

## Investigation of the compatibility between one-dimensional system parameters and the multi-dimensional Solvation parameter model in RP liquid column chromatography

TOMISLAV J. JANJIĆ,<sup>#</sup> GORDANA VUČKOVIĆ,<sup>\*#</sup> and MILENKO B. ČELAP<sup>#</sup>

Faculty of Chemistry, University of Belgrade, P. O. Box 158, 11001 Belgrade, Serbia and Montenegro

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*Abstract:* It has been established that in many cases the system constants used in the Solvation parameter model as well as the corresponding  $\log k$  values can be linearized in the same  $NSP$  and  $NSP'$  scale, respectively, which shows the compatibility of both models.  $NSP$  and  $NSP'$  are one-dimensional system parameters adapted to the chromatographic system used over the phase equilibrium constant.

*Keywords:* system parameters,  $NSP$  parameter,  $NSP'$  parameter, Solvation parameter model,  $\log k$  linearization, system constants.

### INTRODUCTION

It is known that for the calculation of the retention ( $\log k$  values), especially in RP chromatography, the multi-dimensional Solvation parameter model has been successfully used<sup>1–6</sup>:

$$\log k = V_x/100 m + R_2 r + \pi_2^H s + \alpha_2^H a + \beta_2^H b + c \quad (1)$$

In the above equation  $V_x$  is the solute's characteristic volume,  $R_2$  the solute's excess molar refraction,  $\pi_2^H$  the solute dipolarity/polarizability, and  $\alpha_2^H$  and  $\beta_2^H$  are parameters characterizing the solute's hydrogen-bond acidity and basicity, respectively. The above solute solvation parameters (solute descriptors) can be found in the literature for a great number of compounds,<sup>3,5</sup> while the corresponding system constants  $m$ ,  $r$ ,  $s$ ,  $a$ ,  $b$  and  $c$  are determined on the basis of the obtained  $\log k$  values using multiple linear regression analysis.

The main significance of this model is that at a molecular level it provides an interpretation of the retention properties under chromatographic conditions, which would not be possible by other means. However, its disadvantage is that a great number of system constants is necessary to calculate the  $\log k$  values. These constants depend strictly on the chromatographic system used, for example two types of ODS may have considerably different

\* Author for correspondence: (Fax: +381-11-638-785, e-mail: gordanav@helix.chem.bg.ac.yu).

# Serbian Chemical Society active member.

system constants although the same mobile phase is used.<sup>5</sup> The advantage of the described multi-parameter method over many single parameter models, which can be applied only in some of the cases in a restricted range of modifier concentration, is doubtless. However, single parameters can be divided into two groups: those based only on the eluent properties (vol% of modifier, mole fraction of modifier or its logarithm,  $E_{T(30)}$  and others<sup>6</sup>), and those, which are adapted to a given chromatographic system, over phase equilibrium constant, such as, for example,  $SP$  and  $SP'$  system parameters or their normalized  $NSP$  and  $NSP'$  forms.<sup>7-10</sup>

The aim of the present work was to investigate the compatibility of the  $NSP$  and  $NSP'$  scales with the Solvation parameter model. For this purpose several different systems, as is elaborated in the text have been chosen.

## RESULTS AND DISCUSSION

### 1. Consideration of $\log k$ values in the system $CN$ -silica/MeOH-water obtained by Seibert and Pool<sup>1,2</sup>

This system was chosen as the  $\log k$  values for 18 compounds, having quite different solute descriptors, determined in the range 1–100 % v/v of methanol<sup>1,2</sup> as well as the system constants for 1–80 % v/v of methanol are known.<sup>1</sup> This system was investigated in our previous paper<sup>8</sup> and a good linear correlation of the function:  $\log k = f(NSP)$ , where  $NSP = \log [x_1 (K-1) + 1] / \log K$ , was found. The  $K$  value for the mentioned system was 3.4, and  $x_1$  is the mole fraction of the modifier in the mobile phase.

Both of the described models are compatible if a linear dependence between the system constants and the  $NSP$  or  $NSP'$  parameters exists, because in that case the  $\log k$  values calculated by using Eq. (1) are also a linear function of the mentioned parameters. The corresponding dependence is shown in Fig. 1. It is seen that such a correlation exists, and that only in the case of 1 % v/v of methanol and the constants  $a$ ,  $b$  and  $c$  should this point be rejected. Regression and other data are given in Table I. Thus, it can be concluded that the worst correlation coefficients are obtained if the slope of the straight line is small, which is an expected phenomenon discussed previously by some other authors.<sup>11,12</sup>

By substitution of the values for the system constants from the obtained regression equations (Table I) into Eq. (1), Eq. (2) is obtained, which enables the calculation of the slope and intercept of the straight line  $\log k = f(NSP)$  using the corresponding solute descriptors, after rearrangements:

$$\log k = (-2.65 V_x/100 - 0.56 R + 0.135 \alpha_2^H + 2.21 \beta_2^H + 0.46)(NSP) + (2.06 V_x/100 + 0.48 R - 0.29 \alpha_2^H - 1.85 \beta_2^H - 0.70) \quad (2)$$

The comparative data calculated by these two methods are shown in Table II, from which it is obvious that the data are in good agreement. An average  $|\Delta \text{ %}|$  for the slope is 3.5 %, and for the intercept 3.1 %.

