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THE INFLUENCE OF THE SPECIFIC SURFACE AREA OF  
ADSORBENT UPON THE OPTIMIZATION OF THE PROCESS  
OF ADSORPTION THIN-LAYER CHROMATOGRAPHY

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ABSTRACT

An important aspect of the influence of specific surface area of adsorbent on  $R_M$  values of substances obtained in the process of adsorption thin-layer chromatography has been presented in the paper. The experiments have been conducted with four adsorbents, each having different specific surface area, that is, from 50 to 500  $m^2/g$  and with the use of mixed binary solvent mobile phases of benzene-aliphatic alcohol type. It has been proved that  $R_M$  values of investigated substances of group B change regularly according to the specific surface area of adsorbent for individual concentrations of mobile phase. The relationship may be described by means of square trinomial. The parameters of trinomial may be tabulated and the differentiation of the parameters for particular substances is observable at the same time. The relationship in question may be utilized to calculate  $R_M$  values of studied substances on any adsorbent with known specific surface area.

## INTRODUCTION

In chromatographic investigations great attention is paid to adsorbents with different surface structure, in their monographs Geiss (1) and Snyder (2) denoted much attention to the importance of microporous structure of adsorbent in the process of thin-layer chromatography.

The interest in the role of specific surface area of adsorbent in thin-layer chromatography is still current due to the increasing importance of this method as a pilot technique for determining the optimum mixture separation conditions on analytical and preparative scale (3 - 7). The previously observed linear relationships of the difference of  $R_M$  values of substances for pure components of mixed binary solvents mobile phases from the specific surface area of adsorbents are not so convenient to use in the routine process of optimization of separation conditions. In the present paper an analysis of relationships between  $R_M$  values of substances and specific surface area of adsorbent with the preservation of equal concentrations of mobile phase on adsorbents with different size of specific surface area has been made.

## MATERIALS AND METHODS

In order to solve the problem in question the measurements of  $R_F$  ( $R_M$ ) values of model substances have been made by means of the method applied in adsorption thin-layer chromatography. Silica gel f-my Merck (7) with different specific sur-

face area (s) have been used as adsorbent, that is, 500; 400; 150 and 50 m<sup>2</sup>/g. Polycyclic compounds, the molecules of which contained heteroatoms have been used as chromatographed substances. All studied substances under experiment showed electrodonor properties and constant dipole moment. The chromatographed substances were:

Substances	Pimentel and McClellan classification (8)
phenol	AB
acridine	B
quinoline	B
6-methylquinoline	B
7-methylquinoline	B
8-methylquinoline	B

As mobile phases were used binary mixtures of N(B)-AB type solvents, that is, benzene-methanol, benzene-ethanol and benzene-propanol.

The way in which the chromatographic process was conducted and the visualization of the substances under investigations have been presented in many earlier publications (9-12). The results of the experiments performed have given in a form of diagrams of  $R_M$  values according to the size of specific surface area of adsorbent vs  $R_M$  (Figs. 1-4).

## RESULTS AND DISCUSSION

Molecular interactions in chromatographic process are of very complex nature. It is known that  $R_M$  values of chro-

