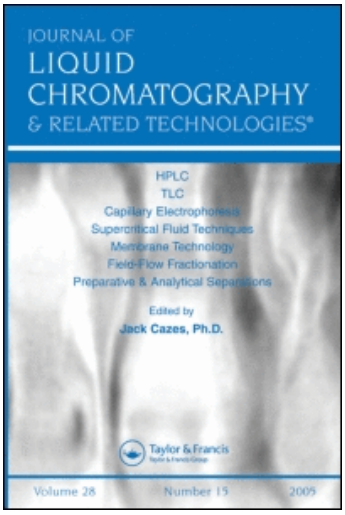

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THE ROLE OF THE SPECIFIC SURFACE AREA OF AN ADSORBENT IN THE OPTIMIZATION OF MIXTURE SEPARATION CONDITIONS IN THIN - LAYER CHROMATOGRAPHY

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ABSTRACT

The very important aspect of effect of the magnitude of specific surface area on R_M values obtained by using TLC method is presented. In experiments were performed on 4 adsorbents of different specific surface areas 50 - 500 m^2/g and with mixed binary mobile phases.

It is shown that R_M values of chromatographed substances aromatic hydrocarbons are lineary dependente upon the specific surface area of adsorbents for each composition of mobile phase. This relationship can be described by a straight line, with the parameters a and b that can be tabularized. These lines can be used to calculate the R_M values of chromatographed substances for any adsorbent if

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is specific surface area is known. The illustrational comparison of experimentally obtained and theoretically predicted R_M values for different chromatographic system are presented.

INTRODUCTION

Adsorbents of different microporous structure (1-5) have been used for a long time in thin-layer chromatography for the separation of mixtures of various substances. The microporous structure of adsorbents is an important affacting optimization of the chromatographic process. The significance of the microporous structure of the adsorbent in the process of thin-layer chromatography was studied by Geiss (6) and Snyder (7) . Practical possibilities of controlling the process of thin-layer chromatography were also indicated by Różyło (8,9). Attemps were also explain the physical-chemical significance of the value of the adsorbent specific surface area in thin-layer chromatography (10) . Recent considerable interest in the role of the specific surface area of the adsorbent in thin-layer chromatography is due to growing importance of this method as a pilot technique for determining the optimum conditions of mixture separation on both analytical and preparative scales. The latter is widely applied for obtaining and purifying of natural origin in research laboratories, as well as in pharmaceutical and food industries, and also in the nature enviroment protection (11).

Linear relations between R_M values of substances for pure components of a mixed e.g. binary mobile phase $R_{M1.2}$

and the specific surface area of the adsorbent, as has already been observed - are not favourable enough to be applied in a routine process of optimization of separation conditions. Therefore, the present paper analyses the relations between the R_M values of substances and the specific surface area of the adsorbent. The values were investigated for identical concentrations of the mobile phase on adsorbents of different values of the specific surface area.

EXPERIMENTAL

Measurements were taken of the R_F (R_M) values of model substances obtained in the process of adsorption thin-layer chromatography on silica gels of different microporous structure, produced by MERCK (12):

pore diameter Å	specific surface area m^2/g
60	500
100	400
200	150
500	50

The chromatographed substances were certain polycyclic aromatic hydrocarbons showing neither electrodonor nor electroacceptor properties: naphthalene, β-methylnaphthalene, pyrene, chrysene, fluoranthene, diphenyl . This selection of model chromatographed substances aimed at eliminating possible additional intermolecular actions with the adsorbent surface and the components of the mobile phase which was composed of four mixed binary solvents: hexane - -benzene, methylcyclohexane - benzene, benzene - methanol

andbenzene - ethanol. The procedure of conducting the chromatographic progess and substance detection were described in several earlier publications (1-4, 8, 13).

RESULTS AND DISCUSSION

It is apparent from the results presented in figures 1-4 that on silica gels of different specific surface area the R_M values of the chromatographed substance change in a regular manner. It turned out that there is a linear dependence of the R_M value on the specific surface of the adsorbent. This dependence can be presented from of a linear equation:

$$R_M = as + b \qquad (1)$$

where s is the specific surface area of the adsorbent, and values "a" and "b" - parameters of the straight line.

