

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

Some Physico-Chemical Problems of Prediction of the Optimum Separation in Adsorption TLC with Mixed Mobile Phase

J. K. Różyło^a; G. Chojnacka^a; B. Ościk-mendyk^a; H. Kołodziejczyk^a

^a Institute of Chemistry M. Curie-Skłodowska University, Lublin, Poland

To cite this Article Różyło, J. K. , Chojnacka, G. , Ościk-mendyk, B. and Kołodziejczyk, H.(1989) 'Some Physico-Chemical Problems of Prediction of the Optimum Separation in Adsorption TLC with Mixed Mobile Phase', *Journal of Liquid Chromatography & Related Technologies*, 12: 1, 247 – 269

To link to this Article: DOI: 10.1080/01483918908049199

URL: <http://dx.doi.org/10.1080/01483918908049199>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SOME PHYSICO-CHEMICAL PROBLEMS OF PREDICTION OF THE OPTIMUM SEPARATION IN ADSORPTION TLC WITH MIXED MOBILE PHASE

J.K. RÓŻYŁO, G. CHOJNACKA,
B. OŚCIK-MENDYK AND
H. KOŁODZIEJCZYK
*Institute of Chemistry
M. Curie-Skłodowska University
20-031 Lublin, Poland*

ABSTRACT

Determination of optimal composition of a mixed mobile phase used in separation of different substances by adsorption TLC methods is performed usually by the experimental trial and error method. In this paper we have presented and discussed equations permitting to determine the relationships between R_M values of the substances and the composition of binary and ternary mobile phases on the basis of measured chromatographic and adsorption parameters and experimentally determined partition coefficients of the substance between the mobile phase components. A good agreement between theoretical and experimental data has been shown. The results of these investigations allow for more precise prediction of the mobile phase optimal composition for the mixture separation.

INTRODUCTION

Adsorption thin-layer chromatography is widely known as a typical analytical method and is used above all in separation of many mixtures. This method is used especially in cases when we are interested in rapid and simple analyses. This relates mainly to the analyses connected with the determination of contamination degree of biotop, biotop protection, pharmaceutical and clinical investigations as well as to pilot investigations for column liquid chromatography [1-3].

Good separation of the mixture can be obtained only in the case when the chromatographic system is characterized by appropriate selectivity. Recently published criteria of optimization of the mixture separation process are of typically mathematical nature [2,4] and in this respect are less useful for practical solution of the problem of choosing optimal chromatographic systems. This is due among others to the fact that in chromatographic techniques mainly multicomponent mobile phases are used. Choice of optimal composition of such phases is very difficult and realized mainly in an experimental way. Some new possibilities of choice of optimal composition of a ternary mobile phase are provided by the analysis of chromatographic parameters of such mobile phases proposed by Różyło and Ościk-Mendyk [5]. In this method the experimental data are presented on the Gibbs triangle in the form of the isolines i.e. the lines connecting the points corresponding to the same R_F values (or R_{F1}/R_{F2} values where subscripts 1 and 2 correspond to individual components of the mixture separated).

Moreover, in spite of knowing adsorption TLC principles and many papers on chromatographic systems optimization

the problem of optimal mobile phases remains still unsolved. In this connection, investigations on simple and useful equations describing adsorption TLC process are necessary. Pery [6] has shown how many valuable conclusions relating to chromatographic practice can be drawn from the equations derived by Snyder [7] and Soczewiński [8].

