EVALUATION OF ADSORPTION AND RETENTION MODELS FOR SEPARATION OF POLYCHLORINATED BIPHENYLS BY HPLC ON REVERSED PHASES

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Adsorption model for separation of polychlorinated biphenyls (PCB) in HPLC on reversed phases (chemically bonded C_{18}) was applied to a series of 15 PCB. The values for adsorption interaction energy were computed employing the method of empirical potential functions according to Dashevskii. The model of interphase partitioning and the partition model of separation are also presented with respect to the optimized geometry of the PCB molecule with an optimal torsion angle. The Gibbs solvation energies in the stationary (octanol) and mobile (water) phases for 15 PCB were computed by means of continuum models. The energy values were correlated with capacity factors and partition coefficients. Correlation analysis indicated the dominant role in PCB separations to be partition processes of the solute in mobile phase; adsorption on these surfaces does not influence considerably the separation process.

The majority of HPLC separations (70–80%) has recently been carried out on chemically bonded reversed phases (RP-HPLC) in which the mobile phase is more polar than the stationary one; e.g. the carrier surface is modified by C_2, C_8 or C_{18} alkyls, water–methanol being the mostly employed mobile phase. The RP-HPLC theory is hitherto not worked up, although the chemically bonded phases are used frequently. The main problem is to find a suitable description for chemically bonded alkyls when contacting the mobile phase and the compound being separated. The dominating process has not been cleared; involved can be partition[1–5] (absorption), adsorption[6–12], combined adsorption–absorption[13], solvophobic adsorption[14], or some other retention mechanisms. Partition between mobile phase and chemically bonded stationary phase is considered by several authors[1,2,15–16] as the effective partition mechanism. The chemically bonded stationary phase is modelled either as a system similar to the liquid alkane[15,16], or as a mixed stationary liquid phase[17,18] with a presumed absorption of the organic component of the mixed mobile phase[1,3,19]. The adsorption mechanism assumes the molecules of the compound being separated to be bonded either directly to the alkyl chains, or adsorbed to the so called "interface" between the bulky phase and the region containing the solvated alkanes.

Whether partition or adsorption mechanisms are involved is quite difficult to evidence unequivocally; prevalence of one of them is considered in papers published so far. Therefore, some authors tried to describe quantitatively the process on non--polar bonded phases, e.g. employing the thermodynamic properties of the system under investigation. This resulted in a series of models[20-31] as e.g. solvophobic model by Melander and Horváth[20-21], partition model by Sentell[22-24], the lattice model by Martire and Boehm[25,26], Dill's model[27] assuming the existence of interphases and statistical–thermodynamic model[28,29]. None of the above-mentioned models describes the HPLC chromatography on reversed phases so as the capacity factors could reliably be calculated from the accessible physicochemical data. Final equations include either parameters accessible with difficulties, or the accordance between theoretical and experimental data was unsatisfactory after simplification. It is, therefore desirable to elaborate a most adequate and detailed description of separation as possible (without simplification) using laws of classical thermodynamics.

High performance liquid chromatography on reversed phases (RP-HPLC) was modelled from the aspect of partition and adsorption separation mechanism. The partition model was based on continuum methods concerning influence of the medium. Preferred were processes involving physical basis of the problem; they have not to be extraordinarily computer-time consuming and consequently, applicable to great molecular systems. Such a model employed with a series of PCB is described in detail in refs[32,33]; in our previous contribution[34], optimization of PCB geometry was examined in an isolated model, in solution and with adsorption. The model of interphase partitioning and partition model of separation for PCB in RP-HPLC were presented in regard to the optimized geometry of the PCB molecule with an optimal torsion angle Θ_{opt}. Computed adsorption energy values from ref.[34] were employed for the adsorption model investigating modelling of the separated compound with the surface of chemically bonded C_{18} (octadecyl) stationary phase basing on the discrete model by the method of empirical potentials according to Dashevskii. Correlation analysis is the tool for evaluation of both models.

THEORETICAL

The frequently occuring interphases are, in addition to the system liquid–liquid also systems liquid–solid and gas–solid on which adsorption, absorption chromatography and processes of heterogeneous catalysis are taking place. From this theoretical viewpoint it is necessary to explain the fundamentals of chemical sorption, processes, to find energetic profiles of sorption processes and to estimate the most stable positions of molecules being adsorbed and finally to interprete theoretically the thermodynamic data characterizing these processes.

