

## **Influence of the stationary and mobile phase composition on solvent strength parameter $\varepsilon^{\circ}$ and *SP* system parameter in NP column chromatography**

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It is shown that *SP* system parameters, previously used for the linearization of  $\log k$  values in *RP* chromatography, can also be used in NP chromatography. A very good linear correlation between *SP* parameter and the earlier described Snyder solvent strength parameter has been established. It was also found that the phase equilibrium constant *K* is independent of the polarity and concentration of the more polar component of binary solvent mixtures.

*Keywords:* NP chromatography, *SP* parameter, solvent strength parameter  $\varepsilon^{\circ}$ .

### INTRODUCTION

In recently published papers,<sup>1,2</sup> it was shown how in *RP* chromatography, by using the Everett equation for ideal phase equilibrium, *SP* parameters can be calculated from their linear dependence on the  $\log k$  values:  $SP = \log x_s/x_1$  ( $x_s$  and  $x_1$  denote the mole fractions of the modifier in the stationary and the mobile phase, respectively). In addition, the determination of the phase equilibrium constant *K* was described.

In the subsequent paper in the same field,<sup>3</sup> the linear correlation  $\log k = f(SP)$  was analyzed and the corresponding separation mechanisms were considered.

Continuing these investigations, the purpose of the present study was to check whether *SP* parameters could also be applied in an analogous way in NP chromatography.

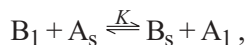
### RESULTS AND DISCUSSION

The most simple way to check the validity of the above-mentioned regularity is to establish if a linear dependence exists between the *SP* parameters and the Snyder solvent strength parameters  $\varepsilon^{\circ}$ . Namely, in numerous cases a linearity between  $\log k$  and  $\varepsilon^{\circ}$  values has already been established. In the case of positive results, the use of *SP* parameters for the linearization of  $\log k$  values not only in *RP* but also in NP chromatography would be confirmed.

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The equilibrium constant in this case corresponds to the phase equilibrium of the binary system modifier(B)/diluent (A):



where 1 represents the mobile and s the stationary phase. The  $SP$  parameter, as in RP chromatography, is the logarithm of the quotient of the mole fraction of the modifier in the stationary and mobile phases,  $SP = \log x_s/x_1$ , but in the present case the modifier is the more polar component of the binary system. All the derived equations are valid also in this case.

As is known,<sup>4</sup> the Snyder solvent strength parameter  $\varepsilon^0$  is of fundamental importance in planning chromatographic separations by NP chromatography. Linear dependence between  $\log k$  values and  $\varepsilon^0$  was established in numerous experiments<sup>4</sup> in which less polar solutes were chromatographed on  $\text{NH}_2$ -silica, alumina and silica with a variety of solvents and their mixtures.

The data for  $\varepsilon^0$ , necessary for the consideration of a possible linearity  $\varepsilon^0 = f(SP)$  and the determination of the corresponding phase equilibrium constants  $K$ , were taken for  $\text{NH}_2$ -silica from the paper by Snyder and Schunk,<sup>5</sup> and for alumina and silica from the tables of binary solvents eluotropic series.<sup>6</sup> The procedure of these considerations was the same as in our previous papers.<sup>1,2</sup> The results obtained are presented as the corresponding regression equations given below (Table I). The cases where one of the experimental points was rejected, due to a great deviation from the regression straight line, are indicated. On the other hand, in some cases, especially when the equilibrium constant  $K$  is large and/or the number of the experimental points low, in order to achieve its better differentiation it was necessary to add the point corresponding to  $\varepsilon^0$  and  $SP$  values for  $x_1 = 0$ . These cases are also indicated.

