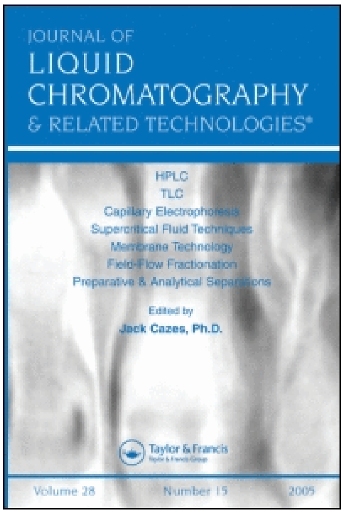

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COMPARISON OF METHODS FOR DETERMINATION OF THE R_M VALUES OF SUBSTANCES IN THIN - LAYER CHROMATOGRAPHY BY USING BINARY MOBILE PHASE

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ABSTRACT

Methods of calculating the function $R_M = f(\varphi_1)$ of some aromatic substances from the data of experimental and theoretically calculated parameters have been compared. It has been shown that there is a possibility to calculate this function with high accuracy on the basis of the measured partition coefficients of the substances chromatographed in partition systems consisting of components of the mobile phase as well as parameters obtained theoretically. Thus obtained results were also compared with the functions $R_{M_{1.2}} = f(\varphi_1)$ obtained experimentally and a high agreement was reached. This in turn contributes to optimization of systems of thin-layer chromatography.

THEORETICAL

Prediction of optimal conditions in partition chromatography of mixtures is one of the most important problems of this analytical method. A number of papers (1-3) on thin-layer chromatography have been published; however, none of the theories dealt with gives satisfactory results. The thermodynamic theory of adsorption from of multicomponent solvent systems, developed by Ościk (4-6) made it possible to combine the R_M values with the composition of the mobile phase and the adsorption parameters of the given chromatographic system, resulting in the general equation:

$$R_{M_{1.2}} = \varphi_1 \Delta R_{M_{1.2}} + (\varphi_1^s - \varphi_1)(\Delta R_{M_{1.2}} + A_z) + R_{M_2} + Y \qquad (1)$$

in which $R_{M_{1.2}}$ is the R_M value of substance "z" obtained by using a binary solvent "1+2"; R_{M_1} and R_{M_2} are R_M values of substance "z" in pure solvents "1" and "2"; the difference $(\varphi_1^s - \varphi_1)$ presents excessive adsorption of component "1" of the mobile phase. This difference can experimentally be determined from isotherms of excessive adsorption (7), or from the distribution function of the mobile phase component (1-6). $\Delta R_{M_{1.2}} = R_{M_1} - R_{M_2}$ is the difference of the R_M values of substances in pure solvents "1" and "2". The value $A_z = \log k_{1.2}^{\infty}$ represents molecular interaction between molecules of the substance chromatographed "z" and those of the components of a miscible solvent. The value A_z can be calculated by fitting this parameter to the two-parameter equation (1),(8). This method, however, does not involve the value of molecular interaction in real systems of the solvents presented. Thus, in the case of totally miscible mobile phases the value $A_z = \log k^{\infty}_{1.2}$ can be obtained indirectly by measuring the partition coefficients of substance "z" between solvent "1" and immiscible solvent x $(k^{\infty}_{1.x})$ and solvent "2" and the same solvent x $(k^{\infty}_{2.x})$ as well as by comparison:

$$k^{\infty}_{1.2} = \frac{k^{\infty}_{1.x}}{k^{\infty}_{2.x}} \qquad (2)$$

The determination of partition coefficients $k^{\infty}_{1.2}$ is a separate analytical problem causing great difficulties. Therefore, the determination of A_z values by this method is not a simple procedure, and the relationship of the A_z values obtained by the two methods is unknown.

The purpose of this method was to compare the relationship $R_{M_{1.2}} = f(\varphi_1)$ of the substances calculated from the experimental partition coefficients $k^{\infty}_{1.2}$ and the relationship $R_{M_{1.2}} = f(\varphi_1)$ calculated from A_z values obtained by the method of fitting this parameter to the two-parameter equation (1).

EXPERIMENTAL

As the components of the binary mobile phase are totally miscible, the coefficients of substance distribution $k^{\infty}_{1.2}$ are therefore determined directly. The coefficients of the distribution of a given substance between component "1" of the mobile phase and water $k^{\infty}_{1.w}$ and between component "2" of this phase and water $k^{\infty}_{2.w}$ were measured. Coefficient

$k^{\infty}_{1.2}$ was calculated from the relation

$$k^{\infty}_{1.2} = \frac{k^{\infty}_{1.w}}{k^{\infty}_{2.w}}$$

The coefficients of distribution of the substances studied between the organic phase and water were measured statistically by determining their distribution isotherms between these phases. The concentration of substances in the water phase was determined by coulometric bromination in the case of 1-naphthol, 3-methylquinoline, quinoline, 2-methylquinoline and 7-methylquinoline for $CHCl_3$-H_2O system and polarografically. The $k^{\infty}_{1.2}$ values determined in this way are presented in Table 1.

