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Theoretical and Experimental Dependence of the R_M Values of Aromatic and Heterocyclic Compounds on the Composition and Kind of the Binary Mobile Phase in Thin-layer Chromatography

Teoretyczne i doświadczalne zależności R_M aromatycznych i heterocyklicznych związków od składu oraz rodzaju dwuskładnikowej fazy ruchomej w chromatografii cienkowarstwowej

Теоретические и экспериментальные зависимости R_M для некоторых ароматических и гетероциклических веществ от состава дикомпонентной подвижной фазы в тонкослойной хроматографии

Finding optimal conditions of the separation of substance mixtures as well as the interpretation of the obtained results are the subject of intensive studies and tests. The procedure which has recently been applied quite frequently is a theoretical determination of certain chromatographic parameters of substance in a given chromatographic system on the basis of substance adsorption from multicomponent mobile phases, e.g. binary solvents used as the mobile phase [6, 7]. These investigations allow for the influence of the following parameters indispensable in the chromatographic process: the kind of the mobile phase, the kind and structure of the adsorbent and the molecular structure of the chromatographed substances. The present tendency is to unify the methods of a theoretical calculation of chromatographic parameters as well as their tabulation which would facilitate an appropriate selection of parameters and substances in various chromatographic systems.

This paper presents the specificity of a molecular interaction between the molecules of the solvent components of the mobile phase and those of the chromatographed substances. An attempt was made to find a relationship between certain parameters of adsorption of the mobile phase components and the amount and kind of substituents in the derivatives of the chromatographed substances: naphthalene and chinoline. Therefore, apart from the obtained experimental values, the values of certain parameters for particular mobile phases were also calculated theoretically with the use of the equation resulting from Ościk's thermodynamic theory of adsorption from multicomponent systems [1, 2, 3, 4]:

$$R_{M1,2} = \varphi_1 \Delta R_{M1,2} + (\varphi_1^s - \varphi_1) (\Delta R_{M1,2} + A_z) + R_{M,1} \quad (1)$$

where:

$$\Delta R_{M1,2} = R_{M,1} - R_{M,2};$$

- $R_{M1,2}$ – the R_M value for the substance obtained when using binary '1+2' solvent;
 $R_{M,1}$ – the R_M value for substance z obtained when using pure solvent '1';
 $R_{M,2}$ – the R_M value for substance z obtained when using pure solvent '2';
 A_z – represents molecular interaction between molecules of the solvent components and those of the chromatographed substance z and is equal to the logarithm of the hypothetical distribution coefficient of $k_{1,2}^\infty$;
 φ_1 – a volume fraction of component '1' of the solvent in the volume phase;
 φ_1^s – a volume fraction of component '1' in the surface phase;
 $(\varphi_1^s - \varphi_1)$ – represents excess adsorption of component '1' of the mobile phase which can be determined from the distribution of the mobile phase components [1, 2]:

$$(\varphi_1^s - \varphi_1) = \frac{\varphi_1 (K_1 - 1) (1 - \varphi_1)}{(1 + \varphi_1) (K_1 - 1)} \quad (2)$$

where: K_1 – is the adsorption equilibrium constant of component '1' of the mobile phase; for ideal and regular solvents it can be assumed that $\log K_1$ equals the $\Delta R_{M1,2}$ mean value.

I. EXPERIMENTAL PART

Experimental R_M values of 17 substances, methylo- and nitro- derivatives of naphthalene and chinoline, were determined on silicagel adsorbent Type 60 produced by Merck, in thermostatic conditions at 21°C, using adsorbent layers 0.3 mm thick, activated for two hours at 135°C, by using ascending technique. The above-mentioned substances were chromatographed in the binary mobile phase systems: trichloroethylene-butyl acetate, trichloroethylene-n-butanol, trichloroethylene-methyl-ethyl ketone, acetone-chloroform, methanol-benzene; the solvents were selected according to Pimentel and McClellan's classification [5] so as to obtain a possibly wide range of the mobile phase activity.

K_1 parameters were calculated for particular chromatographic systems and the A_z values were estimated by the method of selection of parameters appropriate for respective substance groups. Graphs of the dependence of the R_M values on the mobile phase composition were drawn on the basis of the experimental data and theoretical calculations.