TABLE I. The most relevant data of the investigated systems and the regression data of the function: (system

constant)= $f$ (scale)

Example No.	Chromatographic system A) Column B) Eluent (conc. range of modifier vol%) C) Scale	Regression data					
		Syst. const.	Slope	Intercept	<i>n</i>	<i>r</i>	<i>s</i> ×10 <sup>2</sup>
1	A) CN-silica (laboratory made from extraction columns) 250 × 4.6 mm i.d. B) MeOH/water (1–100 % v/v) C) <i>NSP</i> , <i>K</i> = 3.4 <sup>8</sup>	<i>m</i>	-2.6504	2.0572	10	-0.9974	5.05
		<i>r</i>	-0.5648	0.4755	10	-0.9778	3.19
		<i>a</i>	0.1349	-0.2879	9	0.7701	2.81
		<i>b</i>	2.2085	-1.8492	9	0.9911	7.47
2	A) Spherisorb ODS-2 (5 μm) 100 × 5 mm i.d. B) MeOH–phosphate buffer pH 7 (40–90 % v/v) C) <i>NSP</i> , <i>K</i> = 10.88 <sup>7</sup>	<i>m</i>	-4.6581	4.9194	6	-0.9965	6.14
		<i>r</i>	0.1131	0.1841	4	0.8739	0.67
		<i>s</i>	0.9056	-1.2584	6	0.9783	3.02
		<i>a</i>	0.2386	-0.6033	6	0.9583	1.12
3	A) ERC 1000(ODS) 150 × 6 mm i.d. B) 0.01 mol/dm <sup>3</sup> phosphoric acid in CH <sub>3</sub> CN–water mixtures (50–90 % v/v) C) <i>NSP</i> , <i>K</i> = 30 <sup>8,9</sup>	<i>m</i>	-2.2356	2.9723	5	-0.9962	2.28
		<i>r</i>	-0.00035	0.0023	5	-0.0027	1.52
		<i>s</i>	-0.1262	0.0890	5	-0.8390	1.67
		<i>a</i>	0.5873	-0.9462	5	0.9844	1.22
4	A) Spherisorb ODS-2 (5 μm) 100 × 5 mm i.d. B) THF–phosphate buffer pH 7 (20–60 % v/v) C) <i>NSP</i> *, <i>K</i> = 14*	<i>m</i>	-4.9873	4.7649	5	-0.9991	3.24
		<i>r</i>	-0.7600	0.4732	5	-0.8133	8.39
		<i>s</i>	0.8046	-0.8255	5	0.9115	3.52
		<i>a</i>	-0.4761	0.1463	5	-0.9884	1.13
5	A) Unsil Q C18 (ODS) 150 × 4.1 mm i.d. B) 0.01 mol/dm <sup>3</sup> phosphoric acid in CH <sub>3</sub> CN–water mixtures (20–90 % v/v) C) <i>NSP</i> *, <i>K</i> = 12*	<i>m</i>	-5.1136	5.3998	8	-0.9999	1.17
		<i>r</i>	-0.07075	0.2946	8	-0.2833	3.87
		<i>s</i>	0.5223	-0.6495	8	0.9904	1.11
		<i>a</i>	0.5112	-0.5998	8	0.9208	3.50
6	A) ODS-Hypersil (5 μm) 100 × 5 mm i.d. B) MeOH–phosphate buffer pH 7 (20–50 % v/v) C) <i>NSP</i> , <i>K</i> = 10.88 <sup>7</sup>	<i>m</i>	-4.2991	4.5155	4	-0.9970	4.26
		<i>r</i>	-0.1474	0.2518	4	-0.9681	0.49
		<i>s</i>	0.2390	-0.8122	4	0.9961	0.27
		<i>a</i>	-0.04251	-0.3182	4	-0.9304	0.21
7	A) Hypersil ODS (5 μm) 100 × 3 mm or 50 × 4.6 mm i.d. B) MeOH–phosphate buffer pH 2.15 or pH 7 (30–90 % v/v) C) <i>NSP</i> , <i>K</i> = 10.88 <sup>7</sup>	<i>m</i>	-3.7893	4.6533	5	-0.9972	6.00
		<i>r</i>	-0.2945	0.3649	5	-0.9754	1.36
		<i>s</i>	0.5644	-0.9220	5	0.9973	0.85
		<i>a</i>	-0.3155	-0.02562	5	-0.9550	2.00
		<i>b</i>	2.7593	-3.7890	5	0.9976	3.91
		<i>c</i>	-1.1439	-0.0032	5	-0.9474	2.49

\* Estimated in this paper.

TABLE II. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP, K = 3.4)$ , *A*\* and values

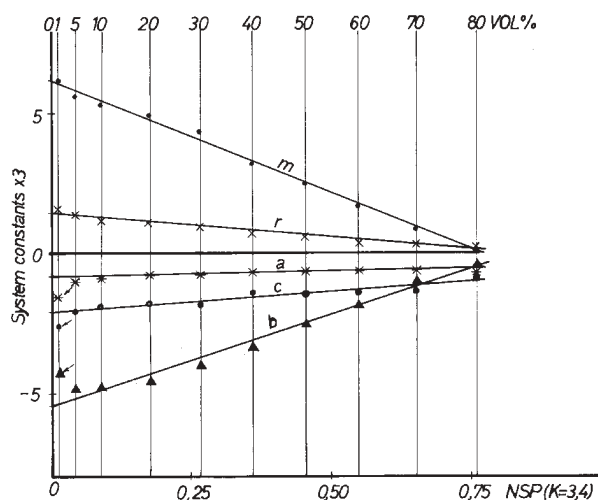


Fig. 1. System constants as a function of *NSP*,  $K = 3.4$  in Example 1. The arrows designate rejected points.

obtained using Eq. (2), *B*. Chromatographic system: CN-silica/methanol-water; ( $n = 10$ )