Some new possibilities in the field of adsorption chromatographic system optimization are provided by the equation derived by Ościk [9]. This equation relates R_M value of the chromatographed substance using a multi-component mobile phase to R_M values of the same chromatographed substance using single components of the mobile phase. For the binary mobile phase this equation is of the form:

$$R_{M_{12}} = X_1 R_{M_1} + X_2 R_{M_2} + (Y_1 - X_1)(\Delta R_{M_{1,2}} + A_{12}) \quad (1)$$

where:

$R_{M_{12}}$, R_{M_1} and R_{M_2} denote R_M values of the chromatographed substance in the binary mobile phase and in pure solvents 1 and 2 respectively, 1 being the more polar solvents;

X_1 and X_2 the molar fractions of the mobile phase components;

Y_1 the molar fraction of a more polar solvent in the surface phase;

$A_{12} = \log k_{12}^\infty$ where k_{12}^∞ denotes a partition coefficient of a given substance between the solvents forming the binary mobile phase;

$$\Delta R_{M_{1,2}} = R_{M_1} - R_{M_2}$$

Particular terms of the equation(1) have the following physico-chemical meaning:

R_{M1} and R_{M2} express the adsorption affinities of the chromatographed substance in solvents 1 and 2 respectively;

A_{12} denotes the parameter characterizing the intermolecular interactions between the chromatographed substance and a component of the mobile phase;

$(Y_1 - X_1)$ - excess adsorption of a more polar component of the mobile phase which permits to evaluate the effect of adsorption phenomena on the chromatographic process mechanism. This quantity is strictly connected with adsorption equilibrium constant in the system in question.

Determination of the equation terms do not cause many difficulties. R_M values of the substance in pure solvents 1 and 2 are determined experimentally. The difference $(Y_1 - X_1)$ may be determined experimentally from the excess adsorption isotherm or from an adsorption equilibrium constant(this second method is significantly simpler because it does not require any additional measurements) using the relationships [10,11] :

$$- \log K_{12} = \Delta R_{M1,2} \quad (2)$$

or

$$K_{12} = 10^{-\Delta R_{M1,2}} \quad (3)$$

and the adsorption isotherm equation proposed by Everett [12]. A_{12} parameter can be calculated by means of its fitting to diparameter equation (1) or from experimentally determined partition coefficients of the chromatographed substance [13,14].

In the considered chromatographic system the term $(R_{M1,2} + A_{12}) = C$ has for each substance a constant value. Thus equation (1) can be presented in the form:

$$R_{M12} = X_1 R_{M1} + X_2 R_{M2} + (Y_1 - X_1) C \quad (4)$$

Assuming the ideality of bulk and surface phases as well as energetical homogeneity of the adsorbents surface, we can transform the equation (4) to the linear form using adsorption isotherm equation proposed by Everett [12]. Equation (4) will have then the following form:

$$G = \frac{X_1 X_2}{R_{M12} - X_1 R_{M1} - X_2 R_{M2}} = \frac{1}{C} \frac{1}{K_{12} - 1} + X_1 = aX_1 + b \quad (5)$$

where

$$a = \frac{1}{C} \quad b = \frac{1}{C(K_{12} - 1)}$$

and thus:

$$K_{12} = \frac{a}{b} + 1 \quad \text{and} \quad A_{12} = \frac{1}{a} - \Delta R_{M1,2} \quad (6)$$

Equation (5) permits to determine K_{12} and A_{12} parameters from $G = f(X_1)$ function and from boundary conditions of the straight lines. This is possible because for $X_1 = 0$ $G = b$, and for $X_1 = 1$ $G = a + b$. Equations (2) and (5) permit to calculate K_{12} values. As starting assumptions used in derivation of these equations are based on different theories [10,11], K_{12} values calculated from equation (2) will be denoted as $K_{12\Delta}$ and the same values calculated from equation (5) as K_{12G} . It has been stated [16,17] that the values of these parameters are strongly dependent on properties of the chromatographed substances. In case of strongly adsorbed substances $K_{12\Delta}$ values are significantly higher than K_{12G} values. When the chromatographed substance does not contain strongly adsorbed groups the $K_{12G} > K_{12\Delta}$. The comparison of $K_{12\Delta}$ and K_{12G} values with K_{12} value ob-

tained from direct measurements of the adsorption of the mobile phase components in the absence of the chromatographed substance [16] shows that these values are significantly lower than K_{12} .