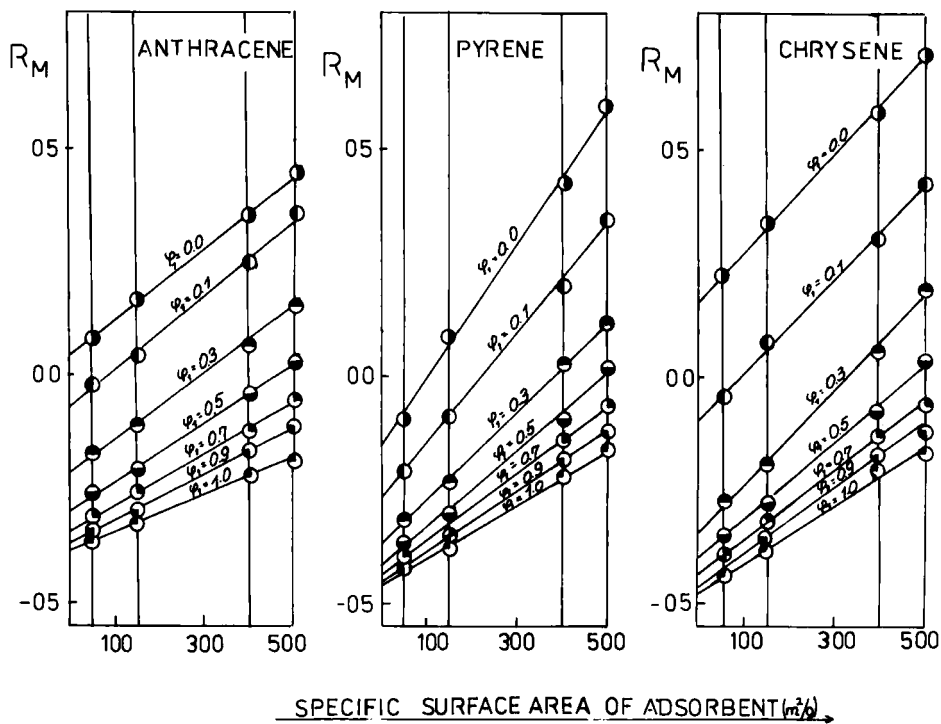


FIGURE 1. Linear relationship  $R_M = f s$  for nonactive chromatographic substances. Mobile phase: methylcyclohexane-benzene.

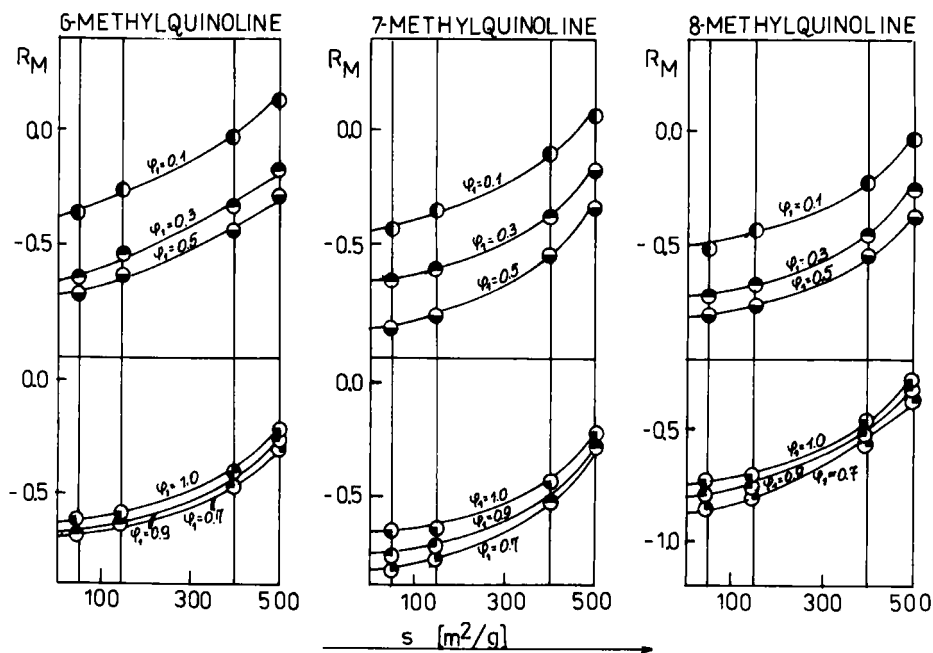


FIGURE 2. Relationship  $R_M = f s$  for active solutes. Mobile phase: benzene-methanol.