No.	Compound	- Slope		$ \Delta \% ^{**}$	Intercept		$ \Delta \% $
		<i>A</i>	<i>B</i>		<i>A</i>	<i>B</i>	
1	Naphthalene	2.5348	2.7237	7.5	1.7500	1.8085	3.3
2	2-Hexanone	1.0374	1.0543	1.6	0.4392	0.4159	5.4
3	Benzaldehyde	1.5455	1.4508	6.1	0.7543	0.7705	2.1
4	Anisole	1.6471	1.7230	4.6	0.9566	0.9903	3.5
5	Benzonitrile	1.4882	1.5344	3.1	0.8051	0.8399	4.3
6	Bromobenzene	2.1170	2.1962	3.7	1.3424	1.3923	3.7
7	Chlorobenzene	1.9736	2.0107	1.9	1.2068	1.2435	3.0
8	Benzyl alcohol	1.1711	1.1349	3.1	0.4056	0.4407	8.7
9	2-Chlorophenol	1.8413	1.6664	9.5	0.9516	0.8910	6.4
10	<i>n</i> -Propylbenzene	2.4523	2.5651	4.6	1.5905	1.6588	4.3
11	Acetophenone	1.6413	1.6023	2.4	0.8907	0.8750	1.8
12	1,2-Dichlorobenzene	2.4269	2.4866	2.5	1.5937	1.6242	1.9
13	2-Phenylethanol	1.3477	1.3182	2.2	0.5701	0.5772	1.2
14	4-Cresol	1.6528	1.6425	0.6	0.7875	0.8233	4.5
15	Phenol	1.3255	1.3006	1.9	0.5312	0.5540	4.3
16	Benzamide	1.2024	1.1260	6.4	0.4014	0.3980	0.8
17	Acetanilide	1.4084	1.4311	1.6	0.6230	0.6279	0.8
18	Nitrobenzene	1.6448	1.7701	7.6	0.9995	1.0355	3.6

\*Taken from our recently published paper<sup>9</sup>; \*\* $|\Delta \%| = |100 (B-A) / A|$

The obtained results show the compatibility of the *NSP* parameter and the Solvation parameter model in the case of the investigated system. The only exception is 1 % v/v of methanol, because, in this case, the system constants *a*, *b* and *c* strongly deviate from linearity. However, in spite of this, the average error in the log *k* values calculated using the two compared methods for 1

% v/v methanol and the compounds in Table II are almost the same, *i.e.*, 0.04 log units.

## 2. Consideration of the log $k$ values in the system ODS/MeOH–water obtained by Smith and Burr<sup>13</sup>

The log  $k$  values for this system in the range 40–90 % v/v of methanol were taken from the mentioned paper. The necessary system constants and solute descriptors were taken from the paper by Abraham and Rosés.<sup>5</sup> As the given interval of methanol concentrations is not wide enough to determine the phase equilibrium constant,<sup>8</sup> the value of 10.88 was taken from the literature<sup>7</sup> where it was determined under similar conditions. As already said, it is necessary for the calculation of the  $NSP$  values.

The applied procedure was the same as that described. First, the linear dependence be-

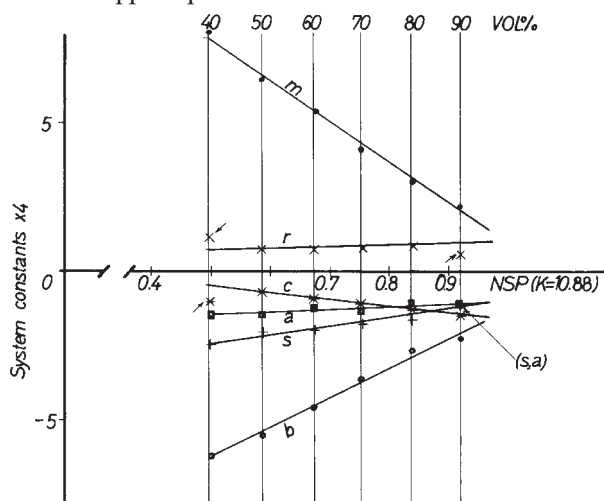


Fig. 2. System constants as a function of  $NSP$ ,  $K = 10.88$  in Example 2. Other data as in Fig. 1.

tween system parameters and  $NSP$  values was found (Fig. 2). The obtained regression data are given in Table I, and by their substitution into Eq. (1) the following is obtained:

$$\log k = (-4.66 V_x/100 + 0.113 R + 0.906 \pi_2^H + 0.239 \alpha_2^H + 3.24 \beta_2^H - 0.813)(NSP) + (4.92 V_x/100 + 0.184 R - 1.26 \pi_2^H - 0.603 \alpha_2^H - 3.69 \beta_2^H + 0.236) \quad (3)$$

A comparison of the slopes and intercepts of the straight lines directly determined from the function  $\log k = f(NSP)$  and those calculated by using Eq. (3) are given in Table III. From Table III it can be seen that the compatibility criterium of the data is met as the average  $|\Delta \%$  in the case of the slope and intercept are 3.7 % and 3.9 %, respectively.

The high values  $|\Delta \%$  of the slopes and intercepts shown in Table III for benzyl chloride are the consequence of the large error in the log  $k$  values calculated by means of Eq. (1). This error is the highest for 40 % v/v of methanol and amounted to 0.16 log  $k$  units, while the average standard deviation in such calculations is about 0.06 log units.<sup>5</sup> The log  $k$  values for benzyl chloride calculated using Eq. (1) are also a good linear function of the  $NSP$  values:  $\log k_{\text{calc}} = -3.4396 NSP + 2.9068$  ( $n = 6$ ,  $r = -0.9996$ ,  $s = 1.45 \times 10^{-2}$ ). The

slope and intercept of the obtained straight line are similar to those calculated by Eq. (3), but quite different from those obtained from the corresponding function with experimental  $\log k$  values (Table III).