In practice, $K_{12\Delta}$ and K_{12G} values depend on the properties of all components of chromatographic system and on the dynamics and kinetics of the chromatographic process. For this reason, under these conditions K_{12G} and $K_{12\Delta}$ values are not the adsorption equilibrium constants, nevertheless they are strictly connected with the process. Defining these values as „adsorption parameters“ appears to be more precise. These values together with $A_{12\Delta}$ and A_{12G} characterize the chromatographic process under consideration. These parameters can provide some information on adsorption TLC and thus be useful in the process optimization.

The main purpose of the investigations described in this paper consists in showing applicability of equations (1), (2) and (5) in TLC system optimization, especially in selection of appropriate multicomponent mobile phases.

METHODS

The R_F values were measured by adsorption TLC for different aromatic compounds. For nitrobenzene, aniline, 2,6-dimethylnitrobenzene, o-nitroaniline, 2,6-dinitroaniline and isomeric dinitrobenzene, nitrotoluenes and toluidines aluminum oxide 150 neutral (Merck) was used as the adsorbent. The solutions tetrahydrofuran, ethyl acetate, methyl ethyl ketone, dioxane and acetone in n-heptane were used as the mobile phases. For heterocyclic bases (Tables 3 and 4), aniline and 1-naphthol the following binary solutions were used as the mobile phases: carbon tetrachloride + n-heptane,

trichloroethylene + carbon tetrachloride, chloroform + benzene, benzene + carbon tetrachloride, chloroform + trichloroethylene. The silica gel G (Merck) was used as the adsorbent.

In case of phenol, 2,3-dichlorophenol, 3,4-dichlorophenol and 2,6-dichlorophenol, ternary solutions chloroform(1) + toluene(2) + carbon tetrachloride(3) were used as the mobile phase. In these mixtures the volume ratio of components 2 and 3 was always kept constant (equal to 1:1).

The chromatographic process was carried out by ascending technique on adsorbent layers of 0.3mm in thickness in glas chambers saturated with mixed solvent vapours. All the measurements were carried out under thermostatic conditions at 298⁰K. The detection of the substances was carried out by reaction with iodine. The R_M values were calculated using the equation of Bate-Smith and Westall.

The partition coefficients k_{12}^{∞} of heterocyclic bases aniline and 1-naphthol in the binary mobile phases were indirectly obtained in the following way. First, the partition coefficient of the substance was measured between component 1 of the mobile phase and water ($k_{1,w}^{\infty}$) and then between component 2 and water ($k_{2,w}^{\infty}$).

From these values k_{12} can be calculated.

$$k_{12}^{\infty} = \frac{k_{1,w}^{\infty}}{k_{2,w}^{\infty}}$$

The partition coefficients of the examined substances between the individual mobile phase components and water were obtained by determining their partition isotherms between the phases for very low concentrations (0.001-0.00025 mol/l). Water was presaturated with the appropriate organic solvents. The concentrations of the substance in the water phase were determined polaro-

graphically and by coulometric bromination. The partition coefficients measured in this way are presented in Tables 3 and 4.

The results of the measurements of and of the theoretical calculations according to equations (1), (2) and (5) are given in Tables 1 - 4 and Figs. 1 - 5,

RESULTS AND DISCUSSION

In the previous paper [18] A_{12} values calculated from the equation (1) were compared with such physico-chemical quantities characterizing the test substances as pKa values or adsorption energy of the functional groups. It has been stated that some correlations between these quantities exist allowing for wider interpretation of A_{12} parameter. In case of adsorption chromatography system optimization, adsorption parameters play a very important role. In this connection a comparison of these parameters with such physico-

TABLE 1

The solvent strength parameter ξ^0 and the solubility parameters [21] of the more active components of the mobile phases