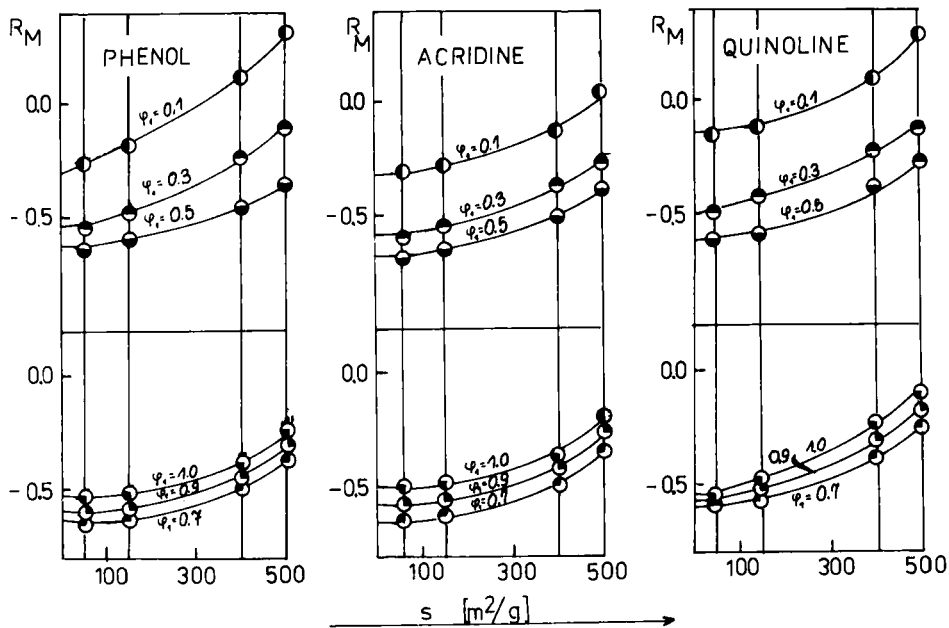


FIGURE 3. Relationship  $R_M = f s$  for active solutes. Mobile phase: benzene-ethanol.

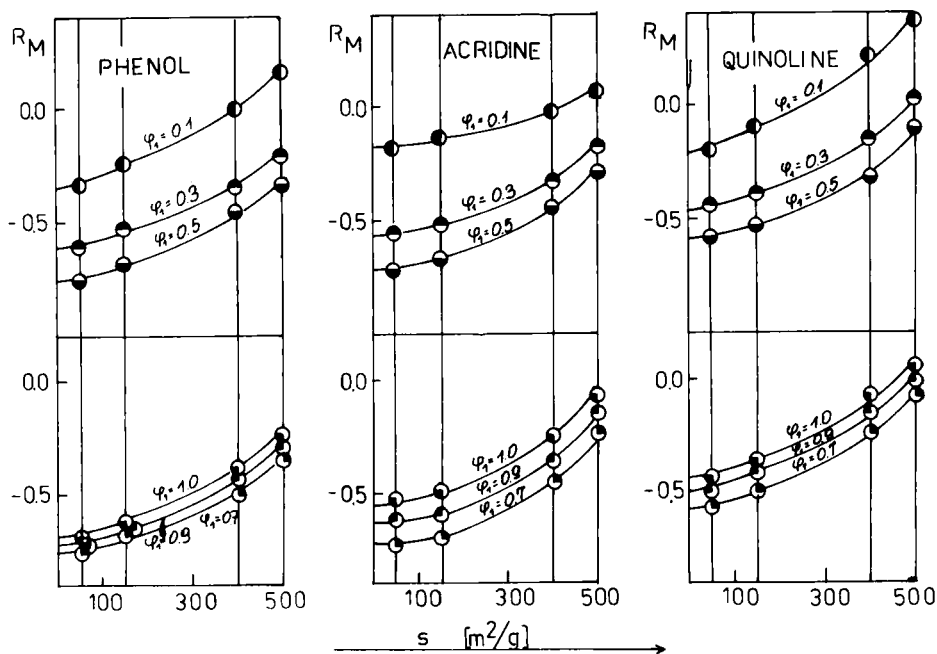


FIGURE 4. Relationship  $R_M = f s$  for active solutes. Mobile phase: benzene-propanol.

