K*

[#] Serbian Chemical Society active member.

^{*} Author for correspondence (Fax: +381-11-638-785, E-mail: evuckogo@ubbg.etf.bg.ac.yu)

value, the following would be possible: 1) to conclude that the investigated chromatographic system behaves in accordance with the Everett equation for an ideal phase equilibrium; 2) to determine the approximate value of the equilibrium constant K and, at the same time, the functional dependence: $x_s = f(x_1)$ as well as 3) to show that SP scales can be applied in such chromatographic systems. The aim of the work reported in this paper was to check the above-mentioned assumptions.

RESULTS AND DISCUSSION

By taking the logarithm of Eq. (29) from Everett's paper² one obtains:

$$SP = \log x_s/x_1 = \log \{K/[x_1 (K-1) + 1]\} \quad (1)$$

This equation enables the calculation of theoretical system scales for different K values. The scale exhibiting the best linear correlation with average $\log k$ values of the investigated group of compounds (for which is previously established common RPP solvent strength scale¹) corresponds to constant K . Due to its significance, Eq. (1) will be considered in detail.

By differentiation Eq. (1) one obtains:

$$d(SP)/d x_1 = -0.43 (K-1) / [x_1 (K-1) + 1] \quad (2)$$

and as:

$$d x / d \log x_1 = 2.3 x_1$$

the following is obtained:

$$d(SP)/d \log x_1 = - [x_1 (K-1)] / [x_1 (K-1) + 1] \quad (3)$$

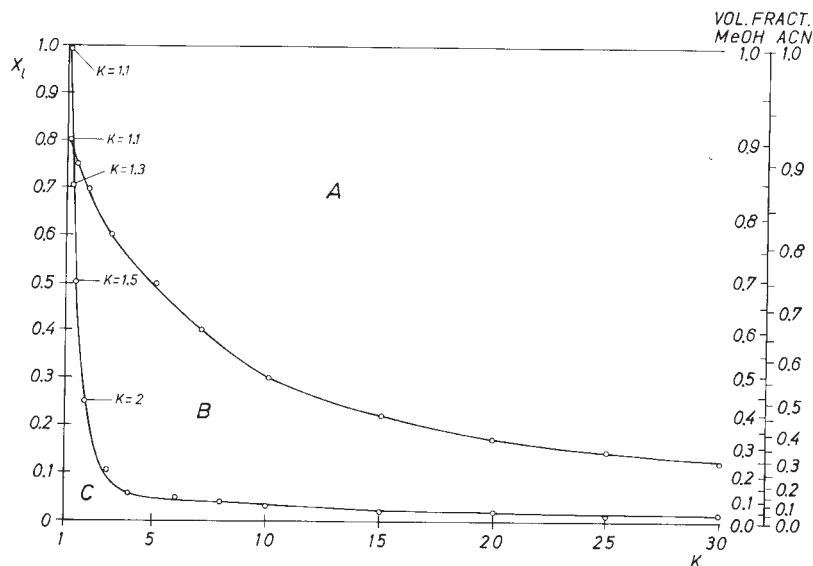


Fig. 1. Regions of the theoretical system scales in which a linear dependence of the SP parameters versus $\log x_1$ (zone A) of x_1 (zone C) exists.

Since neither of the two above-mentioned differential quotients is constant when x_1 is changed, it can be concluded that the SP parameter has, strictly speaking, no linear segments neither in the x_1 nor in the $\log x_1$ scale. However, there are x_1 regions (depending on the value of K) in which these quotients change only a little; in these regions the SP parameter can be considered as a linear function of the x_1 value or $\log x_1$, respectively. To make a clear distinction among these regions, linear regression analysis was applied, the only criterion being r higher than or equal to 0.9996 (Fig. 1). For the construction of this diagram, x_1 values in the interval of 0.001 to 0.05 were used, depending on the need for a better distinction of zones ($n = 8$ to 26). From Fig. 1 it is obvious that the greater part of the field x_1 vs. K belongs to zone A, in which there is a linear dependence of the SP parameter on $\log x_1$. There is a much smaller zone C, where the linearity of SP vs. x_1 exists and, finally, there is an intermediate zone B.