II. DISCUSSION OF RESULTS

In the chromatographic systems of the A-B type according to Pimentel and McClellan [5]: trichloroethylene - methyl-ethyl ketone, trichloroethylene - n-butanol, trichloroethylene - butyl acetate, good separation of the tested substance mixtures was stated. The curves of the R_M dependence on the mobile phase composition for quinoline and its derivatives showed considerable differences of the R_M for pure solvents and had the minimums within the range of 0.3-0.5 of the volume fraction of the more polar component. In the case of naphthalene and its derivatives those curves showed lower R_M values and smaller differences of those coefficients for pure solvents although their minimums fell, as was the case with quinoline derivatives, within the range of 0.3-0.5 of the volume frac-

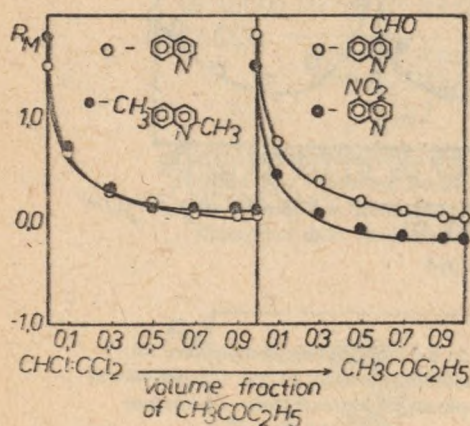


Fig. 1. The dependence of the R_M value on the mobile phase composition for: quinoline, 2,6-dimethylquinoline, quinoline-4-aldehyde and nitroquinoline; points - experimental data, lines - theoretical data. Mobile phase: trichloroethylene - methyl-ethyl ketone

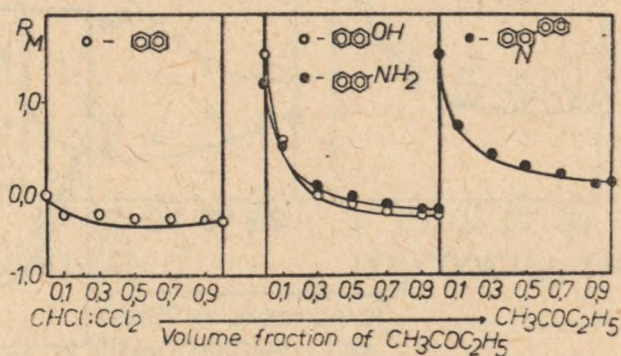


Fig. 2. The dependence of the R_M values on the mobile phase composition for: naphthalene, 2-naphthol, 2-naphthylamine and 2-naphthylquinoline; points - experimental data, lines - theoretical data. Mobile phase: trichloroethylene - methyl-ethyl ketone

tion of the more polar component. Certain differences were also observed between the experimental and the theoretically calculated relationships $R_M = f(\varphi_1)$, particularly for substances capable of forming the hydrogen bonds with the components of the mobile phase [8], e.g. with methanol, butanol and trichloroethylene.

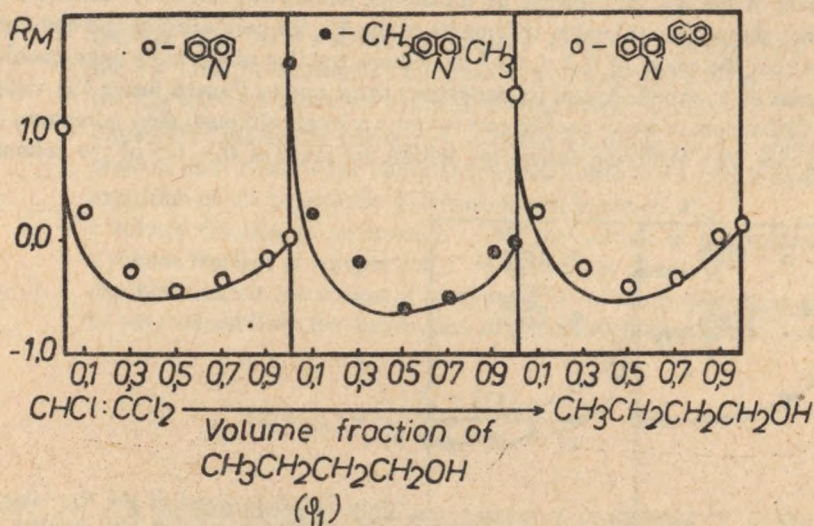


Fig. 3. The dependence of the R_M values on the mobile phase composition for: chinoline, 2,6-dimethylchinoline and 2-naphthochinoline; points – experimental data, lines – theoretical data. Mobile phase: trichloroethylene – n-butanol