TABLE III. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP, K = 10.88)$ ,  $A$  and values obtained using Eq. (3),  $B$ . System: ODS/methanol–water ( $n = 6$ )

No	Compound	– Slope		$\Delta$ %	Intercept		$\Delta$ %
		$A$	$B$		$A$	$B$	
1	Aniline	2.0085	1.958	2.5	1.2094	1.216	0.6
2	Benzene	3.0669	3.172	3.4	2.6109	2.701	3.5
3	Benzonitrile	2.8048	2.713	3.3	2.0658	2.040	1.2
4	Benzyl alcohol	2.2403	2.309	3.1	1.4412	1.529	6.1
5	Benzyl bromide	4.1362	3.972	4.0	3.5559	3.527	0.8
6	Benzyl chloride	3.9569	3.473	12.3	3.3561	2.956	12.0
7	Benzyl cyanide	2.9556	2.944	0.4	2.0835	2.022	3.0
8	Bromobenzene	4.0536	3.914	3.4	3.6294	3.559	2.0
9	Chlorobenzene	3.9054	3.825	2.1	3.4484	3.418	0.9
10	Methyl benzoate	3.4327	3.468	1.0	2.8174	2.880	2.2
11	Nitrobenzene	3.0162	2.954	2.1	2.4057	2.348	2.4
12	Phenol	2.2854	2.412	5.5	1.4485	1.607	10.9
13	Toluene	3.6440	3.815	4.7	3.2710	3.393	3.7
14	Acetophenone	2.8952	2.975	2.8	2.2081	2.331	5.6
15	Anisole	3.1235	3.383	8.3	2.6209	2.858	9.0
16	Benzaldehyde*	2.7004	2.619	3.0	1.9763	2.010	1.7
17	Biphenyl*	5.2695	5.220	0.9	4.8931	4.942	1.0

\* $n = 5$

### 3. Consideration of the $\log k$ values in the system ODS/ $CH_3CN$ –water obtained by Hanai and Hubert<sup>14</sup>

The above authors determined  $\log k$  values for this system in the range 50–90 % v/v of  $CH_3CN$  for 86 compounds.<sup>14</sup> However, from these compounds only 20 for which the corresponding solute descriptors are known could be used.<sup>2,3,5</sup> As the given concentration range of  $CH_3CN$  is not wide enough to determine the phase equilibrium constant,<sup>8,9</sup> this constant was taken from the literature,<sup>8</sup> its value was 30.

In the same way as described above, the linear dependence between the system constants<sup>5</sup> and  $NSP$  values was found (Fig. 3). The obtained regression data are given in Table I and by their substitution into Eq. (1), the following is obtained:

$$\log k = (-2.236 V_x/100 - 0.126 \pi_2^H + 0.587 \alpha_2^H + 2.345 \beta_2^H - 1.486)(NSP) + (2.972 V_x/100 - 0.002 R - 0.089 \pi_2^H - 0.946 \alpha_2^H - 2.979 \beta_2^H + 0.752) \quad (4)$$

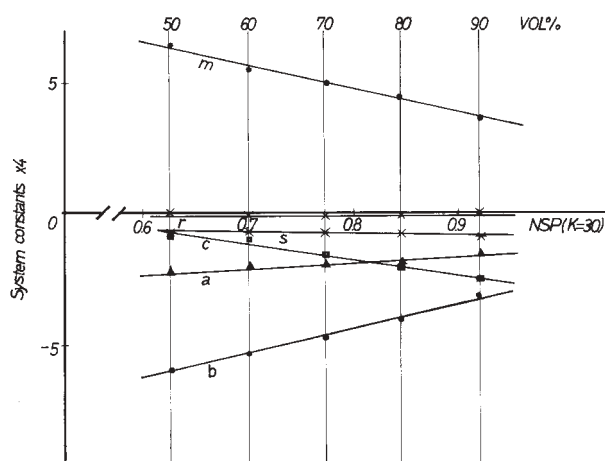


Fig. 3. System constants as a function of  $NSP, K = 30$  in Example 3.

TABLE IV. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP, K = 30)$ ,  $A$  and values obtained using Eq. (4),  $B$ . Chromatographic system: ODS/ $CH_3CN$ -water ( $n = 5$ )

No.	Compound	- Slope		$\Delta$ %	Intercept		$\Delta$ %
		$A$	$B$		$A$	$B$	
1	Benzene	2.9952	2.8242	5.7	2.5842	2.4157	6.5
2	Naphthalene	3.6136	3.5590	1.5	3.3302	3.2918	1.0
3	Toluene	3.2889	3.1401	4.5	2.9707	2.8359	4.5
4	Ethylbenzene	3.6338	3.4305	5.6	3.3808	3.2257	4.6
5	Propylbenzene	3.9831	3.7443	6.0	3.8215	3.6454	4.6
6	Chlorobenzene	3.3146	3.2793	1.1	2.9840	2.9778	0.2
7	1,2-Dichlorobenzene	3.5375	3.6393	2.9	3.2978	3.4185	3.7
8	Bromobenzene	3.3567	3.3592	0.1	3.0645	3.0659	0.1
9	2-Methylphenol	2.7220	2.6338	3.2	2.0585	1.9357	6.0
10	4-Methylphenol	2.6431	2.5823	3.3	1.9540	1.9335	1.1
11	Phenol	2.4459	2.2756	7.0	1.6860	1.5144	10.2
12	2,5-Dimethylphenol	2.9339	2.7641	5.8	2.3459	2.0880	5.8
13	2-Chlorophenol	2.7844	2.6889	3.4	2.1031	2.1140	0.5
14	3-Chlorophenol	2.9095	2.8696	1.4	2.2416	2.2247	0.8
15	4-Chlorophenol	2.8810	2.7667	4.0	2.1970	2.0929	4.8
16	3-Bromophenol	2.9680	2.9692	0.0	2.3274	2.3335	0.3
17	4-Bromophenol	2.7538	2.8956	5.2	2.1341	2.2410	5.0
18	2-Nitrophenol	2.8823	2.8439	1.3	2.3012	2.3294	1.2
19	3-Nitrophenol	2.9297	2.8034	4.3	2.0990	2.0005	4.7
20	4-Nitrophenol	2.7709	2.7343	1.3	1.9465	1.8696	4.0

The comparison between the slopes and intercepts of the straight lines directly determined from the function  $\log k = f(NSP)$  and those calculated by using Eq. (4) are given in Table IV.