matographed substances depend upon the kind of investigated substances, property of solvents constituting mobile phase and property of adsorbent. In the paper an attention has been paid to the size of specific surface area of adsorbents and to  $R_M$  values of chromatographed substances which are connected with them. In earlier works (13) there has been discussed a problem of relationships between  $R_M$  values of chromatographed substances and the specific surface area of adsorbent for substances which exhibit neither electrodonor nor electroacceptor properties (class N) and do not possess significant dipole moment. In the case of such substances in systems of benzene-hydrocarbon (class N-N) and benzene alcohol (class N B - AB types). The relationship between  $R_M$  values of these substances in these mobile phase is given as

$$R_M = as + b \quad 1$$

Values for a and b are chosen in a numerical way. In the paper we deal with the relationship between  $R_M$  values and the specific surface area of adsorbent for substances having electrodonor properties and belonging to groups A and AB according to Pimentel and McClellan. In this case diagrams  $R_M$  vs  $s$  are not straight lines but they have the shape of parabola. This relationship is given as:

$$R_M = as^2 + bs + c \quad 2$$

Graphical relationships of  $R_M$  vs  $s$  have been shown in Figs. 2-4. The parameters a, b and c of equation 2 depend upon the kind of chromatographed substance and applied

mobile phase. For each chromatographed substance there have been calculated and tabulated the values of parameters  $a, b$  and  $c$  according to equation 2 for individual mobile phase compositions. The parameters have been presented in Tab. I-III. Parameter  $a$  denotes specific molecular interactions within chromatographic system. Certain regularities may be observed in systems under investigations. The slightest differences between parameters  $a$  for individual substances appear together with greater concentrations of alcohol in mobile phase. For quinoline and its methyl derivatives the values of parameter  $a$  decrease with the increase of molecular weight of alcohol which is a more active component of mobile phase. It follows from the data in Tab. I-III that the values of parameters  $a$  and  $b$  greatly depend upon the size of the molecular area of chromatographed substances  $A_s$  and upon the configuration of free electrons within the molecule of a given substance. Though acridine and quinoline belong to the same group of compounds according to Pimentel and McClellan classification, we may clearly see the differences in the values of the above mentioned parameters. It is caused by the differences in configurations of free electrons within the molecules of the compound in question.

The values of parameters  $a$  and  $b$  are also greatly different in the case of quinoline and its methyl derivatives. Though the value of adsorption energy of methyl group on  $\text{SiO}_2$  is nearly zero. The differences in the configuration of free electrons in the molecules of substances under in-



Table 1  
Parameters a, b and c (eq 2) . Mobile phase: benzene-methanol

Solute	volume fraction of methanol						
	0.0.	0.1	0.3	0.5	0.7	0.9	1.0
	values of parameter $a \times 10^4$						
phenol	0.025	0.017	0.012	0.005	0.020	0.019	0.019
acridine	0.052	0.006	0.014	0.010	0.010	0.013	0.013
quinoline	0.032	0.004	0.017	0.021	0.025	0.022	0.022
6-methylquinoline	0.003	0.008	0.011	0.013	0.022	0.021	0.019
7-methylquinoline	0.023	0.016	0.023	0.024	0.034	0.036	0.023
8-methylquinoline	0.025	0.021	0.022	0.020	0.028	0.032	0.037
	values of parameter b						
phenol	0.100	0.057	0.052	0.055	0.000	0.004	0.001
acridine	-0.083	0.066	0.024	0.020	0.020	-0.003	0.003
quinoline	-0.022	0.100	0.017	0.011	-0.025	-0.021	-0.021
6-methylquinoline	0.091	0.065	0.046	0.023	-0.024	-0.019	-0.014
7-methylquinoline	0.016	0.029	-0.014	0.004	-0.058	-0.074	-0.017
8-methylquinoline	0.010	0.018	0.018	-0.015	-0.037	-0.065	-0.093
	values of parameter c						
phenol	0.120	-0.500	-0.730	-0.840	-0.890	-0.880	-0.880
acridine	0.610	-0.530	-0.730	-0.750	-0.720	-0.650	-0.640
quinoline	0.910	-0.410	-0.850	-0.770	-0.800	-0.730	-0.700
6-methylquinoline	0.980	-0.410	-0.670	-0.740	-0.720	-0.700	-0.650
7-methylquinoline	0.940	-0.460	-0.690	-0.890	-0.870	-0.800	-0.740
8-methylquinoline	0.460	-0.570	-0.740	-0.820	-0.850	-0.790	-0.740

Table II  
Parameters a, b and c (eq.2). Mobile phase: benzene - ethanol.