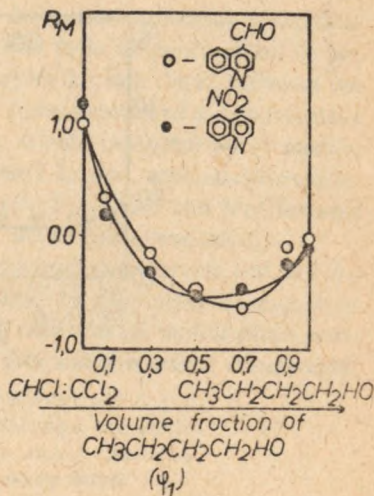


Fig. 4. The dependence of the R_M values on the mobile phase composition for: chinoline-4-aldehyde and nitrochinoline; points – experimental data, lines – theoretical data. Mobile phase: trichloroethylene-n-butanol

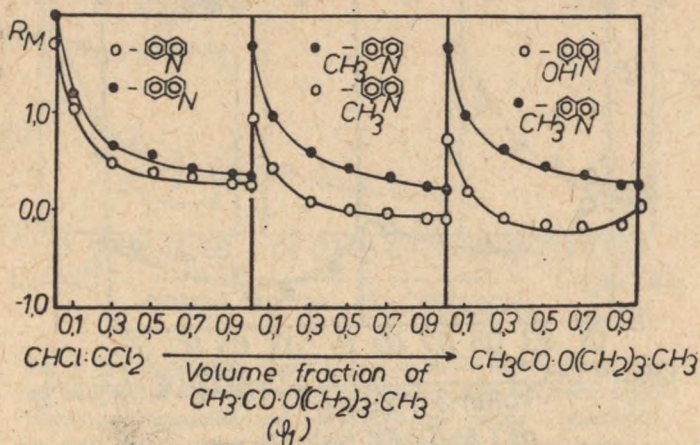


Fig. 5. The dependence of the R_M values on the mobile phase composition for: chinoline, isochinoline, 7-methylchinoline, 8-methylchinoline and 8-hydroxychinoline; points - experimental data, lines - theoretical data. Mobile phase: trichloroethylene - butyl acetate

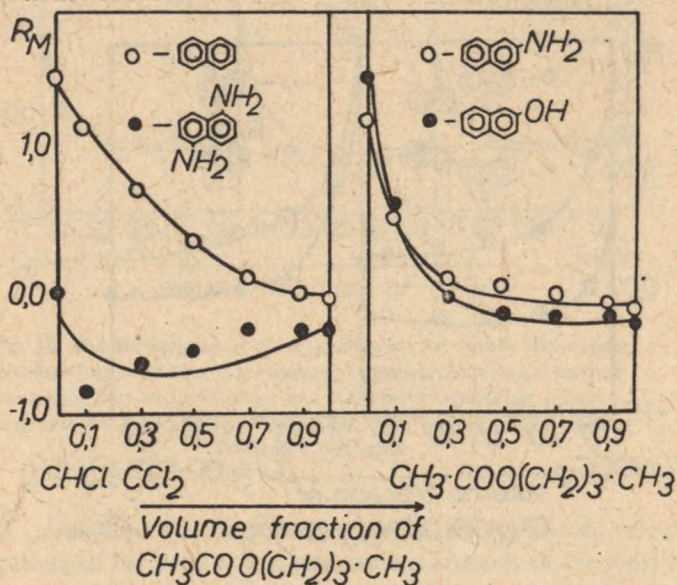


Fig. 6. The dependence of the R_M values on the mobile phase composition for: naphthalene, 2,6-diaminonaphthalene, 2-naphthylamine and 2-naphthol; points - experimental data, lines - theoretical data. Mobile phase: trichloroethylene - butyl acetate