As appears from the graphs, the R_M values obtained from the experiment are laid on a straight line drawn so as get the smallest deviation. Table 1-4 shows the $R_M = f(s)$ straight line parameters which were calculated and tabulated for particular concentrations of the mobile phase and the chromatographed substance.

Tables 1-4 show the $R_M = f(s)$ straight lines parameters, whih were calculated and tabulated for some chosen concentrations of the mobile phase and the chromatographed substance. Tables 1 and 2 show the parameter "a" of the straight line whereas tables 3,4 - the parameters "b".

In the systems methylcycloheksane - benzene and he - benzene inactive mobile phase the "a" values decrease

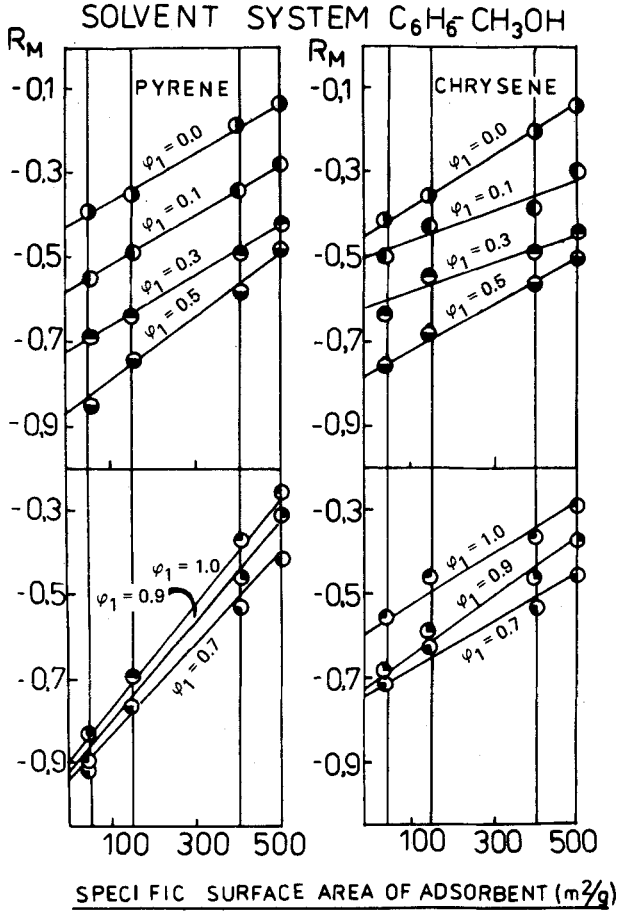

Fig. 1.

Linear relationship between R_M values and specific surface area of adsorbent. Solvent system: benzene--methanol. Points - experimental data, straight line - theoretical data, calculated from eq. 1.