TABLE I. Regression data of linear function  $\varepsilon^0 = f(SP)$ . Sorbents: Nos. 1-5  $\text{NH}_2$ -silica ( $\mu\text{Bondapak-NH}_2$ ), Nos. 6-20 Alumina (activity  $\alpha = 0.6$ ), Nos. 21-30 Silica (activity  $\alpha = 0.7$ )

No.	Mobile phase (A+B)	Conc. range B % (v/v)	$K$	-Slope	Intercept	$n$	$-r$	$s \times 10^{-3}$	Comment
1	Hexane-THF	0.5-60	2.3	0.3170	0.1191	8	0.9981	2.06	
2	Hexane- $\text{CCl}_4$	10-100	1.1	1.8732	$7.821 \cdot 10^{-2}$	4	0.9998	0.35	
3	Hexane- $\text{CH}_2\text{Cl}_2$	5-60	1.7	0.5417	0.1358	5	0.9983	2.10	1
4	Hexane- $\text{CHCl}_3$	5-60	3.2	0.2443	0.1350	5	0.9995	1.09	1
5	Hexane-ethyl acetate	2-50	6.2	0.1198	0.1019	5	0.9997	0.65	
6	Pentane- $\text{CS}_2$	0-100	1.5	0.8491	0.1489	4	0.9998	1.29	
7	Pentane-2-chloropropane	0-77	4	0.4646	0.2781	6	0.9995	2.96	
8	Pentane-benzene	0-83	14	0.2769	0.3152	8	0.9999	1.79	
9	Pentane-ethyl ether	0-81	10	0.3841	0.3814	7	0.9993	4.50	
10	Pentane- $\text{CHCl}_3$	0-100	15	0.3365	0.3966	9	0.9999	1.94	
11	Pentane- $\text{CH}_2\text{Cl}_2$	0-84	11	0.3886	0.4102	9	0.9995	4.15	
12	Pentane-acetone	0-92	30	0.3777	0.5519	10	0.9997	4.16	2

TABLE I. Continued

No.	Mobile phase (A+B)	Conc. range B % (v/v)	<i>K</i>	-Slope	Intercept	<i>n</i>	- <i>r</i>	<i>s</i> × 10 <sup>-3</sup>	Comment
13	Pentane-methyl acetate	0-100	60	0.3317	0.5931	11	0.9996	5.17	
14	Pentane-diethylamine	0-73	700	0.221	0.6341	8	0.9996	5.31	
15	Benzene-acetone	6-93	3	0.4946	0.5586	5	0.9999	6.25	
16	Benzene-methyl acetate	4-100	5	0.3944	0.6003	6	0.9998	1.87	
17	Benzene-diethylamine	2-77	25	0.2248	0.6295	6	0.9998	1.87	
18	Benzene-acetonitrile	0-100	160	0.1491	0.6481	5	0.9999	1.38	3,4
19	Benzene-2-propanol	0-75	250	0.2110	0.8263	7	0.9998	2.93	4
20	Benzene-methanol	0-100	3000	0.1789	0.9415	6	0.9998	5.08	4
21	Pentane-benzene	0-100	14	0.2152	0.2478	6	0.9997	2.36	
22	Pentane-CHCl <sub>3</sub>	0-92	7	0.3004	0.2557	5	0.9998	2.05	5
23	Pentane-CH <sub>2</sub> Cl <sub>2</sub>	0-82	10	0.3132	0.3118	6	0.9998	2.16	6
24	Pentane-ethyl ether	0-56	700	0.1329	0.3784	6	0.9996	3.68	
25	Pentane-ethyl acetate	0-56	650	0.1339	0.3766	6	0.9995	3.90	
26	Pentane-acetone	0-65	3500	0.1308	0.4621	6	0.9998	3.28	4
27	Benzene-acetonitrile	0-65	30	0.1453	0.4660	5	0.9995	2.16	4
28	Benzene-acetonitrile	0-100	100	0.1231	0.4967	5	0.9991	4.08	4
29	Benzene-ethyl ether	0-62	6	0.1687	0.3814	3	1.0000	0.12	4
30	Benzene-ethyl acetate	0-62	6	0.1665	0.3793	3	1.0000	0.49	4

Comments: 1 - Point corresponding to 100 % v/v was rejected; 2 - The point for 1.5 % v/v was rejected and its regression value was 2 % v/v; 3 - The point for 1.5 % v/v was rejected, its regression value being 2.5 % v/v; 4 - The point  $x_1 = 0$  was added for better differentiation; 5 - The point for 26 % v/v was rejected its corresponding regression value being 13.8 % v/v; 6 - The regression straight line showed that the point for 82 % v/v corresponded exactly to  $\varepsilon^0 = 0.30$  and not 0.25, this was taken into account.