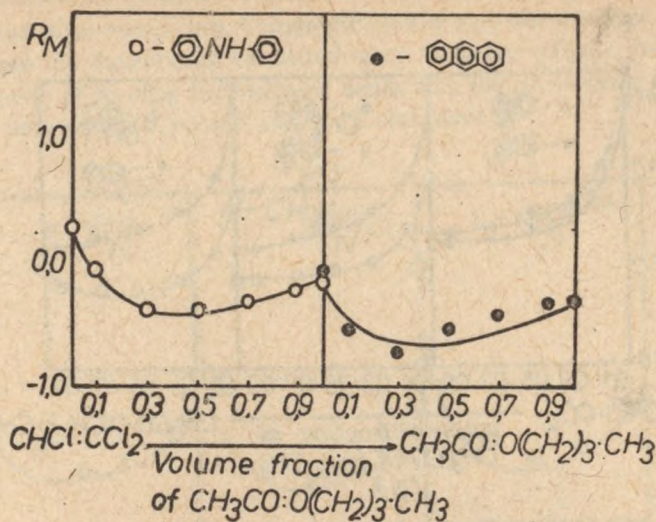


Fig. 7. The dependence of the R_M values on the mobile phase composition for: diphenylamine and anthracene; points – experimental data, lines – theoretical data. Mobile phase: trichloroethylene – butyl acetate

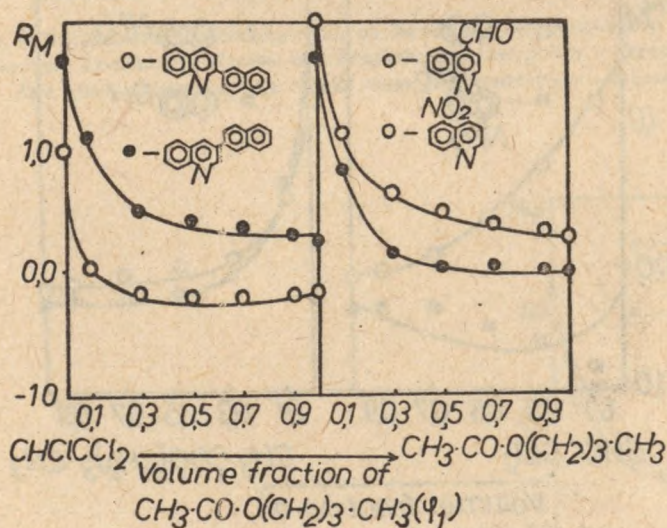


Fig. 8. The dependence of the R_M values on the mobile phase composition for: 1-naphthochinoline, 2-naphthochinoline, chinoline-4-aldehyde and nitrochinoline; points – experimental data, lines – theoretical data. Mobile phase: trichloroethylene – butyl acetate

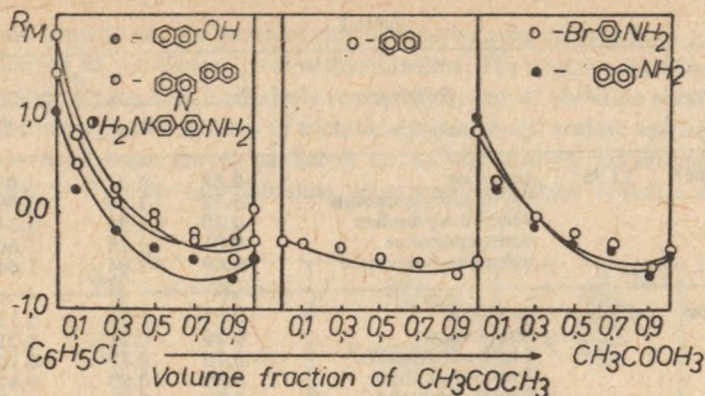


Fig. 9. The dependence of the R_M values on the mobile phase composition for: 2-naphthol; 2-naphthochinoline, diphenylamine, naphthalene, p-bromoaniline and 2-naphthylamine; points – experimental data, lines – theoretical data. Mobile phase: chlorobenzene – acetone