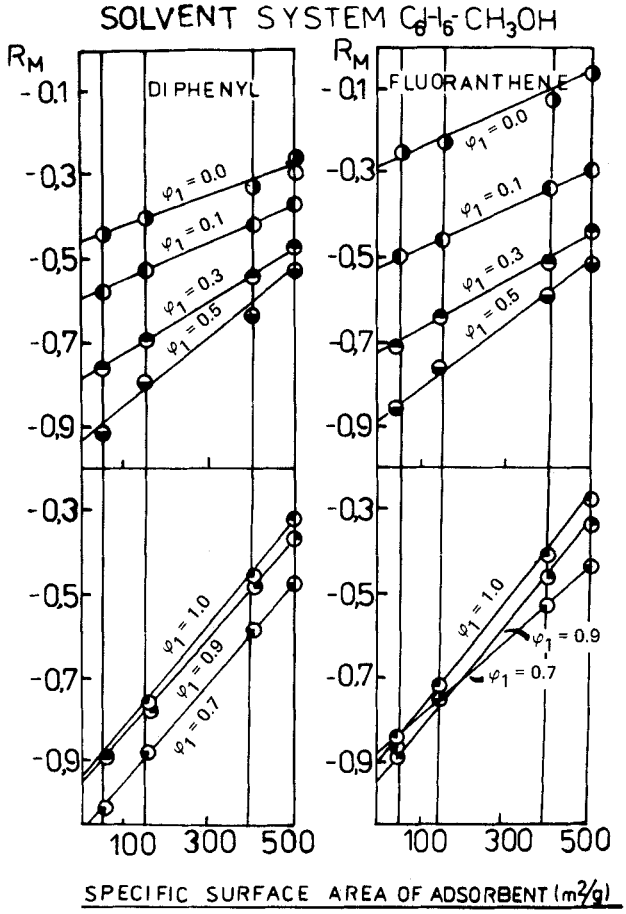

Fig. 2.

Linear relationship between R_M values and specific surface area of adsorbents. Points - experimental data, straight line - theoretical data calculated from eq.1.

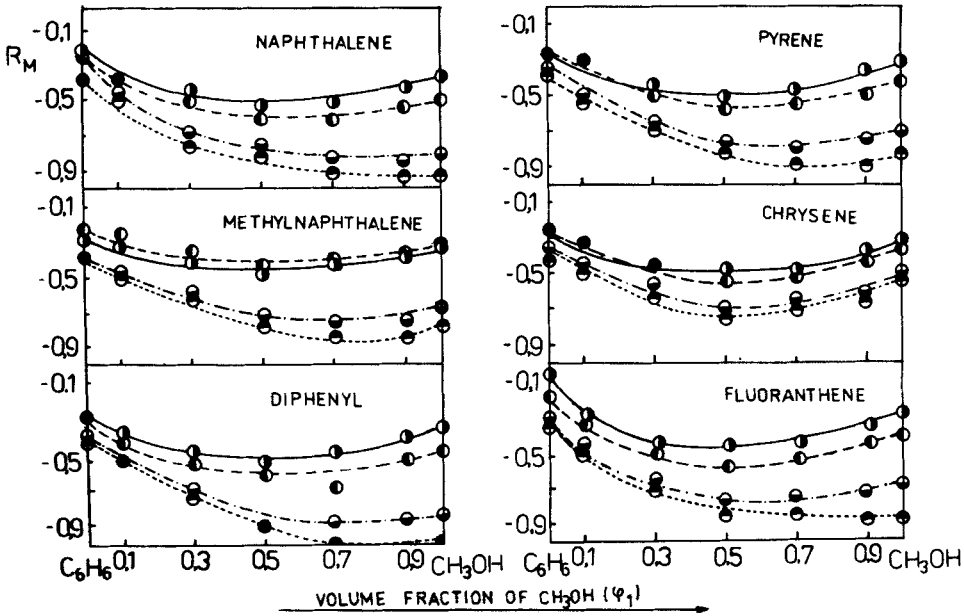

Fig.3. Relationship $R_M = f(\varphi_1)$. Points - experimental data, lines - theoretical data.

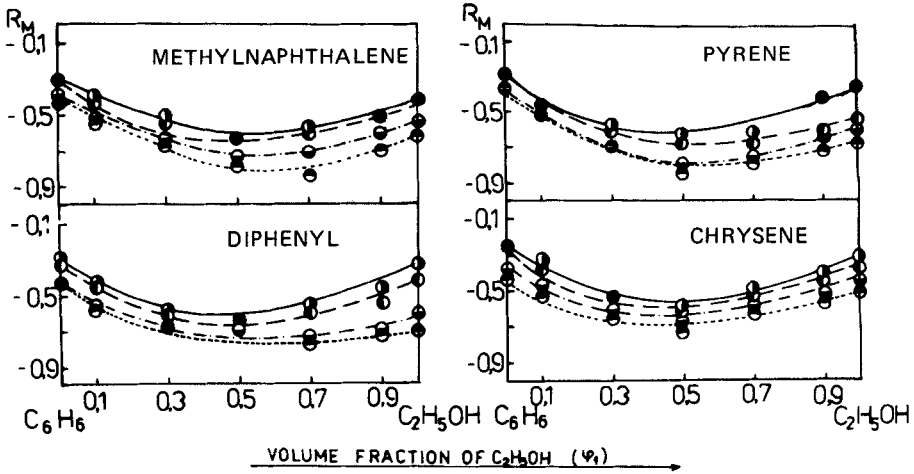

Fig.4. Relationship $R_M = f(\varphi_1)$. ◑ —— - silica gel 60, ◐ · · · · silica gel 100, ◒ - · - · - silica gel 200, ◓ ····· silica gel 500.