All the above mentioned is also valid for $\log k$ values, as well as for those "solvent strength parameters" which are linearly related to the SP parameters. In zone A there is often a linear dependence between the $\log k$ values and the volume fraction of modifier (φ), which is a consequence of the fact that in the significant x_1 regions (which depends on the modifier used) there is a linear dependence $\log x_1 = f(\varphi)$, which can be proved as follows. The following relation between φ and x_1 values exists:

$$\varphi = x_1 A / [x_1 (A-1) + 1] \quad (4),$$

where A is the quotient of the molar volumes of the modifier and water. By differentiation of this equation with respect to $\log x_1$, the following is obtained:

$$d\varphi/d \log x_1 = 2.3 A x_1 / (1 - x_1 + A x_1)^2 \quad (5).$$

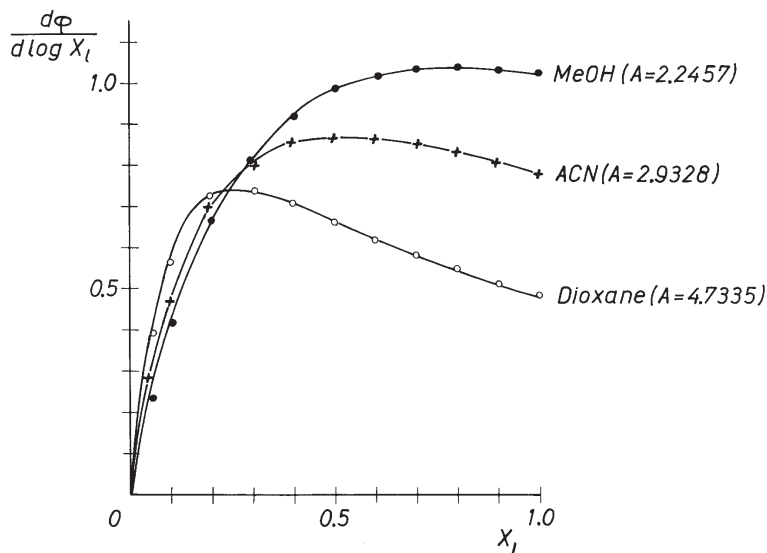


Fig. 2. Functional dependence of the differential quotient $d\varphi/d \log x_1$ on x_1 . The values for A : MeOH 2.2457; ACN 2.9328; dioxane 4.7335.

By the analysis of this equation, it can be concluded that the function $\varphi = f(\log x_1)$ is non-linear, but that there are significant φ ranges in which the differential quotient $d\varphi/d \log x_1$ changes only slightly with respect to the found mean value (Fig. 2). By application of linear regression analysis, the limits of these approximate linear functions for MeOH, ACN and dioxane were determined: MeOH: $\log x_1 = 1.0134 \varphi - 1.0078$ (φ from 0.5–1.0; $x_1 = 0.31 - 1.0$; $r = 0.9995$; $n = 11$; $s = 5.06 \times 10^{-3}$); ACN: $\log x_1 = 1.1986 \varphi - 1.1972$ (φ from 0.4–1.0; $x_1 = 0.185 - 1.0$; $r = 0.9997$, $n = 13$; $s = 6.09 \times 10^{-3}$) and dioxane: $\log x_1 = 1.4263 \varphi - 1.4757$ (φ from 0.5–0.9; $x_1 = 0.17 - 0.65$; $r = 0.9997$; $n = 7$; $s = 5.09 \times 10^{-3}$). The above equations are of importance because they determine the limits of zone A in Fig. 1, in which a linear dependence between $\log k$ and φ values exists. φ Values, although often used in chromatography, are not suitable for the examination of phase equilibria, as can be seen from the Everett equation.

To find the K value which gives the best linearity for the function $\log k = f(SP)$, it is useful to present this correlation graphically. If the chosen K value is higher than the optimal a curve is obtained, the slope ($d \log k / d SP$) of which especially when the values of x_1 are small, *i.e.*, high SP values, decreases with increasing SP parameter. On the contrary, when the chosen K value is smaller than the optimal value the slope of the curve in the mentioned region increases with increasing SP . Thus, after several attempts, the best K value can be found and then confirmed using linear regression analysis. In performing these K value determinations, it is necessary to know the values of $\log k$ (or even better average values of $\log k$) over the widest possible interval of x_1 . If $\log k$ values for x_1 values of only one zone, A or C, are known then the differentiation is not possible, since the SP parameters of one zone for different values of K are in mutual linear correlation.