Interactions between the compound adsorbed and the solid surface can be investigated by two models: (i) modelling the periodic surface, (ii) considering the discrete particles of a certain surface section. We already employed[34] the second method involving empirical potential functions dealing with modelling of PCB adsorption on a model surface represented by a chemically bonded C_{18} phase. The total adsorption Gibbs energy of the separated PCB molecule with the model surface simplified by interaction energy was expressed as a sum of electrostatic dispersion and repulsion contributions:

$$G_{\mathrm{ads}}^{\mathrm{M/S}} \approx E_{\mathrm{ads}}^{\mathrm{M/S}} = E_{\mathrm{el}}^{\mathrm{M/S}} + E_{\mathrm{disp}}^{\mathrm{M/S}} + E_{\mathrm{rep}}^{\mathrm{M/S}}\,, \qquad (1)$$

where M and S stand for the molecule of compound separated and surface, respectively. Procedures dealing with computation of the respective contributions are detailed in refs[34,35–37]; this procedure enables us to find minimal adsorption energy between the sorbed solute molecule and the surface.

The presented adsorption model in the RP-HPLC system considers a separation process of certain solute molecule and also its adsorption on the modelled C_{18} chemically bonded phase and its solvation in mobile phase. Final separation of the compound depends on the mutual difference magnitude of the total adsorption Gibbs energy in stationary phase and solvation Gibbs energy in the mobile phase:

$$\Delta G^{\mathrm{M/S-m}} = \Delta G_{\mathrm{ads}}^{\mathrm{M/S}} - \Delta G_{\mathrm{solv}}^{\mathrm{m}}\,. \qquad (2)$$

For the simplicity it could be assumed $\Delta G_{\mathrm{ads}}^{\mathrm{M/S}} \approx E_{\mathrm{ads}}^{\mathrm{M/S}}$. The member $\Delta G_{\mathrm{solv}}^{\mathrm{m}}$ represents the solvation Gibbs energy in the mobile phase.

Final separation of the compound in this partition model for separation of compounds in an RP-HPLC system or in the model of interphase partitioning depends on the mutual difference magnitude of interaction (solvation) Gibbs energies in the stationary and mobile phases, or in octanol and water:

$$\Delta G^{\mathrm{s/m}} = \Delta G_{\mathrm{solv}}^{\mathrm{s}} - \Delta G_{\mathrm{solv}}^{\mathrm{m}} \qquad (3)$$

$$\Delta G^{\mathrm{o/w}} = \Delta G_{\mathrm{solv}}^{\mathrm{o}} - \Delta G_{\mathrm{solv}}^{\mathrm{w}}\,. \qquad (4)$$

The total Gibbs solvation energy specifying the particular contribution is

$$\Delta G^{\mathrm{s/m}} = (\Delta G_{\mathrm{el}}^{\mathrm{s}} - \Delta G_{\mathrm{el}}^{\mathrm{m}}) + (\Delta G_{\mathrm{dr}}^{\mathrm{s}} - \Delta G_{\mathrm{dr}}^{\mathrm{m}}) + (\Delta G_{\mathrm{cav}}^{\mathrm{s}} - \Delta G_{\mathrm{cav}}^{\mathrm{m}}) \qquad (5)$$

$$\Delta G^{\mathrm{o/w}} = (\Delta G_{\mathrm{el}}^{\mathrm{o}} - \Delta G_{\mathrm{el}}^{\mathrm{w}}) + (\Delta G_{\mathrm{dr}}^{\mathrm{o}} - \Delta G_{\mathrm{dr}}^{\mathrm{w}}) + (\Delta G_{\mathrm{cav}}^{\mathrm{o}} - \Delta G_{\mathrm{cav}}^{\mathrm{w}})\,, \qquad (6)$$

where ΔG_{el}, ΔG_{dr} and ΔG_{cav} are electrostatic, dispersion–repulsion and cavitation terms, respectively. Computation details were already reported in refs[32,38–42].