It can be seen from Table IV that the obtained results show complete compatibility of the  $NSP$  parameter and Solvation parameter model, as the average  $|\Delta \%$  in the slope is 3.4 %, and in the intercept 3.5 %. It is worth mentioning that in all the investigated cases the correlation coefficients of the function  $\log k = f(NSP)$  were better than 0.999. This means that the corresponding regression values of  $\log k$  are very close to the experimentally found values. On the other hand, the  $\log k$  values obtained by using Eqs. (4) and (1) do not differ considerably. Therefore, the difference between the experimentally found  $\log k$  values and those obtained by using Eq. (4) can be approximately calculated as:  $\Delta \log k = \Delta \text{slope } NSP + \Delta \text{interc.}$  In the case of phenol, where  $|\Delta \%$  in the slope and intercept are the highest, this means:  $\Delta \log k = -0.1703 NSP + 0.1716$ . As the  $NSP$  values range from 0.6248 (for 50 % v/v  $\text{CH}_3\text{CN}$ ) to 0.9202 (for 90 % v/v), it is obvious that the greatest  $\Delta \log k$  (0.065) is found in the case of 50 % v/v, which, according to Ref. 5, corresponds to the average standard deviation by using Eq. (1). Almost the same result (0.064) is obtained if in the mentioned case the  $\log k$  value calculated using Eq. (1) is deducted from the experimental value.

#### 4. Consideration of the $\log k$ values in the system ODS/THF–water obtained by Smith and Wang<sup>15</sup>

The above authors determined the  $\log k$  values for this system in the modifier concentration range of 20–60 % v/v for 20 compounds, which have been considered in this paper. On the basis of the average  $\log k$  values, as was described earlier,<sup>9</sup> the phase equilibrium constant  $K = 14$  is determined, using the following regression equation:

$$\log \bar{k} = -3.3799 NSP' + 2.6840 \quad (n = 5, r = -0.99975, s = 1.16 \times 10^{-2})$$

The  $NSP'$  values were calculated using the following equation:<sup>9</sup>

$NSP' = 1 - (K - Q)/(K - 1)Q$ , where  $Q = [x_1(K - 1) + 1]$ , and  $x_1$  is the mole fraction of the modifier in the mobile phase. The correlation coefficients of the function  $\log k = f(NSP')$

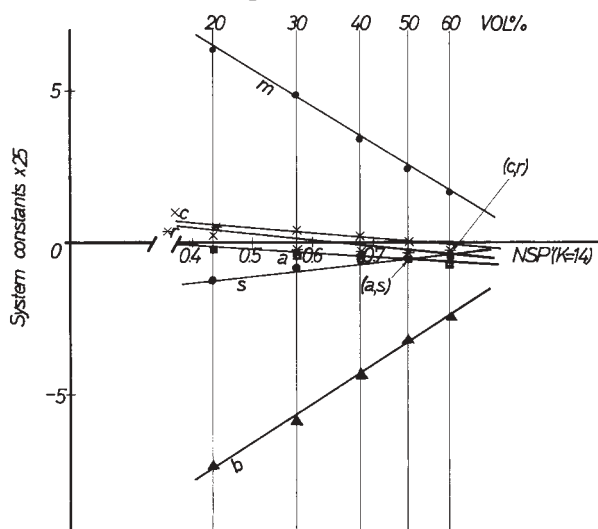


Fig. 4. System constants as a function of  $NSP'$ ,  $K = 14$  in Example 4.



for the individual compounds are worse than those calculated using the average  $\log k$  values, but they are better than  $-0.991$  in all cases.

TABLE V. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP')$ ,  $K = 14$ ,  $A$  and values obtained using Eq. (5),  $B$ . System: ODS/THF–water ( $n = 5$ )

No.	Compound	– Slope		$\Delta$ %	Intercept		$\Delta$ %
		$A$	$B$		$A$	$B$	
1	Acetophenone	2.6252	2.8999	10.5	2.0254	2.2794	12.5
2	Benzene	3.3872	3.4362	1.5	2.9655	2.9698	0.1
3	Toluene	4.1161	4.1321	0.4	3.6425	3.6369	0.2
4	Aniline	2.0646	2.0771	0.6	1.5306	1.3754	10.1
5	Anisole	3.4902	3.5341	1.3	2.9497	2.9824	1.1
6	Benzaldehyde	2.5310	2.6789	5.8	1.9731	2.0941	6.1
7	Benzamide	1.6695	1.6677	0.0	0.7779	0.8249	6.0
8	Benzonitrile	2.8835	2.8364	1.6	2.2765	2.2752	0.1
9	Bromobenzene	4.7187	4.6089	2.3	4.0727	4.0238	1.2
10	Chlorobenzene	4.4832	4.3913	2.1	3.8783	3.8677	0.3
11	<i>N</i> -Ethylaniline	3.5368	3.4681	1.9	3.0503	2.7382	10.2
12	Methyl benzoate	3.3929	3.3617	0.9	2.7607	2.7570	0.1
13	Nitrobenzene	3.5177	3.2959	6.3	2.8878	2.6960	6.6
14	Phenol	2.9848	3.0256	1.4	2.2926	2.2759	0.7
15	Propiophenone	3.3684	3.4838	3.4	2.7815	2.8890	3.7
16	Butyrophenone	4.0922	3.6866	9.9	3.4707	3.3684	3.0
17	Valerophenone	4.8898	4.9358	0.9	4.1784	4.2281	1.2
18	Benzensulfonamide	1.8612	1.7003	8.6	1.1236	0.7620	32.2
19	<i>N,N</i> -Dimethylbenzamide	1.5794	1.2636	20.0	0.7175	0.5171	27.9
20	<i>N</i> -Methylbenzamide	1.7717	2.0068	13.3	0.8742	1.1885	35.9

In the same way as described in earlier examples, the linear dependence between the system constants<sup>5</sup> and the  $NSP'$  values (Fig. 4.) was determined. The obtained data are given in Table I and by their substitution in Eq. (1), the following is obtained:

$$\log k = (-4.987 V_x/100 - 0.760 R + 0.805 \pi_2^H - 0.476 \alpha_2^H + 5.246 \beta_2^H - 0.553)(NSP') + (4.765 V_x/100 + 0.473 R - 0.826 \pi_2^H + 0.146 \alpha_2^H - 5.299 \beta_2^H + 0.439) \quad (5)$$

The comparison of the slopes and intercepts of the straight lines directly determined from the function  $\log k = f(NSP')$  and those calculated using Eq. (5) are given in Table V.