Examples of systems having a linear dependence of the function $\log k = f(SP)$

1) *CN–silica/methanol–water*. The data for this system is the most complete, since there are data for $\log k$ values of 18 compounds in the interval 1–100 % v/v of methanol. The data in the range 1–50 % v/v of methanol have been experimentally determined by Seibert and Poole³ and in the range 50–100 % v/v of methanol they have been calculated by using a quadratic equation and the corresponding parameters given in another paper by the same authors.⁴ We have already investigated this system partially⁵ and found that the $\log k$ values in the interval 1–50 % v/v are a linear function of the x_1 values. In this work, however, we have established that there is a linear correlation between the $\log k$ values in the interval 50–100 % v/v and the $\log x_1$ values (Fig. 3). The analogous data for naphthalene and anisole are shown in Fig. 4. In addition, a list of the investigated compounds and the regression data of the function $\log k = f(\log x_1)$ in the interval 50–100 % v/v for all the 18 investigated compounds is given in Table I.

From the above it can be concluded that for a linear correlation of the $\log k$ values in the interval 1–100 % v/v of methanol, two scales are necessary, *i.e.*, a x_1 scale (1–50 % v/v) and a scale $\log x_1$ (50–100 % v/v). However, the fact that the $\log k$ pair linearity rule^{1,6} can be applied over the whole interval (Fig. 5) points to the existence of a unique solvent strength scale. This apparent contradiction has been solved by the SP scale for $K = 3.4 \pm 0.1$ (Fig. 6) which was established to be the best one. This confirms the regres-

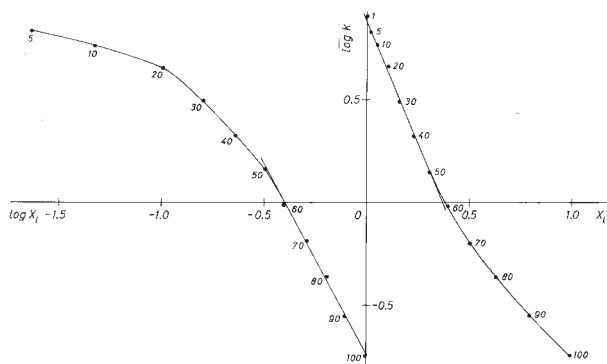


Fig. 3. Functional dependence of the average $\log k$ values for 18 compounds in Table I on the corresponding x_1 values (right), or $\log x_1$ values (left). System: CN-silica/methanol-water. Correlation data: right $r = -0.9982$, $n = 7$, inter. 0.8952, slope = -2.4633 , $s = 1.68 \times 10^{-2}$; left $r = -0.9971$, $n = 6$, inter. -0.7351 , slope = -1.8058 , $s = 2.62 \times 10^{-2}$. The numbers above the curves denote % v/v of methanol.

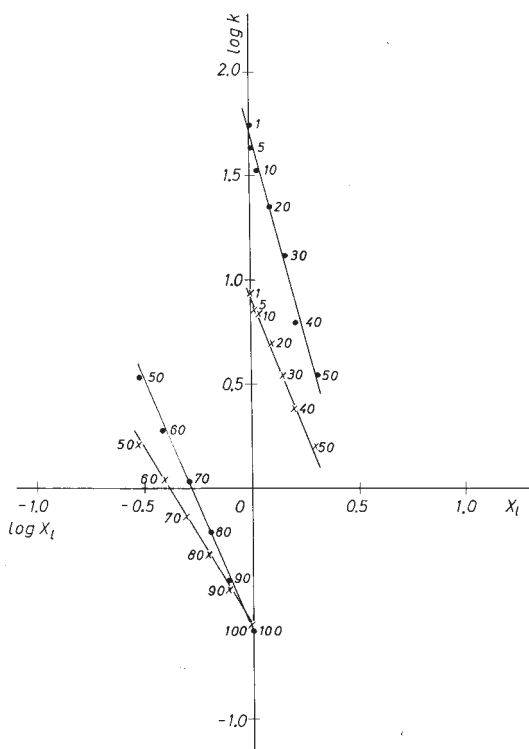


Fig. 4. Dependence of the individual $\log k$ values of anisole (x) and naphthalene (•) on the corresponding x_1 values (right), or $\log x_1$ values (left), respectively. The system is as in Fig. 3. The numbers denote the % v/v of methanol.

sion data given for the 18 investigated compounds in Table I. The results are very satisfactory since they were obtained using the compounds with different solute descriptors used in the Solvation parameter model,^{3,7} *i.e.*, using compounds that differ in their ability to form diverse kinds of interactions in the course of the chromatographic process. Moreover, these results are of importance as they encompass a wide concentration range of methanol in the mobile phase (1–100 % v/v).