Solvent	ξ^0 Al_2O_3	δ_T	δ_d	δ_o	δ_{in}	δ_b
Tetrahydrofurane	0.45	9.1	7.6	3.5	0.8	3.7
Ethyl acetate	0.58	8.9	7.0	4.0	1.0	2.7
Methyl ethyl ketone	0.51	9.5	7.1	4.7	1.2	3.2
Acetone	0.56	9.6	6.8	5.1	1.5	3.0
Dioxane	0.56	10.1	7.8	5.2	1.0	4.6

TABLE 2 K_{12G} and $K_{12\Delta}$ values for systems with aluminium oxide 150 neutral as adsorbent and following mobile phases: 1 - n-heptane+tetrahydrofurane, 2 - n-heptane+ethyl acetate, 3 - n-heptane+dioxane, 4 -n-heptane+methyl ethyl ketone, 5 - n-heptane+acetone.

Mobile phase	1		2		3		4		5	
	K_{12G}	$K_{12\Delta}$	K_{12G}	$K_{12\Delta}$	K_{12G}	$K_{12\Delta}$	K_{12G}	$K_{12\Delta}$	K_{12G}	$K_{12\Delta}$
Nitrobenzene	13.8	-	16.1	6.7	16.6	7.6	18.2	8.4	21.4	13.5
o-Dinitrobenzene	4.8	-	6.1	76.7	6.0	84.9	7.6	94.6	9.8	160.0
m-Dinitrobenzene	4.4	-	7.7	38.5	-	41.8	14.5	48.5	18.4	63.7
p-Dinitrobenzene	-	-	-	66.7	-	71.6	-	82.4	-	126.0
o-Nitrotoluene	13.1	-	-	6.8	17.5	7.3	19.2	8.6	23.1	12.9
m-Nitrotoluene	11.1	-	14.2	8.4	14.2	7.9	18.9	9.0	24.9	14.3
p-Nitrotoluene	12.1	-	14.6	8.5	14.4	9.3	18.0	10.8	23.1	16.9
2,6-Dimethyl-nitrobenzene	13.4	-	15.1	4.7	15.7	4.8	18.3	5.5	21.4	9.9
o-Nitroaniline	5.3	-	9.4	126.8	8.0	133.0	13.5	178.6	21.6	232.0
2,6-Dinitroaniline	4.9	-	8.7	96.2	8.4	91.8	13.2	113.5	20.9	164.4
Aniline	4.6	-	7.3	51.0	7.3	55.2	12.1	66.8	21.9	104.7
o-Toluidine	6.1	-	11.8	39.0	11.2	40.9	17.9	46.7	24.1	79.4
m-Toluidine	5.7	-	8.8	49.2	8.8	51.2	14.0	59.2	20.9	96.8
p-Toluidine	5.3	-	10.7	59.8	10.9	62.2	16.6	69.8	21.2	119.4
2,6-Dimethyl-aniline	8.4	-	12.2	18.8	13.0	18.9	15.8	23.0	21.5	32.5

chemical values a solvent strength parameters [7] and solubility parameters [19-20] of active components of the mobile phases appears to be advisable. The mixtures containing proton acceptor solvents tetrahydrofuran, ethyl acetate, dioxane, methyl ethyl ketone, acetone and nonactive solvent n-heptane were used as the mobile phases in the investigations. In this case, the existence of strong, specific interactions among the mobile phase components can be excluded. Thus K_{12} values will be dependent on competitive interactions: adsorbent-substance and adsorbent-active component of the mobile phase, as well as on the association of molecules of the mobile phase active component (1-1 association) and on the interaction between the molecules of the chromatographed substance and the mobile phase active components (s-1 association). Investigations by Ościk-Mendyk and Różyło [22] have shown that in case of such chromatographic systems (containing alumina, mobile phase of N+B type and the aromatic nitro compounds) association of 1-1 type significantly predominates. As the active solvent strongly interact with the adsorbent surface and its concentration is usually high, association of the active solvents should significantly influence chromatographic parameters. Thus an assumption can be made that a correlation exists between K_{12} parameter and the above mentioned physico-chemical values characteristic for proton donor solvents.