Correlation between the logarithm of capacity factor k', difference of the total adsorption energy and Gibbs solvation energy in the mobile phase

$$\log k' = a\,\Delta G^{\mathrm{M/S-m}} + b\,, \tag{7}$$

between the Gibbs solvation energies in the stationary and mobile phases

$$\log k' = c\,\Delta G^{\mathrm{s/m}} + d\,, \tag{8}$$

and between the logarithm of partition coefficient P and Gibbs solvation energies in octanol and water

$$\log P = e\,\Delta G^{\mathrm{o/w}} + f\,, \tag{9}$$

were sought.

These correlations were then evaluated statistically with respect to the agreement between the theoretical and experimental values and their statistical significance. The correlation coefficient r was employed and the linearity or the correlation function were tested applying the F-criterion[43], viz. by comparison with the critical F-distribution values $F_{\alpha(\nu_1,\nu_2)}$ (S. R.) for degrees of freedom $\nu_1 = k$ and $\nu_2 = n - k - 1$, where k stands for the number of substances in the series, $1 - \alpha$ is the significance level.

The CNDO/2 semiempirical quantum-chemical method[44] was employed for computing both the charge distribution pattern at atoms and the structure optimization. The experimental k' values were taken from ref.[45]. The experimental data for partition coefficients $\log P$ in octanol–water were taken from Shiu and Mackay[46]. The $\log P$ values were determined by methods, the error of which does generally not exceed 10%. Tests showed that such an error in experimental values does not influence the statistical parameters (r, S. R.) to an extent such as to bring about change in the qualitative conclusions.

RESULTS AND DISCUSSION

Numbering of the fundamental biphenyl skeleton and PCB is seen in Fig. 1. Computed were standard geometries taken from ref.[47] excepting the internal torsion angle Θ. The bond length between two phenyl rings of biphenyl and PCB, considered constant during rotation, was taken from ref.[48]. The mutual twist of both phenyl rings of the molecule, characterized by internal torsion angle Θ published in ref.[34] was investigated by the Dashevskii method of empirical potential functions. The total adsorption energy $\Delta G_{\mathrm{ads}}^{\mathrm{M/S}}$ (values taken from ref.[34] are listed in Table I) was computed for optimized position of biphenyl and PCB against the surface (Fig. 2) considering *a*) translation of the molecule against surface, *b*) rotation of the molecule, *c*) change in the torsion angle Θ of the molecule (Figs 3 and 4).

Calculated contributions to the Gibbs free energy of solvation for the homogeneous series of 15 PCB with an optimized torsion angle Θ_{opt} are presented in Table II.

Evaluation of particular contributions detailed in ref.[32] presented the computed individual contributions to Gibbs solvation energy of 15 PCB with a unified torsion angle. Table II lists values for electrostatic (coulombic) part, dispersion – repulsion and cavitation contributions computed according to Sinanoglu or Pierotti for octanol

TABLE I

Optimal torsion angle[a], total Gibbs adsorption energy[a], experimental and log P values[b] for a homogeneous series of 15 PCB

Compound	Θ_{opt}	$\Delta G_{ads}^{M/P}$ kJ mol^{-1}	k'_{exp}	log P
Biphenyl	48	−41·90	–	3·9 ± 0·2
2-Cl	68	−42·39	1·01	4·3 ± 0·5
2,2′-Cl	79	−40·51	1·18	4·9 ± 0·5
2,3′-Cl	68	−45·22	1·36	4·8 ± 0·3
2,6-Cl	73	−43·18	1·30	5·0 ± 0·2
2,5,4′-Cl	68	−52·85	2·80	5·7 ± 0·2
2,4,4′-Cl	68	−56·45	2·90	5·8 ± 0·2
2,5,3′-Cl	67	−48·87	2·91	–
2,3,2′,3′-Cl	78	−52·25	1·91	5·6 ± 0·3
2,3,2′,5′-Cl	79	−54·78	2·20	6·0 ± 0·3
3,4,3′,4′-Cl	47	−63·20	4·14	6·1 ± 0·4
2,5,2′,5′-Cl	79	−45·18	2·58	6·1 ± 0·2
2,5,3′,4′-Cl	67	−54·06	3·92	5·9 ± 0·3
2,4,2′,5′-Cl	79	−47·26	2·92	6·1 ± 0·2
2,4,2′,4′-Cl	79	−51·87	3·14	5·9 ± 0·3
2,3,4,2′,5′-Cl	79	−58·48	3·36	6·5 ± 0·4

[a] Values taken from ref.[32]; [b] from ref.[46].