TABLE I. Functional dependence $\log k = f(\log x_1)$ for 50–100 % v/v of methanol (left) and dependence $\log k = f(SP, K = 3.4)$ for 1–100 % v/v of methanol (right). System: CN–silica/methanol–water

No.	Compound	–Interc.	–Slope	– <i>r</i>	<i>s</i> ×10 ²	–Interc.	+Slope	– <i>r</i>	<i>s</i> ×10 ²
1	Naphthalene	0.6686	2.3625	0.9998	0.90	0.7847	4.7694	0.9977	5.78
2	2-Hexanone	0.5465	0.9733	0.9997	0.45	0.5982	1.9520	0.9956	3.28
3	Benzaldehyde	0.7050	1.3789	0.9996	0.74	0.7912	2.9079	0.9950	5.20
4	Anisole	0.6574	1.7348	0.9985	1.81	0.6905	3.0990	0.9994	1.92
5	Benzonitrile	0.6470	1.5390	0.9988	1.44	0.6831	2.8001	0.9992	2.00
6	Bromobenzene	0.7509	2.3059	0.9980	2.78	0.7746	3.9832	0.9989	3.33
7	Chlorobenzene	0.7682	2.2530	0.9972	3.22	0.7668	3.7135	0.9976	4.60
8	Benzyl alcohol	0.7769	1.4021	0.9963	2.30	0.7655	2.2035	0.9976	2.73
9	2-Chlorophenol	0.8542	1.9419	0.9985	2.03	0.8897	3.4645	0.9994	2.14
10	<i>n</i> -Propylbenzene	0.8251	2.6214	0.9983	2.91	0.8618	4.6141	0.9987	5.21
11	Acetophenone	0.6556	1.4607	0.9999	0.39	0.7506	3.0881	0.9952	5.41
12	1,2-Dichlorobenzene	0.7780	2.5139	0.9988	2.35	0.8332	4.5664	0.9990	3.64
13	2-Phenylethanol	0.7880	1.6170	0.9962	2.69	0.7723	2.5257	0.9971	3.43
14	<i>p</i> -Cresol	0.8580	1.8689	0.9974	2.57	0.8653	3.1099	0.9989	2.60
15	Phenol	0.8152	1.6162	0.9960	2.76	0.7943	2.4939	0.9963	3.84
16	Benzamide	0.7385	1.1072	0.9992	0.84	0.8010	2.2623	0.9956	3.80
17	Acetanilide	0.7390	1.4124	0.9991	1.14	0.7854	2.6499	0.9989	2.22
18	Nitrobenzene	0.6251	1.7947	0.9980	2.16	0.6453	3.0947	0.9996	1.56

2) *Diol–silica/methanol–water*. The $\log k$ values for 27 compounds in the interval 1–50 % v/v of methanol have been determined by Seibert *et al.*⁷ In our earlier investigation of this system, the average $\log k$ values of these compounds were found to be in a good linear relationship with the x_1 values.⁸ From Fig. 1 it follows that such a behaviour is consistent with an *SP* scale for *K* values from 1.1 – 1.8. For a better distinction it would be necessary to have $\log k$ values for methanol concentrations higher than 50 % v/v (*i.e.*, $x_1 > 0.31$). However, these values have not been determined due to the inadequate retention of the solute.³ The same is also the case for the subsequent examples Nos. 3 and 4. As these values are not known, all *SP* scales with *K* values between 1.1 – 1.8 give very similar correlation coefficients of the function $\log k = f(SP)$. For example,