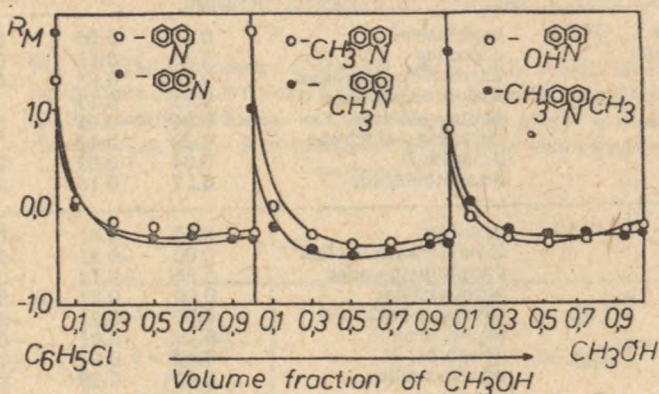


Fig. 10. The dependence of the R_M values on the mobile phase composition for: chinoline, isochinoline, 7-methylchinoline, 8-methylchinoline, 8-hydroxychinoline and 2,6-dimethylchinoline; points – experimental data, lines – theoretical data. Mobile phase: chlorobenzene – methanol

In theoretical calculations the attention was paid to the K_1 and A_2 values (Table 1). The K_1 values calculated for the whole system were positive in all the above mentioned systems within the range of 13.9–13.3 which indicated the presence of active hydrogen atoms and atoms of electrodonor character (oxygen). The A_2 parameter was calculated in every system for each chromatographed substance individually which resulted in changes in the values of that parameter. In the trichloroethylene – n-butanol (A–AB) system, these

Table 1

Mobile phase	K1	Substance	A_z			
			0.3	0.5	0.7	\bar{A}_z
Trichloroethylene- Butanol (A-AB)	13.96	quinoline	-0.82	-1.36	-1.67	-1.28
		2,6-dimethylquinoline	-0.72	-1.58	-1.99	-1.43
		β -naphthoquinoline	-0.79	-1.36	-1.54	-1.23
		o-nitroquinoline	-0.81	-1.20	-1.60	-1.20
		quinoline-4-aldehyde	-0.49	-1.04	-1.64	-1.05
Trichloroethylene- Butyl acetate (A-B)	13.14	quinoline	-0.03	-0.04	0.12	0.04
		isoquinoline	0.26	0.22	0.21	0.23
		8-hydroxyquinoline	-1.70	-0.17	-0.18	-0.68
		7-methylquinoline	0.30	0.90	0.42	0.54
		8-methylquinoline	0.06	0.01	0.02	0.03
		α -naphthoquinoline	0.25	-0.24	-0.32	-0.27
		β -naphthoquinoline	0.07	0.11	0.20	0.13
		o-nitroquinoline	-0.15	-0.08	-0.78	-0.23
		quinoline-4-aldehyde	0.06	0.11	0.20	0.12
		naphthalene	-0.52	-0.32	0.19	-0.21
		β -naphthol	-0.14	-0.12	0.08	-0.06
		β -naphthylamine	0.11	0.27	0.49	0.29
		anthracene	-0.78	-0.57	-0.36	-0.57
		diphenylamine	-0.56	-0.59	-0.63	-0.59
Trichloroethylene- Methyl ethyl ketone (A-B)	13.33	naphthalene	0.15	0.05	0.30	0.16
		quinoline	0.15	0.10	0.10	0.12
		2,6-dimethylquinoline	0.10	0.02	0.06	0.06
		β -naphthoquinoline	0.15	0.15	0.14	0.14
		o-nitroquinoline	0.04	-0.05	0.00	0.00
		quinoline-4-aldehyde	0.23	0.12	0.10	0.15
		β -naphthol	0.04	-0.09	0.02	-0.01
		β -naphthylamine	0.17	0.15	0.03	0.12
Acetone- Chlorobenzene (B-N)	13.90	quinoline	0.02	-0.01	-0.50	-0.12
		2,6-dimethylquinoline	0.00	-0.21	-0.49	-0.23
		β -naphthoquinoline	0.06	-0.12	-0.35	-0.13
		nitroquinoline	0.00	-0.07	-0.19	-0.08
		quinoline-4-aldehyde	-0.05	-0.21	-0.55	-0.27
		naphthalene	0.19	-0.01	-0.21	-0.01
		β -naphthol	0.13	0.04	-0.20	-0.01
		p-bromoaniline	0.42	0.26	0.15	0.27
Methanol- Chlorobenzene (AB-N)	13.30	quinoline	-0.14	-0.05	0.00	-0.06
		isoquinoline	-0.35	-0.38	-0.29	-0.35
		8-hydroxyquinoline	-0.50	-0.38	-0.30	-0.32
		7-methylquinoline	-0.36	-0.43	-0.33	-0.37
		8-methylquinoline	-0.48	-0.50	-0.42	-0.46
		2,6-dimethylquinoline	-0.36	-0.35	-0.23	-0.29
		α -naphthoquinoline	-0.55	-0.30	-0.10	-0.32
		β -naphthoquinoline	-0.40	-0.32	-0.28	-0.33
		nitroquinoline	-0.04	-0.39	-0.32	-0.34
		quinoline-4-aldehyde	-0.04	-0.16	-0.14	-0.10
		naphthalene	-0.06	-0.38	-0.13	-0.09
		2,3,5-trimethylnaphthalene	-0.29	-0.33	-0.50	-0.37
		β -naphthol	0.06	-0.12	-0.08	0.02
		β -naphthylamine	0.06	-0.19	0.00	-0.04
		anthracene	-0.19	-0.16	-0.39	-0.24
1,5-dimethylnaphthalene	-0.46	-0.42	-0.47	-0.45		