As it can be seen from the 30 regression equations with the very good correlation coefficients, *SP* scales can be used for the linearization of  $\log k$  values obtained by binary mobile phases not only in RP, but also in NP chromatography.

By analogous consideration as in our previous paper,<sup>3</sup> the physical meaning of the intercept and the slope of the linear functions  $\varepsilon^0 = f(SP)$  and  $\varepsilon^0 = f(NSP)$ :

$$\varepsilon^0 = [(\varepsilon_A^0 - \varepsilon_B^0) / \log K] SP + \varepsilon_B^0 \quad (1)$$

$$\varepsilon^0 = (\varepsilon_B^0 - \varepsilon_A^0) NSP + \varepsilon_A^0 \quad (2)$$

was found.

The relationships (3) and (4) are valid in the above equations.

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

$$NSP = \log [x_1(K-1)+1]/\log K \quad (4)$$

where  $K$  is the Everett phase equilibrium constant,  $\varepsilon^\circ = \varepsilon_{AB}^\circ$ ,  $\varepsilon_B^\circ > \varepsilon_A^\circ$ . The normalized  $SP$  parameter ( $NSP$ ) is described in a previous paper.<sup>3</sup>

From Eq. (1) it is obvious that the value  $\varepsilon_B^\circ$  equals the intercept of the obtained regression straight lines, while the value  $\varepsilon_A^\circ = \text{slope} \times \log K + \text{intercept}$ . The values of  $\varepsilon_A^\circ$  and  $\varepsilon_B^\circ$  thus estimated were within the range of literature data or deviated only slightly from them. Usually the data given by Geiss<sup>7</sup> was used but in the case of disagreement or when some data was missing literature data from other sources was used. For example, the data for diethylamine  $\varepsilon_B^\circ = 0.63$  (alumina) was taken from Fried and Sherma,<sup>8</sup> and the values for acetonitrile  $\varepsilon_B^\circ = 0.65$  (alumina), trichloromethane  $\varepsilon_B^\circ = 0.26$  (silica) and ethyl acetate  $\varepsilon_B^\circ = 0.38$  (silica) were taken from Schoenmaker.<sup>9</sup> The data for  $\text{NH}_2$ -silica were taken from Snyder.<sup>5</sup>

Although Snyder's  $\varepsilon^\circ$  parameters were used to show that they are linear function of the  $SP$  parameters, that is to prove the applicability of  $SP$  scale also in NP chromatography, it must be pointed out that our results are not in accordance with Snyder's "solvent localization phenomenon". Namely, in all the cases considered, it was found, regardless of the polarity of the more polar component in a binary system B, that the constant  $K$ , as well as the values  $\varepsilon_B^\circ$ , are independent of the mole fraction of component B in the stationary or mobile phase, which was not the case according to Snyder.<sup>10</sup> This is a consequence of the different equations used in both papers. Namely, Snyder used the following equation to connect  $\varepsilon^\circ$  and  $K$ :

$$\varepsilon^\circ = \log [N_B(K-1)+1]/n_B \alpha + \varepsilon_A^\circ \quad (5)$$

To derive this equation two definitions of  $K$  were used: the one of Everett, denoted here as  $K^E$  and that of Snyder, denoted here as  $K^S$

$$K^E = (\theta_B \cdot N_A) / (\theta_A N_B) \quad (6)$$

$$K^S = 10^z, \text{ where } z = \alpha n_B(\varepsilon_B^\circ - \varepsilon_A^\circ) \quad (7)$$

or in the logarithmic form:

$$\log K^S = \alpha n_B(\varepsilon_B^\circ - \varepsilon_A^\circ) \quad (7a)$$

In the above equations  $\theta_B$  and  $N_B$  denote the mole fractions of the more polar component B in the stationary and mobile phase, respectively, and  $\theta_A$  and  $N_A$  have an analogous meaning, but they correspond to the less polar component (A),  $n_B$  denotes the area required by a molecule of solvent B on the adsorbent surface, and  $\alpha$  is the adsorbent activity parameter.  $\varepsilon^\circ$ ,  $\varepsilon_A^\circ$  and  $\varepsilon_B^\circ$  are the solvent strength parameters of the mixed solvent AB, and of the pure solvents A and B, respectively. In Eq. (5), as can be seen from the derivation of this equation in Snyder's paper,<sup>10</sup> the value  $K$  in the numerator of the first term is *de facto*  $K^E$ . The constant  $K^S$  is also represented in the same equation, albeit in a somewhat hidden form, because if in the first term of Eq. (5) both the numerator and denominator are multiplied by  $(\varepsilon_B^\circ - \varepsilon_A^\circ)$  by using Eq. (7a) the following expression is obtained:

$$\varepsilon^{\circ} = \{(\varepsilon_{\text{B}}^{\circ} - \varepsilon_{\text{A}}^{\circ}) \log [N_{\text{B}}(K^{\text{E}} - 1) + 1] / \log K^{\text{S}}\} + \varepsilon_{\text{A}}^{\circ} \quad (8)$$

If the above equation is compared with the one used in this work, which was obtained by substitution of Eq. (4) into Eq. (2) taking into account that  $N_{\text{B}} = x_1$ , as well as that in these equations  $K = K^{\text{E}}$ , it can be seen that this equation is analogous to Eq. (8):

$$\varepsilon^{\circ} = \{(\varepsilon_{\text{B}}^{\circ} - \varepsilon_{\text{A}}^{\circ}) \log [x_1(K^{\text{E}} - 1) + 1] / \log K^{\text{E}}\} + \varepsilon_{\text{A}}^{\circ} \quad (9)$$

The only difference is that in the denominator of the first term of Eq. (8) the value  $\log K^{\text{S}}$  is present whereas in Eq. (9) it is  $\log K^{\text{E}}$ . Hence it is of importance to establish whether these constants ( $K^{\text{S}}$  and  $K^{\text{E}}$ ) are equal, which must be the case, as both of them correspond to the same phase equilibrium. The values  $K^{\text{E}}$  were determined in the present paper for 30 phase equilibria by using reference  $\varepsilon^{\circ}$  values and the procedure described earlier.<sup>2</sup> The values of  $K^{\text{S}}$  were estimated from Snyder's equation (7) on the basis of literature data for  $\alpha$ ,  $n_{\text{B}}$ ,  $\varepsilon_{\text{B}}^{\circ}$  and  $\varepsilon_{\text{A}}^{\circ}$ . However, as these data often differ in the literature, and Eq. (7) is exponential, it was arbitrarily decided that these constants are not equal only in those cases in which they differ by more than a factor of three times. This was the case in the following 10 from the total of 30 considered equations:

*For alumina, systems:*

1. pentane–diethylamine:  $K^{\text{E}}/K^{\text{S}} = 700/32.5$  ( $n_{\text{B}} = 4.0^{10}$ ,  $\varepsilon_{\text{B}}^{\circ} = 0.63^8$ )
2. benzene–diethylamine: 25/5.5 and
3. benzene–acetonitrile: 160/4.1.

In the cases benzene–2-propanol and benzene–methanol,  $K^{\text{S}}$  could not be estimated as there are no data in the literature for  $n_{\text{B}}$ . The data available in Geiss<sup>7</sup> and other literature data are obviously increased in order to achieve better agreement between the experimentally found and the values of  $\varepsilon^{\circ}$  calculated using Eq. (5), which will be discussed later.

*In the case of silica, systems:*

1. pentane–ethyl acetate: 650/54.1
2. pentane–ethyl ether: 700/22.6
3. pentane–acetone 3500/29.5
4. benzene–acetone 30/5.8 and
5. benzene–acetonitrile 100/5.7.