Solute	volume fraction of ethanol						
	0.0	0.1	0.3	0.5	0.7	0.9	1.0
	values of parameter a						
phenol	0.025	0.016	0.008	0.011	0.012	0.020	0.023
acridine	0.052	0.002	0.008	0.011	0.019	0.023	0.024
quinoline	0.032	0.019	0.004	0.012	0.010	0.004	0.008
6-methylquinoline	0.003	0.009	0.007	0.013	0.014	0.008	0.012
7-methylquinoline	0.023	0.023	0.002	0.027	0.030	0.030	0.013
8-methylquinoline	0.025	0.016	0.014	0.014	0.017	0.019	0.025
	values of parameter b						
phenol	0.100	0.048	0.053	0.006	-0.064	-0.043	-0.057
acridine	-0.083	0.047	0.032	0.011	-0.031	-0.047	-0.065
quinoline	-0.022	-0.013	0.054	0.012	0.019	0.064	0.051
6-methylquinoline	0.091	0.027	0.044	0.015	0.007	0.043	0.026
7-methylquinoline	0.016	0.002	0.072	0.013	-0.005	-0.036	0.013
8-methylquinoline	0.010	-0.017	-0.003	-0.006	-0.026	-0.021	-0.065
	values of parameter c						
phenol	0.120	-0.320	-0.570	-0.650	-0.640	-0.600	-0.530
acridine	0.610	-0.320	-0.620	-0.710	-0.670	-0.580	-0.490
quinoline	0.910	-0.170	-0.520	-0.640	-0.620	-0.600	-0.580
6-methylquinoline	0.980	-0.260	-0.600	-0.710	-0.660	-0.600	-0.560
7-methylquinoline	0.940	-0.210	-0.550	-0.660	-0.660	-0.620	-0.550
8-methylquinoline	0.460	-0.320	-0.620	-0.700	-0.710	-0.620	-0.500

Table III  
Parameters a, b and c (eq.2) . Mobile phase: benzene-propanol .

Solute	volume fraction of propanol						
	0.0	0.1	0.3	0.5	0.7	0.9	1.0
	values of parameter a						
phenol	0.025	0.018	0.015	0.016	0.022	0.018	0.012
acridine	0.052	0.007	0.012	0.017	0.026	0.027	0.012
quinoline	0.032	0.011	0.015	0.019	0.019	0.010	0.007
6-methylquinoline	0.003	0.009	0.010	0.007	0.004	0.017	0.002
7-methylquinoline	0.003	0.022	0.017	0.016	0.013	0.013	0.017
8-methylquinoline	0.025	0.017	0.012	0.012	0.007	0.001	0.000
	values of parameter b						
phenol	0.100	0.014	0.002	0.001	-0.021	0.002	0.025
acridine	-0.083	0.011	0.017	0.000	-0.034	-0.039	0.025
quinoline	-0.022	0.062	0.027	-0.006	-0.007	0.045	0.057
6-methylquinoline	0.091	0.022	0.030	0.038	0.074	-0.004	-0.020
7-methylquinoline	0.016	-0.023	-0.008	-0.004	0.019	0.018	0.031
8-methylquinoline	0.010	0.001	0.015	0.012	0.057	0.094	0.013
	values of parameter c						
phenol	0.120	-0.360	-0.610	-0.760	-0.760	-0.720	-0.690
acridine	0.610	-0.180	-0.560	-0.720	-0.720	-0.630	-0.550
quinoline	0.910	-0.210	-0.460	-0.580	-0.530	-0.500	-0.440
6-methylquinoline	0.980	-0.060	-0.460	-0.550	-0.570	-0.450	-0.400
7-methylquinoline	0.940	-0.140	-0.420	-0.540	-0.500	-0.500	-0.560
8-methylquinoline	0.460	-0.260	-0.640	-0.700	-0.720	-0.670	-0.650

vestigations are seen in the values of their dipole moments and that has an influence on the differentiation of parameters  $a$  and  $b$  of multinominal.

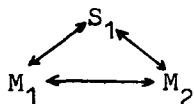
The smaller is the molecule of alcohol which is a more active component of mobile phase the smaller are the differences in the values of parameter  $a$  (from the concentration  $\varphi_1 = 0.7$  of volume fraction). The regularities are most distinctly observed in the case of benzene-methanol mobile phase. It is understood because of the fact that methanol is the solvent of the greatest elution strength among the solvents we used. For benzene-propanol system the relationship is not maintained due to the significantly lower elution strength of the mobile phase.