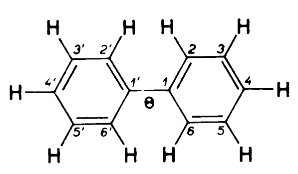

FIG. 1

Basic structure and numbering of atoms in biphenyl

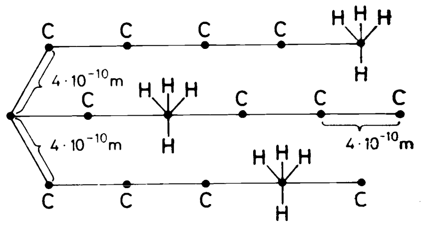

FIG. 2

Top view on the model showing the ***P3*** surface section and water. As seen, values for the respective contributions considered for an optimal torsion angle are a little higher (in absolute values) than those reported in ref.[32].

TABLE II

Contributions to the Gibbs solvation free energy for PCB (kJ mol^{-1}) at optimized torsion angle Θ_{opt} in water and octanol

Compound	$\Delta G^{\mathrm{w}}_{\mathrm{el}}$	$\Delta G^{\mathrm{o}}_{\mathrm{el}}$	$\Delta G^{\mathrm{w}}_{\mathrm{dr}}$	$\Delta G^{\mathrm{o}}_{\mathrm{dr}}$	$\Delta G^{\mathrm{w}}_{\mathrm{cav,s}}$	$\Delta G^{\mathrm{o}}_{\mathrm{cav,s}}$	$\Delta G^{\mathrm{w}}_{\mathrm{cav,p}}$	$\Delta G^{\mathrm{o}}_{\mathrm{cav,p}}$
Biphenyl	−0·92	−0·84	−96·90	−91·36	89·23	33·38	176·79	100·87
2-Cl	−10·45	−9·56	−118·70	−115·76	95·65	35·33	185·40	106·19
2,2′-Cl	−19·71	−18·02	−141·98	−141·64	102·53	37·43	194·87	112·02
2,3′-Cl	−19·26	−17·61	−142·77	−142·46	102·85	37·53	195·41	112·33
2,6-Cl	−18·41	−16·83	−142·61	−142·15	102·50	37·42	194·84	112·00
2,5,4′-Cl	−27·30	−24·97	−164·69	−167·25	110·16	39·76	205·69	118·63
2,4,4′-Cl	−27·52	−25·17	−164·33	−166·92	110·16	39·76	205·69	118·63
2,5,3′-Cl	−26·93	−24·63	−165·70	−168·16	110·30	39·80	205·95	118·78
2,3,2′,3′-Cl	−32·71	−29·91	−187·15	−191·68	115·56	41·40	212·59	122·94
2,3,2′,5′-Cl	−33·88	−30·97	−186·59	−191·49	116·06	41·56	213·42	123·43
3,4,3′,4′-Cl	−32·20	−29·44	−183·86	−188·95	116·23	41·61	213·77	123·63
2,5,2′,5′-Cl	−35·06	−32·06	−188·65	−193·76	117·00	41·84	215·06	124·39
2,5,3′,4′-Cl	−33·82	−30·92	−186·48	−191·51	116·67	41·74	214·56	124·09
2,4,2′,5′-Cl	−35·28	−32·26	−187·97	−193·04	117·00	41·84	215·06	124·39
2,4,2′,4′-Cl	−35·53	−32·49	−188·57	−193·64	116·98	41·84	215·05	124·38
2,3,4,2′,5′-Cl	−39·78	−36·37	−208·39	−215·77	122·42	43·49	222·00	128·72

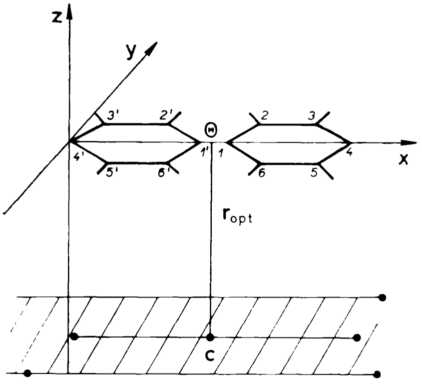

FIG. 3

Interaction of PCB molecule with model surface

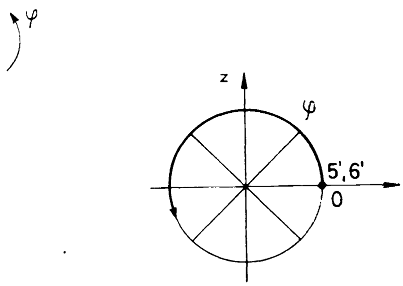

FIG. 4

Projection *y*–*z* of the rotation of PCB molecule

This difference rises proportionally with the increasing molecule hydrophobicity, i.e. with increasing number of chlorine atoms.