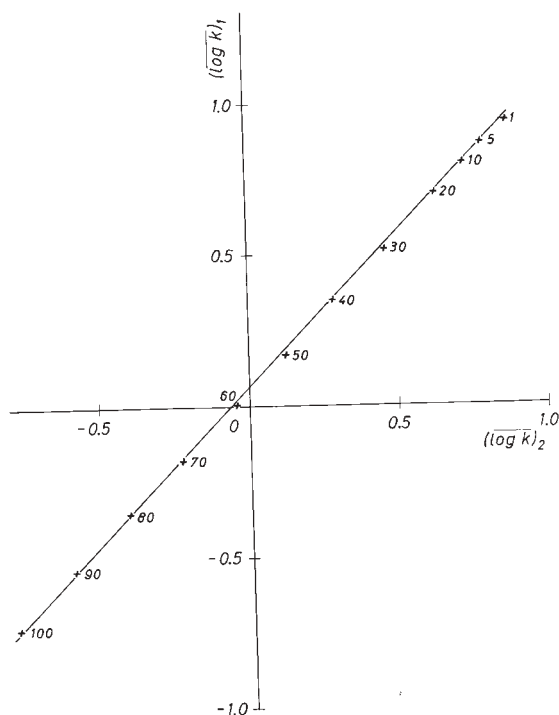


Fig. 5. Dependence of the average $\log k$ values of the first 9 compounds in Table I (ordinate) on the average $\log k$ values of the remaining 9 compounds, (abscissa). The system is as in Fig. 3. Regression data: $r = 0.9999$, $n = 12$, $\text{inter.} = 0.05341$, $\text{slope} = 1.0180$, $s = 9.04 \times 10^{-3}$. The numbers denote the % v/v of methanol.

the linear dependence of the average $\log k$ values for the first 18 compounds from Table II and the SP scale with $K = 1.1$ is shown in Fig. 7 and the correlation coefficients for all 27 compounds are given in Table II, column A. From Table II, column A, it is obvious that the correlation coefficients of the function $\log k = f(SP)$ are better than 0.99 for 21 of the 27 investigated compounds. The reasons for worse values of r were a dispersion of the points (compounds 2 and 17), a large deviation of one of the investigated points (compounds 9, 12 and 15), and only in one case (compound 5) was a slight curvature of the mentioned correlation found. The obtained results are satisfactory as the examined compounds (like in the previous case) differ considerably in their solute descriptors. In such a way we succeeded in explaining the linearity between $\log k$ values and x_1 by the model of the SP scale, which belongs to zone C in Fig. 1.

3) *Diol-silica/ACN-water*. The $\log k$ values for this system for the same 27 compounds were determined in the range of 1–50 % (v/v) of ACN by the same authors as in the second example.⁷ We have already investigated this system and found that their average $\log k$ values are in a good linear relationship with the x_1 values.⁸ As can be seen from Fig. 1, this behaviour is consistent with all SP scales with K values between 1.1 and 2.0. A better distinction, as in the previous case, is not possible since there are no $\log k$ values for ACN concentrations higher than 50 % (v/v), *i.e.*, x_1 values > 0.25 . For example, the linear dependence of the average $\log k$ values (for the first 18 compounds from Table II and the SP scale with $K = 1.1$) is presented in Fig. 8 and the correlation coefficients for all 27 compounds are given in Table II, column B.

TABLE II. Correlation coefficients of the linear function: $\log k = f(SP, K = 1.1)$, for the chromatographic systems considered in the examples 2(A), 3(B) and 4(C). A and B, $n = 7$, C, $n = 6$.

No.	Compound	A	B	C	Note
1	Naphthalene	0.9983	0.9978	0.9932	
2	Benzene	0.9758*	0.9890		B:without 50 % v/v 0.9947
3	<i>n</i> -Propylbenzene	0.9941	0.9986	0.9988	
4	Chlorobenzene	0.9931	0.9976	0.9982	
5	Bromobenzene	0.9894**	0.9990	0.9989	
6	1,2-Dichlorobenzene	0.9937	0.9995	0.9954	
7	1,2-Dibromobenzene	0.9987	0.9967	0.9931	
8	Benzaldehyde	0.9934	0.9923	0.9924	
9	Benzonitrile	0.9799	0.9943	0.9959	A:without 50 % v/v 0.9937
10	Anisole	0.9940	0.9949	0.9967	
11	Acetophenone	0.9907	0.9901	0.9920	
12	Nitrobenzene	0.9817	0.9941	0.9969	A:without 1 % v/v 0.9921
13	Ethyl phenyl ketone	0.9912	0.9924		
14	Methyl benzoate	0.9990	0.9959		
15	Hexan-2-one	0.9584	0.9886	0.9834*	Without 1 % v/v A:0.9942 B:0.9921
16	Octan-2-one	0.9940	0.9950		
17	Phenol	0.9879*	0.9931	0.9908	
18	<i>m</i> -Cresol	0.9944	0.9929		
19	<i>p</i> -Cresol	0.9912	0.9952	0.9956	
20	2-Chlorophenol	0.9954	0.9970	0.9978	
21	1-Naphthol	0.9965	0.9957		
22	4-Phenylphenol	0.9990	0.9953		
23	Benzyl alcohol	0.9904	0.9840	0.9941	B:without 50 % v/v 0.9933
24	2-Phenylethanol	0.9912	0.9929	0.9979	
25	2-Nitroaniline	0.9937	0.9968		
26	Benzamide	0.9991	0.9862	0.9810**	B:without 1 % v/v 0.9962
27	Acetanilide	0.9952	0.9948	0.9912	

* Points are scattered around the regression straight line. ** The function is not linear.