Table 1 lists values characteristic for the mobile phase active components: solvent strength parameter ξ^0 [7] and solubility parameters δ_T and their dispersion δ_d , orientation δ_o , induction δ_{in} and proton acceptor components [19-21].

Table 2 presents $K_{12\Delta}$ and K_{12G} values of the chromatographed aromatic nitro and amino compounds on aluminium oxide 150 neutral. A comparison of these parameters with

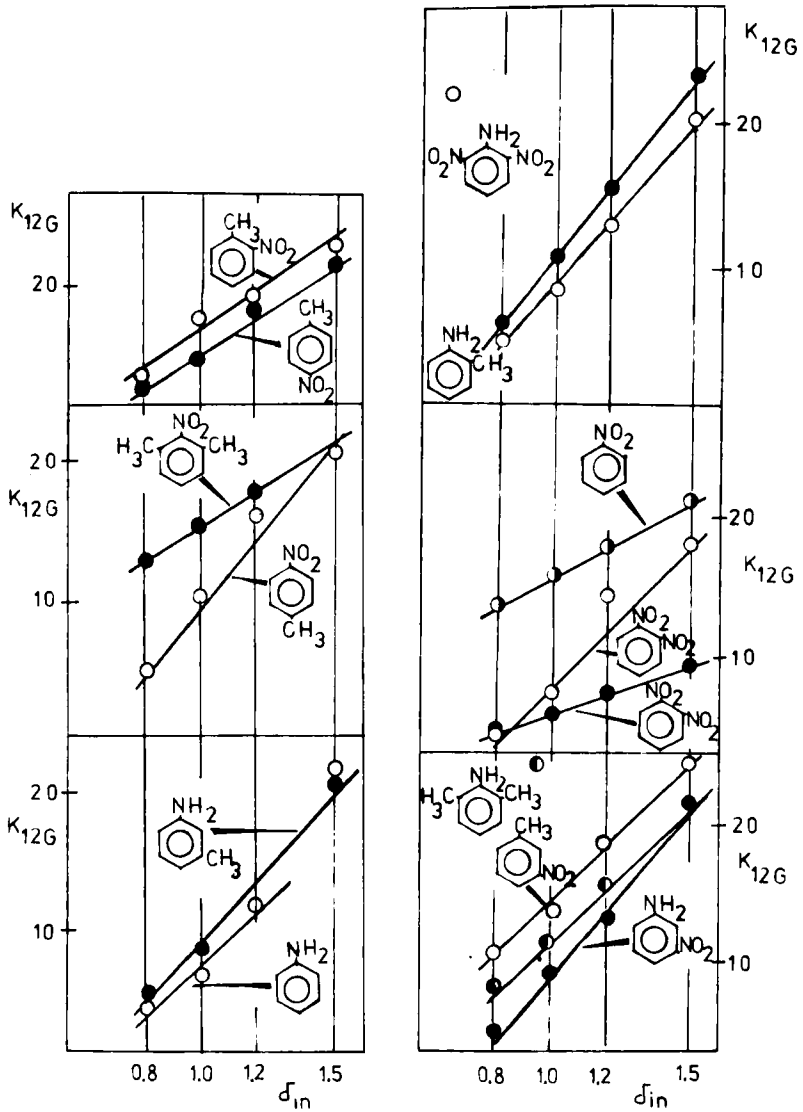


FIGURE 1

Relationships between the adsorption parameters K_{12G} calculated from equation (5) and the δ_{in} values of the preferentially adsorbed component of the binary mobile phases. Adsorbent: aluminium oxide 150 neutral.

