

Application of the Log k pair linearity rule and Proportionality rule to the RPP mobile phase scales estimation on cyano-silica column

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On the basis of literature-reported log k values, the Log k pair linearity rule and the Proportionality rule were found to be also valid in the case of cyano-silica sorbent, when methanol, acetonitrile or propane-2-ol were used as modifiers. The RPP scales, reflecting the solvent strength, are in good linear relationship with the experimentally determined log k values. Furthermore, in the case of methanol and acetonitrile, the linear dependence: $\log k = f(\text{mol \% of modifier})$ was also established. In the function obtained in a such way, the intercept and the slope exhibit an approximate linear dependence. Finally, in the case of methanol, the experimentally obtained log k values are in a satisfactory agreement with the values calculated by the above equation.

Keywords: column chromatography, cyano-silica sorbent, Log k pair linearity rule, Proportionality rule, RPP scale.

INTRODUCTION

In our recently published papers, both the R_M (or log k) pair linearity rule and the Proportionality rule were described.^{1–4} These rules can be used to establish if there is a common solvent strength scale (RPP scale) for a group of compounds chromatographed using the same solvent series. If an RPP scale exists, it can also be determined by the above rules. To date, this procedure has been successfully applied to the log k values obtained on an ODS column using methanol (MeOH) or acetonitrile (ACN) as modifiers,⁴ as well as on a diol-silica sorbent using MeOH, ACN or tetrahydrofuran (THF) as modifiers.⁵

Continuing these investigations, in this study we applied the same procedure to the literature-reported log k values obtained on cyano silica columns using MeOH, ACN or propane-2-ol (IPA) as modifiers.⁶

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RESULTS AND DISCUSSION

The list of the examined compounds, differing in their ability of mutual interaction with the stationary and mobile phase of the chromatographic system, *i.e.*, compounds having different solute descriptors, is shown in Table I.

TABLE I. List of the compounds used

Group I	Group II	Control group
1. Naphthalene	10. Nitrobenzene	19. 1,2-Dibrombenzene
2. <i>n</i> -Propylbenzene	11. 2-Hexanone	20. Ethylphenylketone
3. Chlorobenzene	12. Phenol	21. Methylbenzoate
4. Bromobenzene	13. 4-Cresol	22. 2-Octanone
5. 1,2-Dichlorobenzene	14. 2-Chlorophenol	23. 3-Cresol
6. Benzaldehyde	15. Benzyl alcohol	24. 4-Phenylphenol
7. Benzonitrile	16. 2-Phenylethanol	25. 2-Nitroaniline
8. Anisole	17. Benzamide	
9. Acetophenone	18. Acetanilide	

The regression data and the obtained RPP values are shown in Table II.

TABLE II. Parameters of the linear equation: $\overline{(\log k)}_1 = f(\overline{(\log k)}_2)$, as well as the estimated mobile phase RPP parameters. $\overline{(\log k)}_1$ represents the average $\log k$ values of the first, and $\overline{(\log k)}_2$ of the second group of compounds from Table I ($n = 7$)

Modifier	Intercept	Slope	Cor. coef. (<i>r</i>)	RPP for vol % of modifier*						
				50	40	30	20	10	5	1
MeOH	0.3088	1.4567	0.9981	0.00	0.23	0.46	0.68	0.79	0.89	1.00
ACN	0.1921	1.7073	0.9989	0.00	0.25	0.45	0.57	0.73	0.83	1.00
IPA	0.2464	1.6177	0.9964	0.00	0.26	0.56	0.77	0.83	0.89	1.00
THF	–	–	0.9907	Not estimated**						

*In the system modifier/water; **Because of the fact that the average $\log k$ values for 20, 10 and 5 vol % of modifier differ only slightly

The correlation coefficients of the function: $\log k = f(\text{RPP})$ are given in Table III. Values lower than 0.9900 were found only with compounds 11 and 17 using ACN, and 17 and 24 in the case of IPA.

Linear dependencies $\log k = f(\text{mol \% of modifier})$ for MeOH and ACN are demonstrated in Table IV. These dependencies point to the linear dependence between the RPP values and mol % of modifiers.