From Table II, column B, it is obvious that the correlation coefficients of function $\log k = f(SP)$ are better than 0.99 for 23 of the 27 investigated cases. The reason for the worse r values in the remainder of the cases is the deviation from the regression straight line of one out of the seven determined points (compounds Nos. 2, 15, 23 and 26). These results can be considered as satisfactory, since the investigated compounds differ significantly in their solute descriptors. The earlier established linear dependence between $\log k$ and x_1 can be explained, as in the previous case, by means of the described model (Fig. 1, zone C).

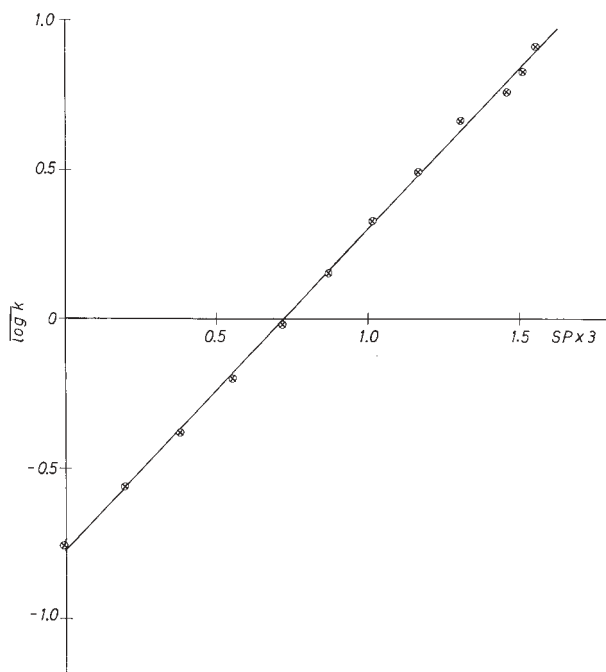


Fig. 6. Linear dependence of the average $\log k$ values of the compounds in Table I on the SP parameters calculated using Eq. (1) with $K = 3.4$. The system is as in Fig. 3. Regression data: $r = 0.9996$, $n = 12$, $\text{inter.} = -0.7703$, $\text{slope} = 3.1845$, $s = 1.67 \times 10^{-2}$.

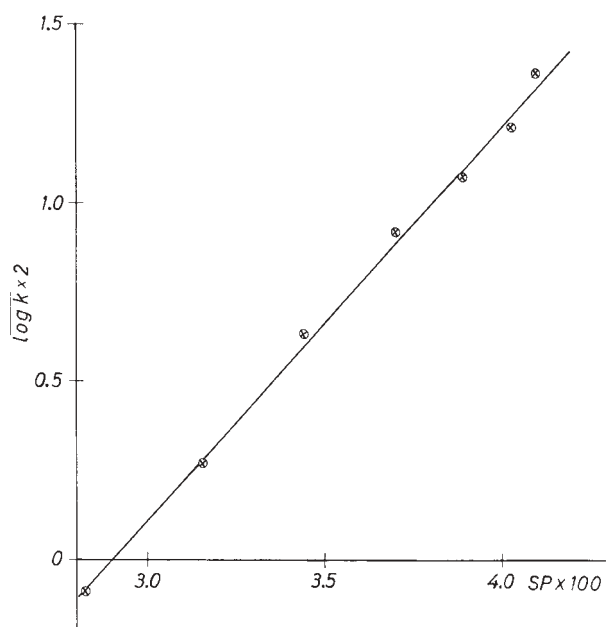


Fig. 7. Linear dependence of the average $\log k$ values for the first 18 compounds in Table II on the SP parameters calculated using Eq. (1) with $K = 1.1$. System: Diol-silica/methanol-water. Regression data: $r = 0.9978$, $n = 7$, $\text{inter.} = -1.5850$, $\text{slope} = 54.6560$, $s = 1.76 \times 10^{-2}$.