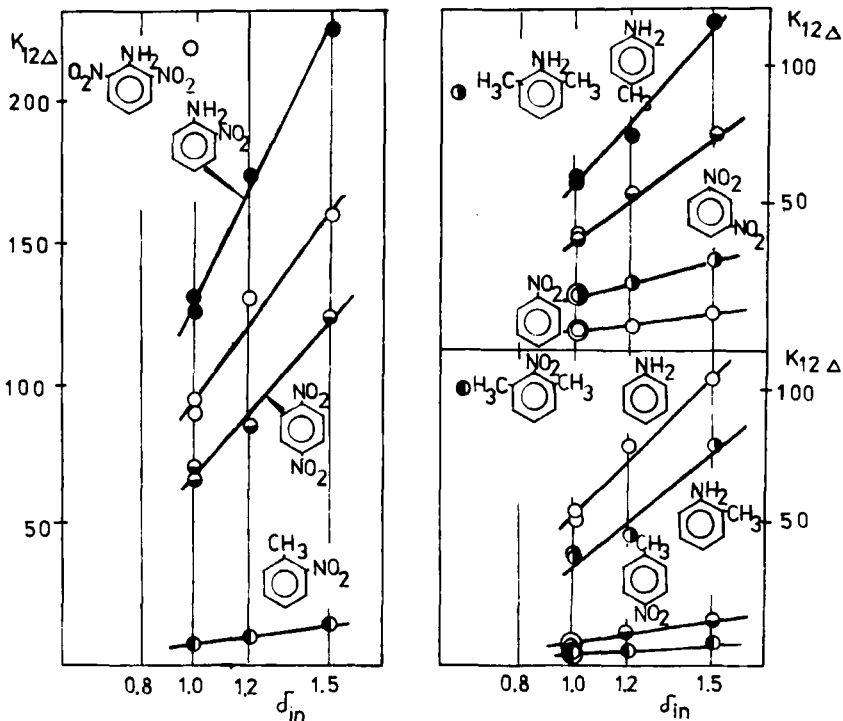


FIGURE 2

Relationships between the adsorption parameter $K_{12\Delta}$ calculated from dependence (2) and the δ_{in} values of more active components of the binary mobile phases. Adsorbent: aluminium oxide 150 neutral.

the data in Table 1 shows the absence of any correlation between ϵ° and $K_{12\Delta}$, and K_{12G} . A comparison of the ϵ° values for ethyl acetate, dioxane, methyl ethyl ketone and acetone with the excess adsorption isotherms of these solvents from n-heptane [23] shows that ϵ° is not connected with the value of surface excess of the mobile phase active component, but with the localiza-

tion of the maximum of the solvent adsorption isotherm. This maximum corresponds to the localization of the minimum on the $R_M = f(X_1)$ curves.

The comparison of $K_{12\Delta}$ and K_{12G} values and the solubility parameters of the proton acceptor mobile phase components indicates to the correlation between these values. A linear relationship between the parameters and the induction component of solubility parameter is observed. It is presented in Figs. 1 and 2. An analogous relationship is also observed when the compounds of a completely different chemical nature (polycyclic aromatic hydrocarbons, naphthols) are used as model substances. Thus, one can suppose that this relationship can be useful in $K_{12\Delta}$ and K_{12G} determination in the chromatographic system containing mobile phases of N+B type and aluminium oxide as adsorbent.

Assuming that ΔR_M values are the measure of the chromatographic system selectivity for mixture of two substance, on the basis of equation (1) the relationship permitting calculation of ΔR_M of the substances can be obtained [24,25]. This relationship has the following form:

$$\Delta R_{M1,2}^{i,j} = \phi_1^d + (\phi_1^s - \phi_1)(d + \Delta A_{12}^{i,j}) + \Delta R_{M2}^{i,j} \quad (7)$$

where

$\Delta R_{M1,2}^{i,j}$ is the difference between the R_M values of substances i and j , when using the binary mobile phase 1+2;

$$d = \Delta R_{M1,2}^i - \Delta R_{M1,2}^j \quad \text{where}$$

$$\Delta R_{M1,2}^i = R_{M1}^i - R_{M2}^i \quad \text{and} \quad \Delta R_{M1,2}^j = R_{M1}^j - R_{M2}^j$$