In addition, high correlation coefficients between the intercept and the slope of the above mentioned linear functions were found, which implies the “approximate congenerity”⁸ of the investigated compounds. The regression data for the function: $(\text{intercept } 10) = f(-\text{slope } 100)$ are: for MeOH ($n = 18$) $r = -0.9598$, intercept -5.7140 , slope 5.9278 , $s = 1.173$; for ACN ($n = 19$) $r = -0.9817$, intercept -1.4872 , slope 3.4704 ,

$s = 0.779$. For comparison, it should be pointed out that for a certainty of 99.9 % the r_{test} values amount to 0.708 ($n = 18$) and 0.693 ($n = 19$), respectively.

Finally, the experimentally determined log k values in the case of MeOH compared with those calculated by means of the Solvation parameters model,^{6,7} as well as by means of the linear dependence $\log k = f(\text{mol \% of MeOH})$ are shown in Table V. The comparison shows a satisfactory agreement.

The presented results show that it is also possible to use the Log k pair linearity rule and the Proportionality rule, as well as the corresponding RPP scales in the case of a cyano-silica sorbent.

TABLE III. Correlation coefficient (r) of the linear function $\log k = f(\text{RPP})$. Ordinal numbers designate the compound in Table I

No.	MeOH	ACN	IPA
1	0.9993	0.9963	0.9962
2	0.9973	0.9982	0.9974
3	0.9954	0.9969	0.9970
4	0.9960	0.9971	0.9926
5	0.9990	0.9962	0.9950
6	0.9969	0.9967	0.9947
7	0.9988	0.9939	0.9993
8	0.9969	0.9980	0.9985
9	0.9967	0.9944	0.9939
10	0.9994	0.9984	0.9985
11	0.9967	0.9891	0.9908
12	0.9989	0.9954	0.9961
13	0.9970	0.9980	0.9997
14	0.9992	0.9996	0.9992
15	0.9988	0.9978	0.9953
16	0.9994	0.9993	0.9975
17	0.9937	0.9861	0.9858
18	0.9939	0.9938	0.9909
19	—	0.9963	0.9937
20	—	—	0.9914
21	—	—	0.9980
22	—	—	0.9983
23	—	—	0.9986
24	—	—	0.9883
25	—	—	0.9977

TABLE IV. Regression data of the linear function $\log k = p(\text{mol \% of modifier}^*) + q$ for MeOH ($n = 7$) and ACN ($n = 6$)** obtained with cyano-silica sorbents

Compound No. from Table I	MeOH			ACN		
	$-p$ 100	q 10	$-r$	$-p$ 100	q 10	$-r$
1	4.05	17.54	0.9989	4.69	14.25	0.9932
2	3.42	15.35	0.9978	4.07	13.32	0.9988
3	2.58	11.40	0.9964	2.96	9.904	0.9982
4	2.92	12.90	0.9984	3.39	10.95	0.9989
5	3.53	15.55	0.9980	4.21	13.06	0.9954
6	2.43	7.668	0.9932	1.84	5.459	0.9924
7	2.20	7.834	0.9957	1.94	6.092	0.9959
8	2.39	9.291	0.9983	2.26	7.306	0.9967
9	2.83	9.152	0.9931	2.34	6.414	0.9920
10	2.29	9.611	0.9980	2.31	7.598	0.9969
11	1.87	4.579	0.9925	1.23	3.184	0.9834
12	1.65	4.744	0.9980	1.44	3.554	0.9908
13	2.34	7.476	0.9976	2.05	5.387	0.9956
14	2.63	9.172	0.9980	2.56	6.957	0.9978
15	1.53	3.628	0.9954	1.30	2.633	0.9941
16	1.73	5.184	0.9969	1.72	4.072	0.9979
17	2.03	4.139	0.9879	1.68	2.503	0.9810
18	2.16	6.136	0.9924	1.99	4.338	0.9912
19	–	–	–	4.99	15.21	0.9931