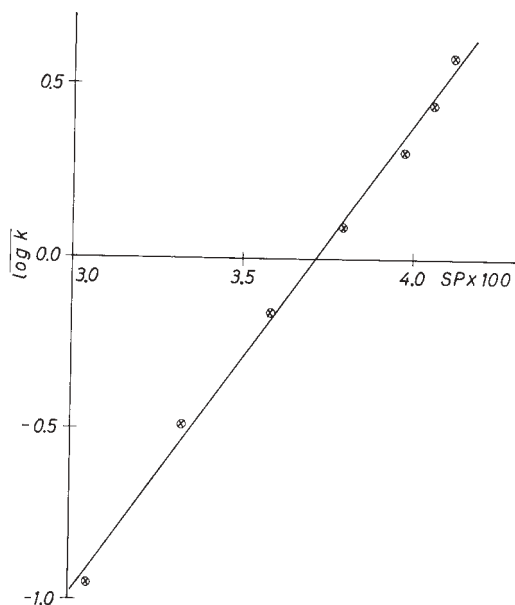


Fig. 8. Linear dependence of the average $\log k$ values for the first 18 compounds from Table II on the SP parameters calculated using Eq. (1) with $K = 1.1$. System: Diol-silica/ACN-water. Regression data: $r = 0.9977$, $n = 7$, inter. = -5.0675 , slope = 1.3613×10^2 , $s = 3.71 \times 10^{-2}$.

4) *CN-silica/ACN-water*. The $\log k$ values for this system in the interval 1–50 % (v/v) for 19 compounds were determined by Seibert and Poole.³ We have already partially investigated this system and found that the average $\log k$ values are a linear function of x_1 in the range 5–50 % (v/v).⁵ From Fig. 1 it follows that such a behaviour is in agreement with the SP scale with $K = 1.1$ –2.0. A better distinction is not possible without $\log k$ values corresponding to the concentrations of ACN higher than 50 % (v/v),

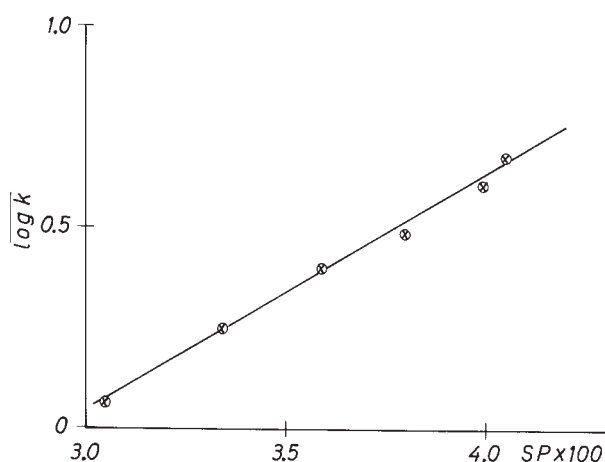


Fig. 9. Linear dependence of the average $\log k$ values for the 19 compounds in Table II/C on the SP parameters calculated using Eq. (1) with $K = 1.1$. System: CN-silica/ACN-water. Regression data: $r = 0.9980$, $n = 6$, inter. = -1.7013 , slope = 58.2394 , $s = 1.44 \times 10^{-2}$.

i.e., $x_1 > 0.25$. For example, a linear correlation of the function average $\log k = f(SP, K = 1.1)$ is presented in Fig. 9. The point corresponding to 1 % v/v of ACN deviates significantly from the regression line and was omitted. The correlation coefficients of the function of $\log k = f(SP)$ for all 19 examined compounds are given in Table II, column C. The r values are better than 0.99 in 17 cases. The worse r values are caused by the dispersion of the points around the regression line (compound 15) or the non-linearity of the mentioned relationship in the range of $\phi < 0.2$ (compound 26).

5) *ODS/ACN-water*. The $\log k$ values for this system were determined for 32 compounds by Bosch *et al.*⁹ In 5 cases the $\log k$ values covered the full range of ACN-water mobile phase compositions ($x_1 = 0.0-1.0$). On the basis of the results obtained, they postulated a mobile phase polarity parameter P_m^N , which, as was confirmed, was in linear correlation with the $\log k$ values in the investigated concentration range. With regard to good linearity between $\log k$ and P_m^N it is, in principle, irrelevant which value would be chosen for our considerations. However, since the P_m^N values encompass the whole concentration range of the ACN-water system, and since by using Eq. (10), presented in the paper by Bosch *et al.*,⁹ P_m^N values can be calculated even for the concentration range 0–10 % v/v of ACN, the $\log k$ values of which have not been determined, although essential for a good distinction of K , we chose the P_m^N values for our considerations. The best linearity of the function $P_m^N = f(SP)$ is found for $K = 30$ (Fig. 10) but only if the ACN concentrations are lower than 80 % v/v. The range of