From Table V, for the compounds 1–17 it can be seen that the obtained results show the complete compatibility of the  $NSP'$  parameter and the Solvation parameter model, as the average  $|\Delta \text{ %}|$  in the slope is 4.1 % and in the intercept 2.5 %. The large  $|\Delta \text{ %}|$  values in the case of compounds 1,4 (intercept),11 (intercept), as well as 18–20, are due to the fact

that the  $\log k$  values could not be calculated with the necessary accuracy using Eq. (1), which is incorporated in Eq. (5). It is concluded from the large errors when Eq. (1) is used. The errors for 20 and 60 % v/v THF are acetophenone  $-0.126/-0.020$ ; aniline  $0.132/0.150$ , *N*-ethylaniline  $0.231/0.218$ , benzenesulfonamide  $0.266/-0.045$ ; *N,N*-dimethylbenzenamide  $0.075/-0.045$ ; *N*-methylbenzenamide  $-0.192/-0.097$ . These errors are often much higher than the average standard deviation obtained by using Eq. (1), *i.e.*, 0.06 log units.<sup>5</sup> In the last three cases the high  $|\Delta \ %|$  values in Table V are partially due to low values of the slope and intercept.

##### 5. Consideration of the $\log k$ values in the system ODS/CH<sub>3</sub>CN–water obtained by Hanai and Hubert<sup>6</sup>

These authors determined  $\log k$  values for 61 compounds from the phenol group over a large range of CH<sub>3</sub>CN concentrations (up to 90 % v/v). Out of the 61 compounds were considered 18, for which the solute descriptors were known.<sup>2,3,5</sup> In the same way as described above, the linear dependence between the system constants<sup>5</sup> and  $NSP'$  values were found for  $K = 12$  (Fig. 5 and Table I). The correlation coefficients of the function  $\log k = f(NSP')$  in the case of compounds 4, 16, 17 and 18 are better than  $-0.996$ , and in the case of the remainder they are better than  $-0.999$ .

By substitution of the regression data from Table I into Eq. (1), the following is obtained:

$$\log k = (-5.114 V_x/100 - 0.071 R + 0.522 \pi_2^H + 0.511 \alpha_2^H + 3.896 \beta_2^H - 0.189)(NSP') + (5.400 V_x/100 + 0.295 R - 0.650 \pi_2^H - 0.600 \alpha_2^H - 4.046 \beta_2^H - 0.164) \quad (6)$$

The comparison between the slopes and intercepts of the straight lines directly determined from the function  $\log k = f(NSP')$ , and those calculated using Eq. (6) are given in Table VI. From Table VI it can be seen that only in the case of the compounds 16 and 18, which have the lowest slope and intercept of the function  $\log k = f(NSP')$ , is  $|\Delta \ %|$  about 10 %, while in the other cases it is lower than 5.4 %, which shows the compatibility of the compared methods.

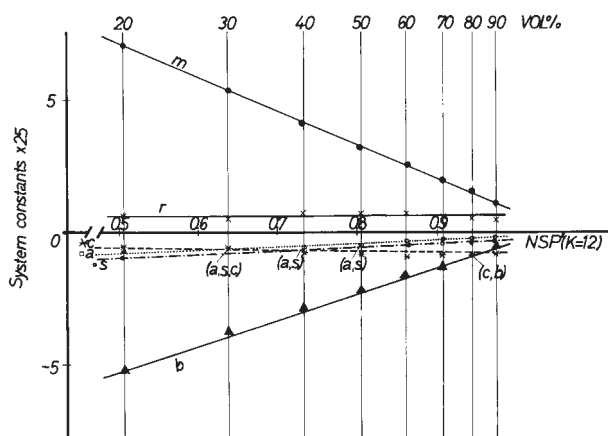


Fig. 5. System constants as a function of  $NSP'$ ,  $K = 12$  in Example 5.

It is interesting to mention that the  $\log k$  values of the considered compounds in the third Example (in which many are phenols) are a linear function of the  $NSP$  parameter, which we believe is the consequence of the different sorbents (Table I). It suggests a different separation mechanism in the mentioned cases.<sup>8,9</sup>

TABLE VI. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP, K = 12)$ ,  $A$  and values obtained using Eq. (6),  $B$ . Chromatographic system: ODS/CH<sub>3</sub>CN–water ( $n = 8$ )

No.	Compound	– Slope			Intercept		
		$A$	$B$	$ \Delta \text{ %} $	$A$	$B$	$ \Delta \text{ %} $
1	Phenol	2.2037	2.2700	3.01	2.0795	2.1067	1.31
2	2-Methylphenol	2.9027	2.9785	2.61	2.8126	2.9454	4.72
3	3-Methylphenol	2.8503	2.8565	0.22	2.7376	2.7323	0.09
4	4-Methylphenol	2.9424	2.9785	1.23	2.8002	2.8625	2.22
5	2,4-Dimethylphenol	3.5199	3.4460	2.10	3.4652	3.3760	2.57
6	2,5-Dimethylphenol	3.5732	3.5238	1.38	3.4985	3.4565	1.20
7	2-Chlorophenol	3.0579	3.0087	1.61	2.9506	2.9159	1.18
8	3-Chlorophenol	3.3876	3.3530	1.02	3.2799	3.2408	1.19
9	4-Chlorophenol	3.3296	3.1585	5.14	3.2125	3.0392	5.39
10	2-Bromophenol	3.2501	3.2935	1.34	3.1544	3.2232	2.18
11	3-Bromophenol	3.5659	3.5417	0.68	3.4725	3.4644	0.23
12	4-Bromophenol	3.5344	3.3922	4.02	3.4318	3.3134	3.45
13	2-Nitrophenol	3.0886	3.1006	0.39	3.0689	3.0521	0.55
14	3-Nitrophenol	2.8886	2.9990	3.82	2.7285	2.8469	4.34
15	4-Nitrophenol	2.8100	2.7899	0.72	2.6309	2.6159	0.57
16	1,3-Dihydroxybenzene	1.3029	1.7729	9.44	1.0864	0.9720	10.53
17	1,2-Dihydroxybenzene	1.5325	1.5041	1.85	1.3511	1.3163	2.57
18	1,4-Dihydroxybenzene*	1.0039	1.0727	6.85	0.7860	0.8610	9.54