From the given data it can be seen that there are several systems on alumina and silica for which the  $K^{\text{E}}$  and  $K^{\text{S}}$  values differ to a great extent. Since the  $K$  value, in the numerator and denominator of the first term of Eq. (8) corresponds to the same phase equilibrium, both  $K$  values,  $K^{\text{E}}$  and  $K^{\text{S}}$ , have to be the same. Therefore, in the case of a significant difference in these values, it is not possible to substitute  $\log K^{\text{S}} = \alpha n_{\text{B}} (\varepsilon_{\text{B}}^{\circ} - \varepsilon_{\text{A}}^{\circ})$  in the denominator of Eq. (8), or which is the same in the denominator of Eq. 5, to use the Table data for  $n_{\text{B}}$  and  $\alpha$ , and after substitution of the experimental data  $\varepsilon^{\circ}$ , to calculate  $K$  which is in the numerator. In such a way, the false conclusion could be reached that the equilibrium con-

stant can change with changing  $\theta_B$  (or  $N_B$ ). The “constant” calculated in such a manner has no physical meaning, hence it is incorrect to substitute it in Eq. (7) for the estimation of  $\varepsilon_B^\circ$ , or to substitute it in Eq. (6) to estimate  $\theta_B$  for the corresponding values of  $N_B$ . This phenomenon, called by Snyder “solvent localization”, according to which, in cases when component B is very polar, the equilibrium constant and the value  $\varepsilon_B^\circ$  change with changing  $\theta_B$  is in our opinion just fiction.

The derivation of the Snyder equations is described in the literature,<sup>10</sup> where the “solvent localization phenomenon” is presented and explained using the system: alumina ( $\alpha = 0.63$ )/pentane-acetonitrile as an example. It was established by application of Eq. (7) that the  $\varepsilon_B^\circ$  values fall from 0.65 (100 % v/v ACN) to 1.3 (0 % v/v ACN), corresponding to a change of the  $K$  value from 18.6 to 346, respectively, when  $n_B = 3.1$  and  $\varepsilon_A = 0$ . In opposition to this, our regression equation  $\varepsilon^\circ = f(SP)$ , obtained on the basis of the same experimental data for  $\varepsilon^\circ$ , is given by:

$$\varepsilon^\circ = -0.2084 SP + 0.6486 \quad (K = 1280)$$

$$\text{conc. range } 0 - 100 \% \text{ v/v, } n = 8, r = -0.9996, s = 5.48 \times 10^{-3}$$

$$\varepsilon_A^\circ \text{ estimated}/\varepsilon_A^\circ \text{ by definition} = 0.001/0.000$$

$$\varepsilon_B^\circ \text{ estimated}/\varepsilon_B^\circ \text{ experimental}^{9,10} = 0.649/0.650.$$

From the above equation it can be seen that the equilibrium constant equals 1280, and that it is valid over the whole concentration range of the modifier. The same is valid for the  $\varepsilon_A^\circ$  and  $\varepsilon_B^\circ$  values, estimated from the slope and intercept of the regression straight line in accordance with Eq. (1).

An interesting observation described in the already mentioned paper<sup>10</sup> is that if the value of  $n_B$  increases with respect of the value according to the definition, for example, if multiplied by a factor  $\Psi$ , Snyder's Eq. (5) can be then applied for the estimation of  $\varepsilon^\circ$  with extreme accuracy. Thus, if in the given example, the  $n_B$  value of 3.10 is multiplied by  $\Psi = 2.45$ , the new  $n_B$  value of 7.6 gives excellent agreement between the experimental and calculated  $\varepsilon^\circ$  values. However, in this procedure the  $n_B$  value is not increased artificially, as according to Snyder, but  $\log K^S$  is recalculated into  $\log K^E$ :

$$\alpha \Psi n_B (\varepsilon_B^\circ - \varepsilon_A^\circ) = \Psi \log K^S = (\log K^E / \log K^S) \log K^S = \log K^E \quad (10)$$

The value  $\Psi$  calculated from the relation  $\Psi = \log K^E / \log K^S = \log 1280 / \log 18.6 = 2.45$ , it is completely consistent with the value empirically found by some other authors.<sup>10</sup>