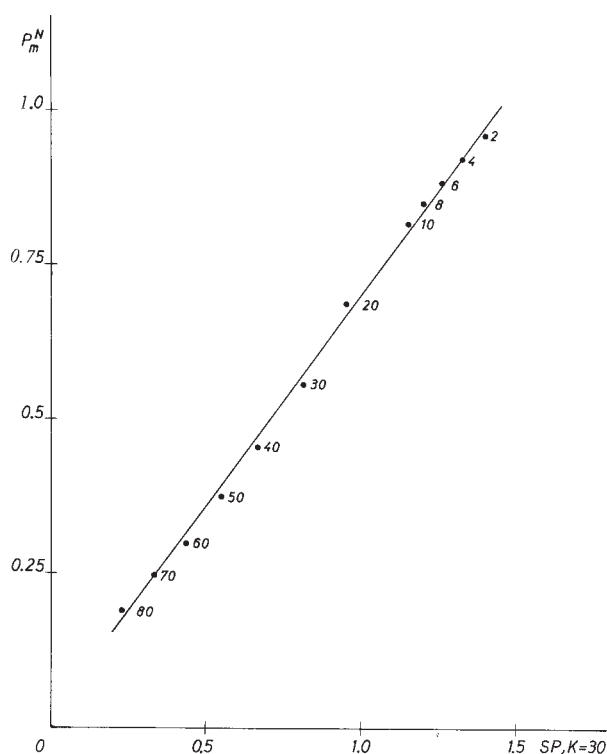


Fig. 10. Linear dependence of the function $P_m^N = f(SP)$ for $K = 30$. System: ODS/ACN-water. The numbers on the straight line denote the % v/v of ACN in water. Regression data: $r = 0.9990$, $n = 12$, $\text{inter.} = 0.0125$, $\text{slope} = 0.6828$, $s = 1.26 \times 10^{-2}$.

ACN concentration higher than 80 % v/v were considered as an exception until good linearity between P_m^N and SP' parameter for the same value of K ($SP' = x_s/x_1 = 10^{SP}$) was established. This is caused by a change of the separation mechanism, which will be considered in a future paper.

6) *ODS/dioxane-water*. Finally, as the last of the examined systems, this one was studied with three homologous series of organic compounds by Jandera.¹⁰ He found a close linear dependence between $\log k$ and ϕ , if the mobile phase contains more than 40–50 % v/v of dioxane. Unfortunately, $\log k$ values were given only for the ϕ interval 0.50–0.75 for which the correlation coefficients between the mentioned values were about 0.9990. As in this region an ideal linear correlation between $\log x_1$ and ϕ values ($r = -0.99999$) exists, it is evident that in this range linearity between $\log k$ and $\log x_1$, as well as for $\log k$ and SP parameters exists for all the phase equilibrium constants values higher than 20. This is concluded on the basis of Fig. 1, from which it can be seen that when $K > 20$, $x_1 > 0.175$ ($\phi > 0.5$), the SP parameters fall in the zone A range where a linear dependence between $\log k$ values and $\log x_1$ exists. Consequently, these investigations could not be used for the determination of K , as no $\log k$ values corresponding to the low ϕ values have been reported in the literature.

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ИЗВОД

УТИЦАЈ САСТАВА СТАЦИОНАРНЕ И МОБИЛНЕ ФАЗЕ НА ФАКТОРЕ ЗАДРЖАВАЊА И ПАРАМЕТРЕ ЈАЧИНЕ РАСТВОРАЧА У РФ ХРОМАТОГРАФСКИМ СИСТЕМИМА У КОЈИМА ВАЖИ ЕВЕРЕТОВА ЈЕДНАЧИНА

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

Хемијски факултет, Универзитет у Београду, б. бр. 158, 11001 Београд

Показано је како се у РФ хроматографији применом Еверетове једначине за идеалне фазне равнотеже могу израчунати SP вредности ($SP = \log x_s/x_1$, где x_s и x_1 представљају молске фракције модификатора у стационарној и мобилној фази), које стоје у линеарној зависности са $\log k$ вредностима. Описана процедура обухвата и одређивање приближне фазне равнотежне константе K . Анализом Еверетове једначине утврђено је да у пољу x_1/K постоје области линеарне зависности SP параметра, односно $\log k$ вредности, и молске фракције модификатора, односно његовог логаритма. Због тога само у овим областима два различита хроматографска система могу имати исту скалу јачине растварача: x_1 , односно $\log x_1$.

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