Table 1

$k^{\infty}_{1.2}$ VALUES OF SUBSTANCES OF $CHCl_3$-CCl_4 SYSTEM

SUBSTANCE	$k^{\infty}_{1.2}$
1-naphthol	1.50
quinoline	2.86
2-methylquinoline	2.69
4-methylquinoline	1.62
6-methylquinoline	2.96
7-methylquinoline	1.60
8-methylquinoline	3.51
3-methylisoquinoline	1.65

In the course of the investigations the relationship of the values $R_{M_{1.2}} = f(\varphi_1)$ for 1-naphthol, quinoline and methylquinoline derivatives was determined experimentally by adsorption thin-layer chromatography.

Magnesium silicate (Woelm) and aluminium oxide (Merck) were used as stationary phase. The mobile phase was a binary solution of different concentration, consisting of chloroform and carbon tetrachloride. The chromatograms were developed by the ascending technique on the adsorbent layers 0.3 mm thick in glass chambers saturated with vapours of appropriate mobile phase. All measurements were carried out in a thermostatic room at 25°C. Substances were detected by means of iodine vapours.

The results of experimental and theoretical calculations of the relationship $R_{M_{1.2}} = f(\varphi_1)$ are given in Table 2 and 3 and in diagrams Fig. 1-3.

Table 2

BASIC PARAMETERS, ON THE BASIS OF WHICH, THE $R_{M_{1.2}}$ VALUES OF CHROMATOGRAPHED SUBSTANCES HAVE BEEN CALCULATED

ADSORBENT: ALUMINIUM OXIDE

SUBSTANCE	$\Delta R_{M_{1.2}}$	A_z^c	A_z^e	φ_1	$R_{M_{1.2}}^e$	$R_{M_{1.2}}^t$	$R_{M_{1.2}}^c$
7-methylquinoline	-1.28	0.56	0.20	0.2	0.40	0.15	-0.09
				0.4	-0.04	-0.02	-0.22
				0.6	-0.28	-0.16	-0.29
				0.8	-0.40	-0.28	-0.35
8-methylquinoline	-1.40	0.61	0.54	0.2	-0.23	-0.44	-0.48
				0.4	-0.56	-0.62	-0.66
				0.6	-0.82	-0.77	-0.80
				0.8	-	-	-

A_z^c - chromatographic data, A_z^e - experimental data,

$R_{M_{1.2}}^e$ - experimental data, $R_{M_{1.2}}^t$ - theoretical data,

$R_{M_{1.2}}^c$ - calculated on the basis of experimental A_z values.

Table 3

BASIC PARAMETERS, ON THE BASIS OF WHICH, THE $R_{M_{1.2}}$ VALUES OF SUBSTANCES HAVE BEEN CALCULATED.

ADSORBENT: MAGNESIUM SILICATE

SUBSTANCE	$R_{M_{1.2}}$	A_z^c	A_z^e	1	$R_{M_{1.2}}^e$	$R_{M_{1.2}}^t$	$R_{M_{1.2}}^c$
1-naphthol	-1.06	0.22	0.18	0.2	1.10	0.79	0.76
				0.4	0.75	0.68	0.65
				0.6	0.56	0.60	0.59
				0.8	0.42	0.55	0.54
quinoline	-1.80	0.53	0.46	0.2	1.06	0.79	0.74
				0.4	0.65	0.59	0.55
				0.6	0.40	0.44	0.42
				0.8	0.20	0.32	0.30
2-methylquinoline	-1.78	0.39	0.43	0.2	0.72	0.52	0.54
				0.4	0.38	0.33	0.35
				0.6	0.16	0.21	0.22
				0.8	0.06	0.11	0.12
4-methylquinoline	-1.53	0.55	0.21	0.2	1.06	0.77	0.54
				0.4	0.65	0.58	0.40
				0.6	0.40	0.44	0.32
				0.8	0.22	0.32	0.25
6-methylquinoline	-1.92	0.65	0.47	0.2	0.88	0.77	0.65
				0.4	0.62	0.57	0.44
				0.6	0.32	0.36	0.30
				0.8	0.14	0.22	0.19
7-methylquinoline	-1.62	0.33	0.20	0.2	1.08	0.82	0.73
				0.4	0.70	0.65	0.58
				0.6	0.51	0.55	0.49
				0.8	0.28	0.46	0.43
8-methylquinoline	-2.25	0.79	0.54	0.2	0.42	0.43	0.26
				0.4	0.20	0.15	0.02
				0.6	-0.08	-0.05	-0.11
				0.8	-0.24	-0.23	-0.28
3-methylisoquinoline	-1.62	0.42	0.22	0.2	1.12	0.87	0.74
				0.4	0.78	0.70	0.59
				0.6	0.52	0.57	0.50
				0.8	0.33	0.48	0.44