values were negative for the group of chinoline derivatives, ranging from -1.05 for chinoline-4-aldehyde to -1.43 for 2,6-dimethylchinoline. The negative A_z values may be connected, among others, with a relatively strong adsorption of the more polar component of the mobile phase. In the systems of trichloroethylene-butyl acetate and trichloroethylene - methyl-ethyl ketone, the A_z parameter turned into positive one ranging from 0.23 for isoquinoline to 0.00 for nitrochinoline. Most probably, there occurs a decrease in the

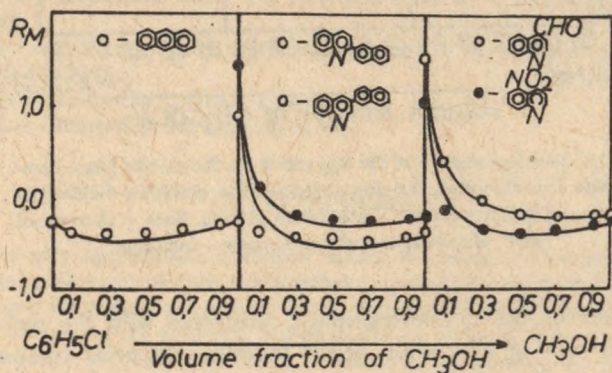


Fig. 11. The dependence of the R_M values on the mobile phase composition for: naphthalene, 1,5-dimethylnaphthalene, 2-naphthol, 2,3,5-trimethylnaphthalene and 2-naphthylamine; points - experimental data, lines - theoretical data. Mobile phase: chlorobenzene - methanol

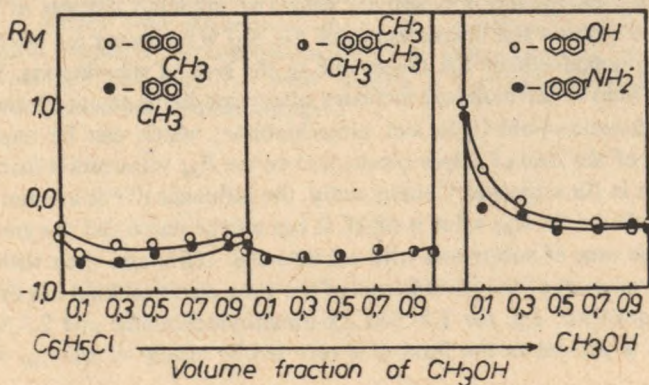


Fig. 12. The dependence of the R_M values on the mobile phase composition for: anthracene, 1-naphthochinoline, 2-naphthochinoline, chinoline-4-aldehyde and nitrochinoline; points - experimental data, lines - theoretical data. Mobile phase: chlorobenzene - methanol