\* $n = 7$

#### 6. Consideration of the $\log k$ values in the system ODS/MeOH–water obtained by Smith and Finn<sup>17</sup>

These authors determined the  $\log k$  values in the range of modifier concentrations 20–50 % v/v for 27 compounds. Since the range of modifier concentration was not wide enough for the determination of the phase equilibrium constant  $K$ , a value 10.88 was taken from the literature.<sup>7</sup> A linear dependence between the  $\log k$  values and the  $NSP$  parameter was found for the given  $K$  value. Only in the case of nitromethane, the compound with the smallest slope of the mentioned function, a bad correlation coefficient was found ( $r = -0.9739$ ), whereas in 14 cases  $|r| > 0.99$  and in 12  $|r| > 0.999$ . The investigation of the compatibility of the mentioned methods was possible only in 7 of the cases, for which the solute descriptors were known.<sup>2,3,5</sup> Using the already described procedure, a linear dependence between the system constants<sup>5</sup> and the  $NSP$  parameters was found (Fig. 6 and Table I). By substituting the regression data from Table I into Eq. (1) the following is obtained:

$$\log k = (-4.299 V_x/100 - 0.147 R + 0.239 \pi_2^H - 0.0425 \alpha_2^H + 1.325 \beta_2^H + 0.691)(NSP) + (4.516 V_x/100 + 0.252 R - 0.812 \pi_2^H - 0.318 \alpha_2^H - 2.551 \beta_2^H - 0.543) \quad (7)$$

TABLE VII. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP, K = 10.88)$ ,  $A$  and values obtained using Eq. (7),  $B$ . Chromatographic system: ODS/MeOH–water ( $n = 4$ )

No.	Compound	– Slope		$\Delta$ %	Intercept		$\Delta$ %
		$A$	$B$		$A$	$B$	
1	Acetophenone	3.0902	2.8976	6.23	2.2381	2.1973	1.82
2	Propiophenone	3.5598	3.4760	2.35	2.8358	2.8032	1.15
3	Butyophenone	4.1140	4.0946	0.47	3.4592	3.4637	0.13
4	Toluene	2.7512	2.7693	0.66	2.7234	2.7006	0.84
5	<i>p</i> -Cresol	2.8794	2.7646	3.99	2.1239	2.1218	0.10
6	Nitrobenzene	2.5906	2.6236	1.27	2.0764	2.0846	4.00
7	2-Phenylethanol	2.7849	2.9018	4.20	2.0026	2.0000	0.14

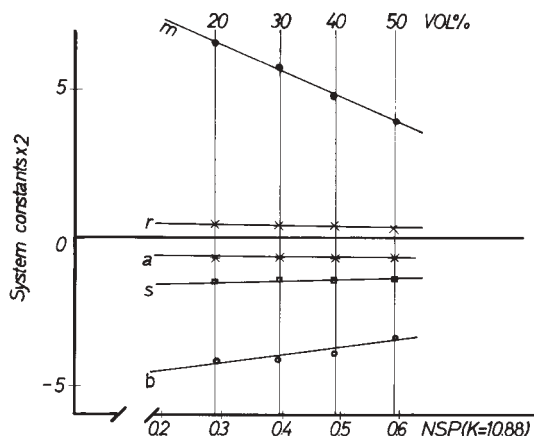


Fig. 6. System constants as a function of  $NSP, K = 10.88$  in Example 6.

The comparison between the slope and intercept of the straight lines determined directly from the function  $\log k = f(NSP)$ , and those calculated using Eq. (7) are given in Table VII. From Table VII it can be seen that only in the case of the slope of compound 1, was the value  $|\Delta \text{ %}|$  somewhat higher than 5 %, which shows the compatibility of the compared methods.

### 7. Consideration of the $\log k$ values in the system ODS/MeOH–water obtained by Hafkenschied<sup>18</sup>

This author determined the  $\log k$  values for this system in the modifier concentration range 30–90 % v/v for 34 compounds. From these compounds, 17, for which the solute descriptors<sup>2,3,5</sup> were available, were considered. As the investigated concentration range was insufficient for the determination of the phase equilibrium constant, a value  $K = 10.88$  was taken from the literature.<sup>7</sup> Then it was established that there is a linear dependence between the  $\log k$  values and the  $NSP$  parameters where  $|r| > 0.999$ . By means of the described procedure, the linearity between the system constants<sup>5</sup> and  $NSP$  parameters was established (Fig. 7 and Table I). By substitution of the regression data from Table I in Eq. (1) the following is obtained:

$$\log k = (-3.789 V_x/100 - 0.295 R + 0.564 \pi_2^H - 0.316 \alpha_2^H + 2.759 \beta_2^H - 1.144)(NSP) + (4.653 V_x/100 + 0.365 R - 0.922 \pi_2^H - 0.0256 \alpha_2^H + 3.789 \beta_2^H - 0.0032) \quad (8)$$

The comparison between the slope and intercept of the straight lines directly determined from the function  $\log k = f(NSP)$ , and those calculated by Eq. (8), are given in Table VIII. From Table VIII it can be seen that only in the case of the slope or intercept for compounds 5, 10 and 16 is  $|\Delta \%$  somewhat higher than 5 %, which confirm the compatibility of the compared method. Very high  $|\Delta \%$  value in the intercept of compound 15 (hydroquinone) is the result, as in many other cases, of the fact that Eq. (1) does not yield accurate enough  $\log k$  values. Thus, by application of this equation to the case of 30 % v/v of methanol it was found of that the value of  $\log k$  is 0.34 log units higher than those experimentally found, while the corresponding regression value of the function  $\log k = f(NSP)$  (calculated with the values given in Table VIII, column A), is only 0.02 log units higher than the experimental values.