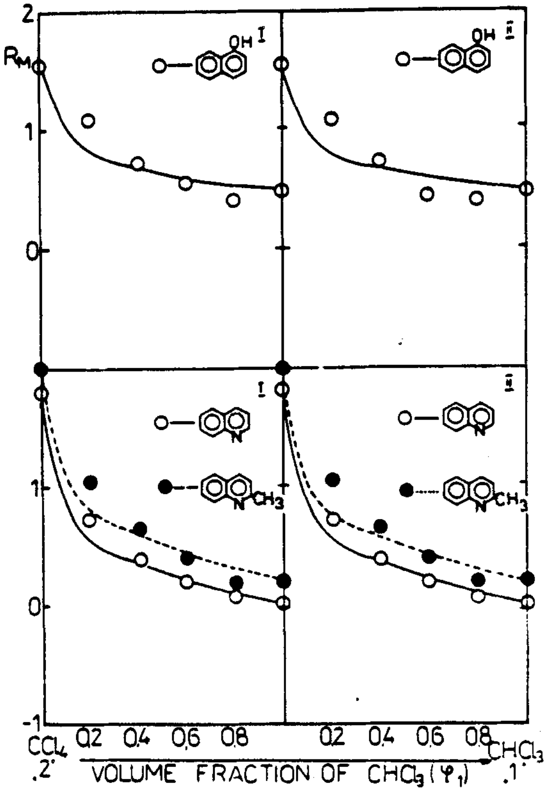

Fig. 1

Theoretical (lines) and experimental (points) function $R_{M_{1,2}} = f(\varphi_1)$

I - calculated from equation (1) by fitting the parameter A_z

II - calculated from this equation on the basis of measured values of the partition coefficients $k^{\infty}_{1,2}$

Adsorbent: magnesium silicate.

DISCUSSION

From the determined partition isotherms the partition coefficients summarized in Table 1 have been calculated. They

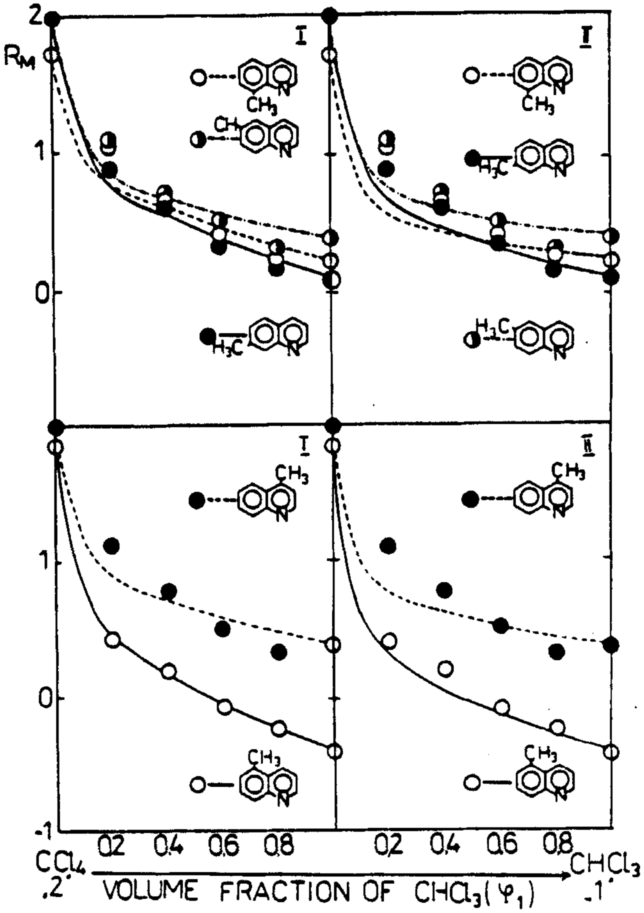

Fig. 2

Theoretical (lines) and experimental (points) function

$R_{M_{1,2}} = f(\varphi_1)$

I - calculated from equation (1) by fitting the parameter A_z

II - calculated from this equation on the basis of measured values of the partition coefficients $k^{\infty}_{1,2}$

Adsorbent: magnesium silicate.