A more detailed information about evaluating the relationship between structure of the molecule and retention (partition, adsorption) properties offer total Gibbs energies of solvation (or their differences in two-phase systems), total Gibbs energies of adsorption and differences between the particular contributions. It is, therefore important to examine trends of changes in series of compounds, i.e. to compare relative changes with experimental data. Table III presents differences in Gibbs energies of solvation contributions for the system octanol–water.

Partition between Two Phases

Correlation dependences and their statistical characteristics were established for single-parameter equations of the log $P = f(\Delta G^{o/w})$ type, where $\Delta G^{o/w}$ is the difference in the total Gibbs free energies of solvation in two variants – with application of the Sinanoglu or Pierotti approaches to calculation of the cavitation contribution (Table IV). For 15 PCB derivatives following correlations were found:

$$\log P = -0{\cdot}0790\, \Delta G_S^{o/w} - 0{\cdot}0835 \qquad (10)$$

$$r = 0{\cdot}980 \quad n = 15 \quad \text{S.R.} = 319{\cdot}99 \quad 1 - \alpha > 99{\cdot}99\%$$

TABLE III

Differences between contributions to the Gibbs free energy of solvation (kJ mol^{-1}) in water and octanol

Compound	$\Delta G_{cl}^{o/w}$	$\Delta G_{dr}^{o/w}$	$\Delta G_{cav,s}^{o/w}$	$\Delta G_{cav,p}^{o/w}$
Biphenyl	0·08	5·54	−55·85	−75·92
2-Cl	0·89	2·94	−60·32	−79·21
2,2′-Cl	1·69	0·34	−65·10	−82·85
2,3′-Cl	1·65	0·31	−65·32	−83·08
2,6-Cl	1·58	0·46	−65·08	−82·84
2,5,4′-Cl	2·33	−2·56	−70·40	−87·06
2,4,4′-Cl	2·35	−2·59	−70·40	−87·06
2,5,3′-Cl	2·30	−2·46	−70·50	−87·17
2,3,2′,3′-Cl	2·80	−4·53	−74·16	−89·65
2,3,2′,5′-Cl	2·91	−4·90	−74·50	−89·99
3,4,3′,4′-Cl	2·76	−5·09	−74·62	−90·14
2,5,2′,5′-Cl	3·00	−5·11	−75·16	−90·67
2,5,3′,4′-Cl	2·90	−5·03	−74·93	−90·47
2,4,2′,5′-Cl	3·02	−5·07	−75·16	−90·67
2,4,2′,4′-Cl	3·04	−5·07	−75·14	−90·67
2,3,4,2′,5′-Cl	3·41	−7·38	−78·93	−93·28

$$\log P = -0{\cdot}0955\,\Delta G_P^{o/w} - 2{\cdot}8101 \qquad (11)$$

$$r = 0{\cdot}981 \quad n = 15 \quad \text{S.R.} = 335{\cdot}70 \quad 1 - \alpha > 99{\cdot}99\%\,.$$

A better correlation was obtained by employing the Pierotti method to express the cavitation contribution. The high quality of correlation indicates the formulated theory to reflect well the reality of experimental conditions.

Chromatographic Retention

The polar mobile phase consisting prevalently of aqueous methanol was, for simplification, modelled as water in chromatographic separation in the RP-HPLC system; attempts to set up a model for this mixed mobile phase did not result in a noticeable correlation improvement between the Gibbs free energy of partition and the retention data. Modelling of the stationary phase is more complicated, the RP-HPLC systems involve chemically bonded stationary phase with highly non-polar C_{18} alkyl chains. Some unreacted OH groups remain, however, on the support surface after its alkylation and play a role in separation of substances. Because of this, modelling of the RP-HPLC stationary phase by octanol, having a non-polar carbon chain and a polar OH group, was successful.