Table 1

Values of parameter "a" for inactive mobile phase.

Substance	concentration of benzene						
	mobile phase: methylcycloheksane - benzene						
	0.0	0.1	0.3	0.5	0.7	0.9	1.0
diphenyl	0.14	0.09	0.09	0.08	0.07	0.03	0.03
naphthalene	0.09	0.09	0.07	0.04	0.02	.0.02	0.02
2,6-dimethyl-naphthalene	0.10	0.10	0.08	0.08	0.07	0.07	0.04
fluoranthene	0.09	0.07	0.05	0.03	0.02	0.02	0.03
anthracene	0.12	0.08	0.07	0.05	0.05	0.05	0.04
chrysene	0.11	0.10	0.09	0.08	0.08	0.07	0.03
pyrene	0.15	0.11	0.10	0.08	0.08	0.07	0.06
	mobile phase : heksane - benzene						
diphenyl	0.18	0.15	0.12	0.12	0.09	0.07	0.03
naphthalene	0.12	0.09	0.08	0.05	0.02	0.01	0.02
2,6-dimethyl-naphthalene	0.15	0.12	0.10	0.05	0.05	0.04	0.04
fluoranthene	0.12	0.12	0.11	0.05	0.04	0.04	0.03
anthracene	0.17	0.14	0.11	0.05	0.04	0.08	0.04
chrysene	0.16	0.15	0.12	0.06	0.08	0.06	0.03
pyrene	0.18	0.13	0.12	0.11	0.10	0.08	0.06

[x]Paramiter "a" values are presented as $ax10^{-2}$

with the increase in the concentration of benzene which is the more active component of the mobile phase.

In the systems where the second component most active has the ability to formation of hydrogen bonds (benzene--methanol, benzene - ethanol) the slope of the straight line parameter "a" increase with the increasing concentration of alcohol. It is possible that this behaviour of the parameter "a" is to some extent influenced by the association of alcohol that occurs in such systems.

Table 2

Values of parameter "a" for active mobile phase

Substance	concentration of alcohol						
	mobile phase: benzene - Methanol						
	0.0	0.1	0.3	0.5	0.7	0.9	1.0
naphthalene	0.02	0.03	0.07	0.07	0.09	0.11	0.13
methylnaphthalene	0.02	0.05	0.05	0.07	0.10	0.11	0.12
chrysene	0.03	0.04	0.04	0.06	0.08	0.08	0.06
pyrene	0.06	0.06	0.06	0.07	0.11	0.11	0.12
diphenyl	0.03	0.04	0.06	0.09	0.15	0.16	0.15
fluoranthene	0.03	0.05	0.06	0.08	0.12	0.12	0.13
	mobile phase: benzene - ethanol						
methylnaphthalene	0.02	0.05	0.04	0.03	0.06	0.06	0.05
chrysene	0.03	0.05	0.02	0.05	0.03	0.04	0.04
pyrene	0.06	0.04	0.03	0.05	0.04	0.07	0.07
diphenyl	0.03	0.04	0.02	0.02	0.04	0.04	0.08

x parameter "a" values are presented as $ax10^{-2}$

Tables 3 and 4 cantain the parameter "b" for considered systems. The parameter "b" may give information about the molecular action between mobile phase and chromatographed substance for the surface s = 0.

The straight lines described can be used for the calculation oi the R_M values of substances on any adsorbent with a specific surface area. A series of arduous measurements can be avoided in this way. It is enough to take two measurements of possibly extreme R_M values in order to draw straight lines $R_M = f(s)$. When parameters "a" and "b" are known for two different substances, the separability of such mixture can be calculated with good approximation, with the use of the given mobile phase.