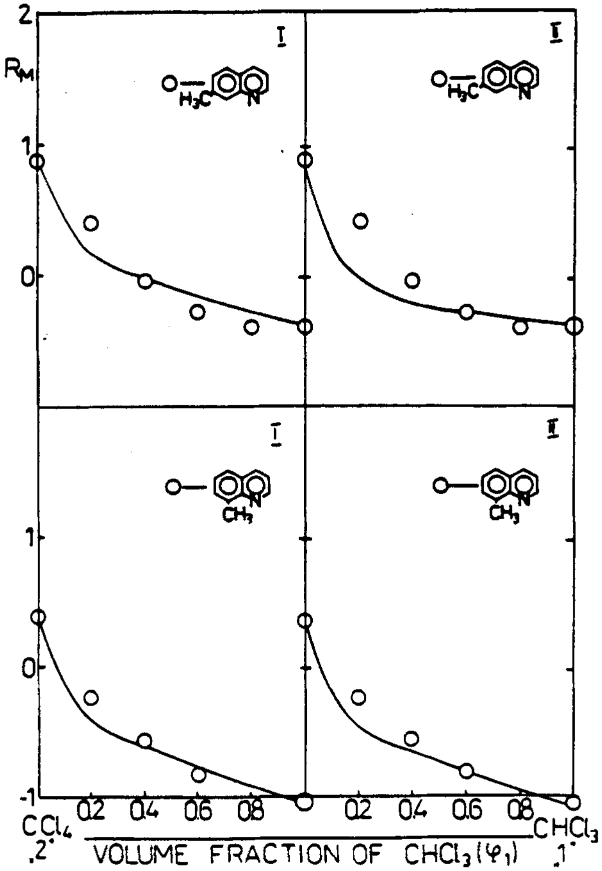

Fig. 3

Theoretical (lines)and experimental (points) function $R_{M_{1,2}} = f(\varphi_1)$

I -calculated from equation(1)by fitting the parameter A_z

II - calculated from this equation on the basis of measured values of the partition coefficients $k^{\infty}_{1,2}$

Adsorbent: aluminium oxide.

have served then to calculate the A_z values listed in Table 2 and 3. It should be noted that the A_z values of substances, calculated theoretically by fitting this parameter to equation (1) as well as from the partition coefficients measured, are approximate bath with respect to the order and value of this parameter. However, the values A_z calculated from the partition coefficients measured experimentally are more differentiated in relation to the chemical structure of the substance chromatographed. This leads to a deeper interpretation of molecular interactions in such partition systems.

Figure 1 and 2 present the functions $R_{M_{1.2}} = f(\varphi_1)$ for 1-naphthol and a number of methylquinoline derivatives, obtained by using a mixture of carbon tetrachloride + + chloroform as binary mobile phase, magnesium silicate being the adsorbent. In this system attention is drawn by a relatively good agreement of the functions $R_{M_{1.2}} = f(\varphi_1)$ calculated theoretically and obtained experimentally. This results from not too strong molecular interactions in this chromatographic system. The comparison of the functions $R_{M_{1.2}} = f(\varphi_1)$ calculated from equation (1) by fitting the parameter A_z (Fig. 1 I, 2 I) and calculated from this equation on the basis of measured values of the partition coefficients $k^{\infty}_{1.2}$ (Fig. 1 II, 2 II) shows that a high agreement of these functions can be obtained. Small differences in the functions $R_{M_{1.2}} = f(\varphi_1)$ calculated by fitting the parameter A_z to the equation (1) as well as in the experimental data of the partition coefficients result from differences between partition and adsorption systems in chromatography. Under such conditions, a proper choice of adsorption systems of weak molecular interactions of the mobile phase and of substances chromatographed with the adsorbent can give a picture of molecular interactions in the partition system in which no action is exerted by the adsorbent.

In order to demonstrate that the results obtained do not depend on the kind of the adsorbent used, functions $R_{M_{1.2}} = f(\varphi_1)$ were estimated on aluminium oxide (Fig. 3). It appeared that also in this case a high agreement of the functions $R_{M_{1.2}} = f(\varphi_1)$ was obtained which were calculated theoretically and experimentally parameter A_z values.

The studies carried out and the results obtained are of great significance for our further investigations. It was found that parameter A_Z, which is of primary importance in equation (1) can be calculated in a simple way from experimental data. As these data can be summarized in Tables, there exists a possibility of a simple and fast calculation of the functions $R_{M_{1.2}} = f(\varphi_1)$ from readily measurable experimental data. Therefore the interpretation of the process of thin-layre chromatography it self will be more exact.

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