*Mole % of modifiers were calculated according to the equation: $(\text{mol \%})^{-1} = A(\% \text{ v/v})^{-1} + 0.01(1-A)$, where A in case of MeOH is 2.2475 and ACN 2.9352. **The point for 1 % v/v of modifier is omitted

TABLE V. A comparative review of the experimentally found and calculated log *k* values for some compounds: (a) Experimentally found values⁶; b) The values calculated by Solvation parameter model^{6,7}; c) The values calculated by equation: $\log k = f(\text{mol \% of modifier})$ using parameters *p* and *q* from Table IV

Compound	Vol % (mol %) of methanol in the mobile phase							
	50 (30.79)	40 (22.88)	30 (16.02)	20 (10.01)	10 (4.711)	5 (2.288)	1 (0.4474)	
Naphthalene	a)	3.35	6.35	13.03	22.50	34.38	45.06	58.50
	b)	3.44	6.43	12.88	22.45	33.17	42.59	59.61
	c)	3.21	6.71	12.75	22.32	36.60	45.88	54.49
1,2-Dichlorbenzene	a)	2.91	5.34	10.33	17.32	22.75	28.56	35.70
	b)	2.99	5.52	9.96	16.95	23.13	27.73	31.90
	c)	2.94	5.59	9.77	15.92	24.49	29.82	34.63
Benzonitrile	a)	1.29	1.90	2.60	3.85	4.67	5.07	6.44
	b)	1.31	1.83	2.70	3.88	4.86	5.52	6.75
	c)	1.28	1.91	2.70	3.66	4.78	5.41	5.94
Anisole	a)	1.59	2.35	3.43	5.05	6.83	7.06	8.43
	b)	1.52	2.35	3.47	5.16	6.56	7.51	9.16
	c)	1.56	2.41	3.52	4.90	6.55	7.49	8.29
Nitrobenzene	a)	1.86	2.68	3.86	5.39	6.73	8.15	9.47
	b)	1.60	2.33	3.71	5.22	7.16	8.33	10.26
	c)	1.80	2.74	3.93	5.39	7.13	8.10	8.93
Benzyl alcohol	a)	0.79	1.02	1.32	1.62	1.87	2.05	2.44
	b)	0.79	1.04	1.33	1.77	2.13	2.37	2.83
	c)	0.78	1.03	1.31	1.62	1.95	2.13	2.27
2-Propylethanol	a)	0.98	1.29	1.77	2.30	2.65	2.88	3.39
	b)	0.88	1.19	1.65	2.25	2.80	3.19	4.28
	c)	0.97	1.35	1.74	2.21	2.73	3.01	3.24
<i>n</i> -Propylbenzene	a)	2.93	5.46	10.33	17.32	22.50	27.83	32.30
	b)	2.96	5.58	10.49	18.19	24.83	29.74	37.06
	c)	3.03	5.66	9.72	15.59	23.67	28.65	33.11

ИЗВОД

ПРИМЕНА ПРАВИЛА ЛИНЕАРНОСТИ $\log k$ ПАРОВА И ПРАВИЛА
ПРОПОРЦИОНАЛНОСТИ ЗА ИЗРАЧУНАВАЊЕ RPP СКАЛА МОБИЛНИХ ФАЗА НА
ЦИЈАНО-СИЛИКА КОЛОНИ

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

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На основу литературних $\log k$ - вредности потврђено је важење Правила линеарности $\log k$ парова и Правила пропорционалности у случају цијано-силика сорбента када се као модификатори употребе метанол, ацетонитрил или пропан-2-ол. Одређене RPP скале, које одражавају снагу растварача, биле су у доброј линеарној зависности са експерименталним $\log k$ вредностима. У случају метанола и ацетонитрила утврђена је такође и линеарна зависност: $\log k = f(\text{mol \% модификатора})$. Одсечак и нагиб тако добијених правих показивали су приближну линеарну зависност. Најзад, у случају метанола експерименталне $\log k$ вредности показале су задовољавајућу сагласност са израчунатим вредностима применом наведене једначине.

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