Table 3

Values of parameter "b" for nanactive mobile phase

Substance	concentration of benzene						
	mobile phase: methylcycloheksane - benzene						
	0.0	0.1	0.3	0.5	0.7	0.9	1.0
diphenyl	-0.16	-0.22	-0.36	-0.45	-0.49	-0.48	-0.48
naphthalene	-0.04	-0.14	-0.27	-0.32	-0.33	-0.35	-0.35
2,6-dimethyl-naphthalene	-0.11	-0.22	-0.36	-0.42	-0.43	-0.47	-0.45
fluoranthene	0.07	-0.05	-0.17	-0.31	-0.36	-0.38	-0.38
anthracene	0.05	-0.07	-0.11	-0.30	-0.34	-0.38	-0.38
chrysene	0.02	-0.28	-0.35	-0.42	-0.47	-0.48	-0.48
pyrene	-0.16	-0.10	-0.37	-0.41	-0.43	-0.45	-0.47
	mobile phase: heksane - benzene						
diphenyl	-0.14	-0.30	-0.43	-0.59	-0.58	-0.56	-0.48
naphthalene	-0.15	-0.20	-0.28	-0.37	-0.36	-0.37	-0.37
2,6-dimethyl-naphthalene	-0.15	-0.27	-0.41	-0.40	-0.45	-0.45	-0.45
anthracene	0.01	-0.13	-0.30	-0.37	-0.39	-0.40	-0.40
fluoranthene	0.02	-0.13	-0.30	-0.37	-0.39	-0.40	-0.40
chrysene	-0.15	-0.17	-0.21	-0.42	-0.47	-0.47	-0.48
pyrene	-0.07	-0.26	-0.40	-0.55	-0.50	-0.47	-0.47

It results from the graphs 3 and 4 of dependencies $R_{M1.2} = f(\varphi_1)$ presented in figures 3 and 4, that and theoretically on the basis of the equation 1 are within the range of a permissible experimental error, i.e. that those theoretical R_M values are adequate representations of real R_M values.

The obtained results seem to suggest thst it is possible to tabulate values "a" and "b" in order to calculate the dependence of $R_M = f(s)$. It has also been stated that there is a general dependence of the parameters of the straight

Table 4

Values of parameter "b" for active mobile phase

Substance	concentration of alcohol						
	mobile phase: benzene - methanol						
	0.0	0.1	0.3	0.5	0.7	0.9	1.0
naphthalene	-0.35	-0.53	-0.65	-0.81	-0.90	-0.94	-1.12
-methyl-naphthalene	-0.41	-0.53	-0.79	-0.86	-0.98	-0.99	-1.03
chrysene	-0.48	-0.51	-0.62	-0.79	-0.73	-0.72	-0.58
pyrene	-0.47	-0.57	-0.72	-0.85	-0.85	-0.87	-0.84
diphenyl	-0.48	-0.59	-0.79	-0.94	-1.06	-0.05	-1.13
fluoranthene	-0.38	-0.44	-0.64	-0.90	-0.89	-0.96	-0.92
	mobile phase: benzene - ethanol						
-methyl-naphthalene	-0.41	-0.63	-0.68	-0.80	-0.71	-0.71	-0.62
chrysene	-0.48	-0.53	-0.64	-0.73	-0.53	-0.58	-0.52
pyrene	-0.47	-0.52	-0.74	-0.86	-0.76	-0.76	-0.72
diphenyl	-0.48	-0.61	-0.79	-0.71	-0.75	-0.75	-0.73

line $R_M = as + b$ on the difference of the elution strenght of the components of the mobile phase, the surface on the adsorbent, occupied by the chromatographed substance and the molecular of the components of the mobile phase. This affords a wider range of possibilities of optimizing the thin-layer chromatography process.

The dependencies described above can undergo changes in the case of sieve effect leading to a non-linear from of equation 1. Consequently, the applicability of the obtained dependencies should be limited to the values of the specific surface 50 - 500 m^2/g (14).

It seems that investigations presented above can be of great importance in transforming the chromatographic data

of thin-layer chromatography to the conditions of liquid column chromatography, due to frequent differences in the properties of the stationary phase in both methods, resulting from their nature.

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