It is to be understood that the 31 linear regression equations given in the present paper can be used for the calculation of the mole or volume fraction of component B (in the system A-B), necessary to achieve the wanted value of  $\varepsilon^\circ$  and *vice versa*. From the excellent linear correlation of the function  $\varepsilon^\circ = f(SP)$ , it follows that for the linearization of  $\log k$  values in NP chromatography, besides  $\varepsilon^\circ$ ,  $SP$  parameters can be applied, as well. For this purpose it is necessary to have a series of the corresponding  $\log k$  values to be able to determine the phase equilibrium constant, necessary for the calculation of  $SP$  parameters.<sup>2</sup> In this case, the polarity of the more polar component of the binary mobile phase is not signif-

icant. Besides, it is not necessary to know either the activity of the adsorbent ( $\alpha$ ) or the other parameters used in the determination or calculation of  $\varepsilon^{\circ}$  values.

## GLOSSARY

$K$  – Phase equilibrium constants in the system: adsorbent/binary eluent,  $K^E$  Everett's definition (Eq. (6), and  $K^S$  Snyder's definition (Eq. (7) and (7a)).

$n_B$  – Molecular area of solvent molecule B

$N_A, N_B$  – Mole fraction of A and B in the mobile phase, respectively

$\alpha$  – Adsorbent activity parameter

$\varepsilon^{\circ}, \varepsilon_A^{\circ}, \varepsilon_B^{\circ}$  – Solvent strength parameters in mixtures A-B, pure A and pure B solvent in NP chromatography, respectively

$\theta_A, \theta_B$  – Mole fraction of A and B in the stationary phase, respectively

$x_s, x_1$  – Mole fraction of modifier in the stationary and mobile phase, respectively. In NP chromatography equal with  $\theta_B$  and  $N_B$ , respectively

$SP$  – Parameter described in ref. 1 and 2, defined by Eq. (3)

$NSP$  – Parameter described as normalized  $SP$  parameter in Ref. 2, defined by Eq. (4).

## ИЗВОД

УТИЦАЈ САСТАВА СТАЦИОНАРНЕ И МОБИЛНЕ ФАЗЕ НА ПАРАМЕТАР  
ЈАЧИНЕ РАСТВАРАЧА  $\varepsilon^{\circ}$  И  $SP$  СИСТЕМ ПАРАМЕТАР У НФ ХРОМАТОГРАФИЈИ  
НА КОЛОНИ

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

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Показано је да се  $SP$  параметри, раније употребљени за линеаризацију  $\log k$  вредности у РФ хроматографији, могу употребити и у НФ хроматографији. Утврђена је врло добра линеарна зависност између  $SP$  параметра и раније описаног Снајдеровог параметра јачине растварања  $\varepsilon^{\circ}$ . Такође је нађено да је фазна равнотежна константа  $K$  независна од поларности и концентрације поларније компоненте бинарне смеше растварања.

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## REFERENCES

1. T. J. Janjić, G. Vučković, M. B. Čelap, *J. Serb. Chem. Soc.* **65** (2000) 725
2. T. J. Janjić, G. Vučković, M. B. Čelap, *J. Serb. Chem. Soc.* **66** (2001) 671
3. T. J. Janjić, G. Vučković, M. B. Čelap, *J. Serb. Chem. Soc.* **67** (2002) 179
4. F. Geiss, *Fundamentals in Thin-Layer Chromatography (Planar Chromatography)* Huthig Verlag, Heidelberg, 1987, p. 257
5. L. R. Snyder, T. G. Schunk, *Anal. Chem.* **54** (1982) 1764
6. L. R. Snyder, *Principles of Adsorption Chromatography*, Edward Arnold, London, 1968, pp. 378, 379
7. As reference 4, p. 254
8. B. Fried, J. Sherma, *Thin-Layer Chromatography: Technique and Applications*, 2<sup>nd</sup> Edition, Chromatogr. Sci. Series, Vol. 35, 1986, p. 81, Marcel Dekker Inc., New York
9. P. J. Schoenmakers, *Optimization of Chromatographic Selectivity*, *J. Chromatography Library*, Vol 35, 1989, p. 100, Oxford, Russ. transl, Mir, Moscow
10. L. R. Snyder, J. L. Glajch, *J. Chromatogr.* **214** (1981) 1 and references cited therein.