TABLE VIII. Comparison of the slope and intercept of the linear function:  $\log k = f(NSP, K = 10.88)$ , A, and values obtained using Eq. (8), B. Chromatographic system: ODS/CH<sub>3</sub>CN–water ( $n = 5$ )

No.	Compound	– Slope		$ \Delta \%$	Intercept		$ \Delta \%$
		A	B		A	B	
1	Benzene	3.2706	3.3588	2.70	2.5183	2.5430	0.98
2	Toluene	3.7915	3.8901	2.60	3.1430	3.1953	1.63
3	Chlorobenzene	4.0276	3.9743	1.32	3.3079	3.2973	0.32
4	Nitrobenzene	3.4469	3.3784	1.99	2.4405	2.3762	2.63
5	Phenol	3.0592	3.1783	3.89	1.7988	1.9245	6.99
6	Aniline	2.6500	2.6795	1.11	1.3640	1.3569	0.52
7	<i>p</i> -Xylene	4.3669	4.3723	0.12	3.8219	3.7795	1.11
8	<i>p</i> -Chlorotoluene	4.6398	4.4930	3.16	4.0058	3.9297	1.90
9	<i>p</i> -Nitrotoluene	3.9461	3.9123	0.86	3.0398	3.0319	0.26
10	<i>p</i> -Cresol	3.5786	3.6908	3.13	2.2481	2.5669	5.72
11	<i>p</i> -Toluidine	3.1955	3.1446	1.59	2.0004	1.9345	3.29
12	<i>p</i> -Chlorophenol	3.8778	3.8654	0.32	2.7885	2.7361	1.88
13	<i>p</i> -Nitrophenol	3.5823	3.6282	1.28	2.2976	2.2125	3.71
14	<i>p</i> -Nitroaniline	3.2294	3.2659	1.13	1.7750	1.8416	3.75
15	Hydroquinone	2.7046	2.7462	1.54	0.6854	1.0173	48.4
16	Methylparaben	3.8410	3.8998	1.53	2.4773	2.6034	5.09
17	Naphthalene	4.6350	4.5812	1.16	3.9780	3.9302	1.20

It is worth mentioning here that in the cases where the  $\log k$  values were determined over modifier concentration ranges insufficient for an estimation of the phase equilibrium constant  $K$  (Examples 2, 3, 6 and 7), this constant was taken from the literature, where it had been determined for analogous chromatographic systems. However, this does not mean that both chromatographic systems have the same  $K$  values, but that the investigated

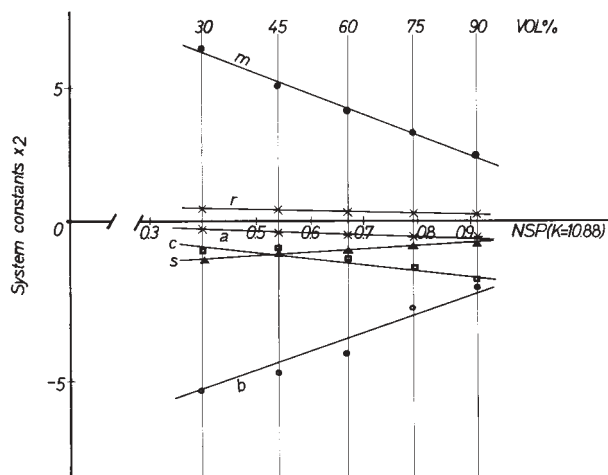


Fig. 7. System constants as a function of  $NSP$ ,  $K = 10.88$  in Example 7.

concentration range falls in zone  $C$  of the field  $x_1 / K$  (Fig. 1 in Ref. 8) in which the  $NSP$  parameters calculated for different  $K$  values are in mutual linear correlation. For this reason the determination of  $K$  values in such cases is not possible.

In the case of linear functions  $\log k = f(NSP \text{ or } NSP')$  assuming that linear extrapolation is possible, the following relations: intercept =  $\log k (x_1 = 0)$  and (intercept+slope) =  $\log k (x_1 = 1)$  are valid.<sup>9</sup> The full analogy is valid also in the case of the function: (system constant) =  $f(\text{scale})$  (See Table I).

Finally, to the best of our knowledge,  $NSP$  and  $NSP'$  parameters are unique one-dimensional adaptable parameters. They are also parameters for which compatibility with the multi-dimensional Solvation parameter model has definitely been proved.

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#### ИЗВОД

### ИСПИТИВАЊЕ САГЛАСНОСТИ ИЗМЕЂУ ЈЕДНОДИМЕНЗИОНАЛНИХ СИСТЕМСКИХ ПАРАМЕТАРА И ВИШЕДИМЕНЗИОНАЛНОГ СОЛВАТАЦИОНО-ПАРАМЕТЕРСКОГ МОДЕЛА У РФ ТЕЧНОЈ КОЛОНСКОЈ ХРОМАТОГРАФИЈИ

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

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

Утврђено је да у многим случајевима системске константе, које се користе код солватационо-параметерског модела, као и одговарајуће  $\log k$  вредности могу да буду линеаризоване у истој  $NSP$ , односно  $NSP'$  скали, што показује сагласност оба поменута модела.  $NSP$  и  $NSP'$  су једнодимензионални системски параметри, усклађени са одговарајућим хроматографским системом преко фазне равнотежне константе.

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