TABLE IV

Differences between the total Gibbs free energies of solvation (kJ mol^{-1}) in octanol and water for the different approaches to the computation of the cavitation contribution

Compound	$\Delta G_S^{o/w}$	$\Delta G_P^{o/w}$
Biphenyl	−50·23	−70·30
2-Cl	−56·49	−75·38
2,2′-Cl	−63·07	−80·82
2,3′-Cl	−63·36	−81·12
2,6-Cl	−63·04	−80·81
2,5,4′-Cl	−70·63	−87·29
2,4,4′-Cl	−70·64	−87·30
2,5,3′-Cl	−70·66	−87·33
2,3,2′,3′-Cl	−75·89	−91·38
2,3,2′,5′-Cl	−76·49	−91·98
3,4,3′,4′-Cl	−76·95	−92·47
2,5,2′,5′-Cl	−77·27	−92·78
2,5,3′,4′-Cl	−77·06	−92·60
2,4,2′,5′-Cl	−77·21	−92·72
2,4,2′,4′-Cl	−77·17	−92·70
2,3,4,2′,5′-Cl	−82·90	−97·25

Considering the nature of the stationary and mobile RP-HPLC phases model, the computed distributions to the Gibbs free energy of solvation in octanol and water can also be employed when modelling the chromatographic process. Although this process is more complex than partition in the octanol–water system, the correlation $\log k' = f(\log P)$ was linear with statistical parameters $r = 0{\cdot}90$, $n = 14$, S.R. = 40·05, $1 - \alpha > 99{\cdot}99\%$, thus evidencing a major role of lipophilic properties in the RP-HPLC separation.

For 15 PCB derivatives following correlations were obtained:

$$\log k' = -0{\cdot}0225\,\Delta G_{\mathrm{S}}^{\mathrm{o/w}} - 1{\cdot}2578 \qquad (12)$$

$$r = 0{\cdot}851 \quad n = 15 \quad \mathrm{S.R.} = 34{\cdot}04 \quad 1 - \alpha > 99{\cdot}99\%$$

$$\log k' = -0{\cdot}0273\,\Delta G_{\mathrm{P}}^{\mathrm{o/w}} - 2{\cdot}0435 \qquad (13)$$

$$r = 0{\cdot}857 \quad n = 15 \quad \mathrm{S.R.} = 36{\cdot}2 \quad 1 - \alpha > 99{\cdot}99\%\,.$$

These are worse than those with $\log P$. Nevertheless, correlation equation of the type $\log k' = f(\Delta G^{\mathrm{o/w}})$ possess a high level of significance. Correlations with $\log P$ have higher statistical parameters (r, F) than those with $\log k'$, due to complexity of the process associated with chromatographic separation.

On the other hand, statistical evaluation of the adsorption model

$$\log k' = 0{\cdot}0065\,(\Delta G_{\mathrm{ads}}^{\mathrm{M/S}} - \Delta G_{\mathrm{solv,s}}^{\mathrm{w}}) + 0{\cdot}1207 \qquad (14)$$

$$r = 0{\cdot}72 \quad n = 15 \quad \mathrm{S.R.} = 15{\cdot}01 \quad 1 - \alpha > 99{\cdot}5\%$$

showed the weak interaction (Eq. (*14*)) to be due to total adsorption energy values. The total adsorption energies correlate worse than the Gibbs solvation energies. It could be, therefore assumed that the dominant role in separation of PCB on C_{18} phase play partition processes and adsorption does not influence considerably the separation process.

REFERENCES

1. Knox J. H., Pryde A.: J. Chromatogr. *112*, 171 (1975).
2. Kikta E. J., Grushka E.: Anal. Chem. *48*, 1098 (1976).
3. Scott R. P. W., Kučera P.: J. Chromatogr. *142*, 213 (1977).
4. Lochmüller C. H., Wilder D. R.: J. Chromatogr. *17*, 574 (1979).
5. Nikolov R. N., Darzhalieva M. M.: J. Chromatogr. *370*, 377 (1986).
6. Telepchak M. J.: Chromatographia *6*, 234 (1973).
7. Kirkland J. J.: J. Chromatogr. Sci. *9*, 171 (1975).
8. Hanai T., Fujimura K.: J. Chromatogr. Sci. *14*, 140 (1976).
9. Unger K. K., Becker N., Roumeliotis P.: J. Chromatogr. *125*, 115 (1976).