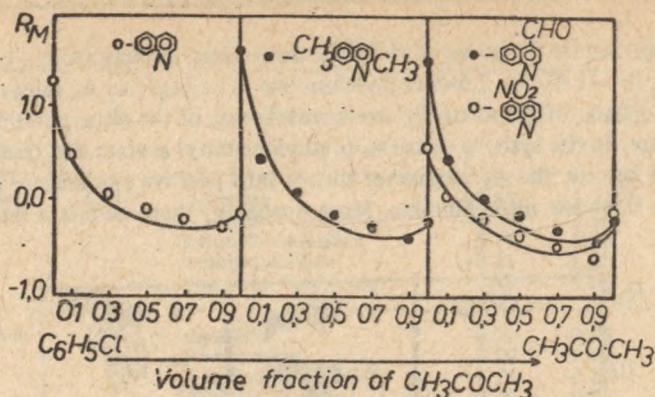


Fig. 13. The dependence of the R_M values on the mobile phase composition for: chinoline, 2,6-dimethylchinoline, chinoline-4-aldehyde and nitrochinoline; points – experimental data, lines – theoretical data. Mobile phase: chlorobenzene – acetone

molecule interaction of the chromatographed substances with the molecules of the mobile phase while strong interaction begins between the polar components of the mobile phase.

In the systems of the B–N and AB–N types, i.e. acetone – chlorobenzene and methanol – chlorobenzene the relationships $R_M = f(\varphi_1)$ were similar to those found in the A–B type systems. Considerable differences occurred also in the R_M values for pure solvents while the minimums fell within the range of 0.5–0.7 of the volume fraction of the more polar component. The K_1 value did not change in comparison with the former systems and was 13.3 and 13.9. It can be noticed, therefore, that the K_1 and A_z values are determined by the solvent of greater polarity and capability of forming hydrogen bonds [8], since an addition a component low activity causes no apparent changes of these values.

In each of the systems the lowest values of the R_M were found for naphthalene and anthracene being nonadsorbent substances due to the lack of substituents. The presence of two aromatic rings in the molecule increases adsorption in the cases of 1- and 2-naphthochinoline and chinoline-4-aldehyde and nitrochinoline, which can be explained by a greater influence of the kind of active substituent on the R_M value rather than the amount of aromatic rings in the molecule. Consequently, the influence of the amount of aromatic rings in a molecule on the R_M value is slight. It can also be stated that the greatest adsorption occurs in the case of substances with substituents –OH, and then with –NH₂ and –CH₃, while the amount of the substituents of the same chemical kind has little effect on the adsorption quantity, e.g. for 1,5- and 2,6-dimethylchinoline and 2,3,5-trimethylchinoline, which is present in the form of a very similar course of the $R_M = f(\varphi_1)$ relationships.

On the basis of the investigations one can notice that the knowledge of the chromatographic and adsorption parameters for given substances makes it possible to predict the separation of the compounds which are similar in character and chemical structure to those of the tested compounds, and to plan an appropriate selection of mobile phases.

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STRESZCZENIE

Wyznaczanie z góry optymalnych warunków rozdziału mieszanin w chromatografii cienkowarstwowej do tej pory praktycznie w dużej mierze odbywa się drogą kolejnych prób.

W przedstawionej pracy pokazano metodę teoretycznego wyznaczania wartości R_M substancji aromatycznych i heterocyklicznych w oparciu o dane parametry adsorpcji tych substancji i składników ruchomej fazy mieszanej o różnej aktywności. Wykazano dobrą zgodność teoretycznie obliczonych i doświadczalnie otrzymanych wartości R_M badanych substancji. Pokazano nowe możliwości przyjętej teorii optymalizacji procesów adsorpcyjnej chromatografii cienkowarstwowej.

РЕЗЮМЕ

В работе представлено метод экспериментального и теоретического определения зависимости R_M от состава подвижной фазы ($R_M=f(\varphi_1)$) для некоторых ароматических и гетероциклических веществ, опираясь на параметры адсорбции этих веществ и состав этой подвижной фазы. В исследованных системах обнаружено хорошее согласие экспериментальных и теоретических функций $R_M=f(\varphi_1)$. Представлено возможности этой теории в процессе оптимизации адсорбционной тонкослойной хроматографии.