In the investigated systems the smallest values of parameter  $a$  appear for acridine. It is also seen that for phenol the values of parameters  $a$  and  $b$  greatly differ from the value of these parameters for remaining solutes. It may be explained by the different ability of phenol to make hydrogen bonds with the remaining substances of group B.

The values of parameter  $c$  denote molecular interactions at specific surface area of adsorbent equal to 0 ( $s=0$ ) in a given chromatographic system, that is, the interactions of the type: chromatographed substance  $S_1$  - component "1" of mobile phase ( $M_1$ ) and chromatographed substance ( $S_1$ ) - component "2" of mobile phase ( $M_2$ ). In a graphical form, the interactions may be shown as follows:

Table IV  
Experimental and theoretical  $k_M$  values of solutes on different adsorbent.

s m <sup>2</sup> /g	volume fraction of the stronger component of mobile phase ( $\varphi_1$ )												
	0.0	0.1	0.3	0.5	0.7	0.9	1.0	$R_M^{th}$	$R_M^{exp}$	$R_M^{th}$			
solvent system: benzene-methanol, chromatographed substance - acridine													
500	1.51	1.50	0.05	0.05	-0.25	-0.25	-0.39	-0.40	-0.37	-0.37	-0.34	-0.34	-0.30
400	1.12	1.11	-0.17	-0.17	-0.40	-0.40	-0.50	-0.52	-0.48	-0.48	-0.45	-0.45	-0.42
150	0.74	0.60	-0.41	-0.42	-0.63	-0.65	-0.67	-0.70	-0.65	-0.67	-0.62	-0.61	-0.60
50	0.63	0.63	-0.50	-0.49	-0.69	-0.70	-0.73	-0.73	-0.70	-0.71	-0.64	-0.63	-0.64
solvent system: benzene-ethanol, chromatographed substance - quinoline													
500	1.59	1.60	0.24	0.24	-0.15	-0.15	-0.28	-0.28	-0.27	-0.27	-0.18	-0.18	-0.11
400	1.33	1.33	0.08	0.08	-0.24	-0.24	-0.40	-0.40	-0.38	-0.38	-0.28	-0.28	-0.24
150	1.02	0.94	-0.02	-0.02	-0.43	-0.43	-0.60	-0.59	-0.56	-0.57	-0.51	-0.51	-0.48
50	0.94	0.91	-0.17	-0.17	-0.50	-0.52	-0.62	-0.63	-0.62	-0.61	-0.59	-0.59	-0.55
solvent system: benzene-propanol, chromatographed substance - phenol													
500	0.98	1.00	0.16	0.16	-0.22	-0.22	-0.34	-0.34	-0.33	-0.33	-0.28	-0.28	-0.27
400	0.66	0.68	-0.22	-0.02	-0.36	-0.36	-0.48	-0.50	-0.50	-0.50	-0.44	-0.44	-0.40
150	0.28	0.32	-0.25	-0.29	-0.53	-0.57	-0.68	-0.72	-0.72	-0.74	-0.69	-0.72	-0.62
50	0.16	0.18	-0.35	-0.35	-0.63	-0.60	-0.77	-0.76	-0.75	-0.76	-0.73	-0.72	-0.70



The values of parameter  $c$  change with the composition of mobile phase due to the fact that systems we investigated are non-ideal. The diagrams of relationships  $c$  vs  $\varphi_1$  correspond in their shapes to relationships  $R_M$  vs  $\varphi_1$ ; but the values of parameter  $c$  are in each case lower than the corresponding  $R_M$  values.

In table IV there have been shown  $R_M$  values for chosen chromatographed substances obtained experimentally and calculated from equation 2. As it is seen from the given data there exists satisfactory agreement between theoretical and experimental data. The connection of the values of parameter  $a, b$  and  $c$  with physico-chemical quantities being characteristic of chromatographic system will allow us to avoid the series of tiring experimental measurements and to obtain greater universality of chromatographic data.

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