10. Hemetsberger H., Maasfeld W., Ricken H.: Chromatographia *9*, 303 (1976).
11. Hemetsberger H., Kellermann M., Ricken H.: Chromatographia *10*, 726 (1977).
12. Colin H., Guiochon G.: J. Chromatogr. *158*, 183 (1978).
13. Řehák V., Smolková E.: Chromatographia *9*, 219 (1976).
14. Karger B. L., Gant J. R., Hartkopf A., Weiner P. H.: J. Chromatogr. *128*, 65 (1976).
15. Kirkland J. J., de Stefano J. J.: J. Chromatogr. Sci. *8*, 309 (1970).
16. Locke D. C.: J. Chromatogr. Sci. *11*, 120 (1973).
17. Colin H., Guiochon G.: J. Chromatogr. Sci. *18*, 54 (1980).
18. Karch K., Sebatian I., Halasz I., Engelhardt H.: J. Chromatogr. *122*, 171 (1976).
19. Lochmüller C. H., Wilder D. R.: J. Chromatogr. Sci. *17*, 17 (1979).
20. Horváth Cs., Melander W., Molnár I.: Anal. Chem. *49*, 142 (1977).
21. Horváth Cs., Melander W., Molnár I.: J. Chromatogr. *125*, 129 (1977).
22. Ying P. T., Dorsey J. G., Dill K. A.: Anal. Chem. *61*, 2540 (1989).
23. Sentell K. B., Dorsey J. G.: J. Chromatogr. *461*, 193 (1989).
24. Sentell K. B., Dorsey J. G.: Anal. Chem. *61*, 930 (1989).
25. Martire D. E., Boehm R. E.: J. Liq. Chromatogr. *3*, 753 (1980).
26. Martire D. E., Boehm R. E.: J. Phys. Chem. *87*, 1045 (1983).
27. Dill K. A.: J. Phys. Chem. *91*, 1980 (1987).
28. Jaroniec M., Martire D. E.: J. Chromatogr. *351*, 1 (1986).
29. Jaroniec M., Martire D. E.: J. Chromatogr. *387*, 55 (1987).
30. Hildebrand J. H., Praussnitz J. M., Scott R. L.: *Regular and Related Solutions*. Van Nostrand, New York 1970.
31. Karger B. L., Gant J. R., Hartkopf A.: J. Chromatogr. *128*, 65 (1976).
32. Jakuš V., Miertuš S.: Collect. Czech. Chem. Commun. *56*, 2833 (1991).
33. Miertuš S., Jakuš V.: Chem. Papers *44*, 793 (1990).
34. Jakuš V., Miertuš S.: Chem. Papers *44*, 589 (1990).
35. Miertuš S., Miertušová J.: J. Chromatogr. *286*, 31 (1984).
36. London F.: Z. Phys. *63*, 245 (1930).
37. Born M., Mayer J. E.: Z. Phys. *75*, 1 (1932).
38. Miertuš S., Kyseľ O., Krajčí M.: Chem. Papers *35*, 3 (1981).
39. Miertuš S., Scrocco E., Tomasi J.: Chem. Phys. *55*, 117 (1981).
40. Miertuš S., Májeková M., Frecer V.: Theochem, J. Mol. Struct. *179*, 354 (1988).
41. Sinanoglu O.: Ann. N.Y. Acad. Sci. *158* 308 (1969).
42. Pierotti R. A.: J. Phys. Chem. *69*, 281 (1965).
43. Gattnarová E.: *Inžinierska štatistika*, p. 71. Slovak Technical University, Bratislava 1985.
44. *Program GEOMO. Quantum Chemistry Program Exchange.* Bloomington, Indiana 1977.
45. Lehotay J., Garaj J., Buzinkaiová T., Rattay V., Dzurov J., Škultétyová M., Bartalos L., Chovancová M.: Hospodárska zpráva n. 86/83, p. 13. Slovak Technical University, Bratislava 1983.
46. Shiu W. Y., Mackay D.: J. Phys. Chem. Ref. Data *15*, 911 (1986).
47. Pople J. A., Beveridge L.: *Aproximatívna teória molekulových orbitálov*, p. 86. Alfa, Bratislava 1979.
48. Golebiewski A., Parczewski A.: Z. Naturforsch., A *25*, 1710 (1970).

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