R_{M1}^i ; R_{M2}^i and R_{M1}^j , R_{M2}^j show the R_M values of substance

i and j , when using the pure solvent 1 and 2 as the mobile phase, respectively;

ϕ_1^s and ϕ_1 - volume fractions of the active component of the mobile phase in the surface and bulk phase, respectively;

$$\Delta A_{12}^{i,j} = \log k_{12}^{i,\infty} - \log k_{12}^{j,\infty} \quad \text{where } k_{12}^{i,\infty} \text{ and } k_{12}^{j,\infty}$$

are hypothetical partition coefficients of the substances i and j among the mobile phase components;

$$\Delta R_{M_2}^{i,j} = R_{M_2}^i - R_{M_2}^j \quad \text{in pure solvent 2.}$$

In equation (7) the concentration of the mobile phase is expressed in the form of a volume fraction. In case of high size differences of molecules forming the mobile phase this way of expressing the concentration is more reasonable.

As for determination of each equation term, as mentioned above, R_M values of the substances in pure solvents 1 and 2 are experimentally determined. The term $(\phi_1^s - \phi_1)$ can be determined from experimentally determined excess adsorption isotherm or calculated from equation (2).

The determination of A_{12}^i and A_{12}^j parameters provides some problems. They can be determined by fitting them to diparameter equation (1). However this procedure is time-consuming. A_{12} is equal to the logarithm of the hypothetical partition coefficient of the substance between totally miscible binary mobile phase components. For this reason the values of the partition coefficient of the substance between pure components of the mobile phase and the liquid immiscible with these components can be used (the procedure is described in METHODS). A_{12} values calculated by this procedure are listed in Table 3. The analysis of the data listed in this Table shows that a full agreement be-

TABLE 3 Parameters A_{12} of the substance calculated on the basis of experimental partition coefficients (A_{12p}) and determined by fitting them to equation (1) ($A_{12\Delta}$).

Mobile phase	$C_7H_{16}+CCl_4$		$CHCl=CCl_2+CCl_4$		$C_6H_6+CCl_4$		$CHCl_3+CHCl=CCl_2$		$CHCl_3+C_6H_6$	
	$A_{12\Delta}$	A_{12p}	$A_{12\Delta}$	A_{12p}	$A_{12\Delta}$	A_{12p}	$A_{12\Delta}$	A_{12p}	$A_{12\Delta}$	A_{12p}
Quinoline	0.072	0.245	-0.149	-0.836	0.212	0.266	-0.040	0.110	-	-
8-Methyl-quinoline	-0.042	-0.331	0.101	-0.063	0.134	-0.179	0.463	0.207	0.320	0.324
8-Hydroxy-quinoline	0.733	0.577	-0.001	-0.003	0.594	0.122	0.542	0.193	0.088	0.068
Isoquinoline	0.410	0.079	0.399	0.276	0.638	0.465	0.120	0.055	0.066	-0.134
3-Methyliso-quinoline	0.325	0.140	0.048	0.194	0.351	0.217	0.393	-0.138	-0.112	-0.161
Aniline	-0.066	-0.108	-	-	-	-	-0.308	-0.263	-0.227	-0.815
1-Naphthol	-	-	0.305	0.188	-0.032	-0.035	-	-	-	-

tween A_{12p} and $A_{12\Delta}$ values does not exist. For some substances the difference between these values can be relatively high (e.g. for 8-hydroxyquinoline chromatographed by using the solution of chloroform in trichloroethylene or aniline chromatographed in benzene + chloroform mixture). These differences are probably due to the conditions in which the partition process occurs. It relates mainly to the values of the ratio of the surface area of the liquid-liquid interface to the volume of the phases and disturbances taking place during the partition process. These disturbances may be due to different interactions of the liquid, used for determination of the hypothetical partition coefficient. Moreover, they can be caused by the chromatographic process dynamics. Adsorption of the chromatographed substance on the liquid-liquid interface can play an important role [14,26,27]. All the factors, mentioned above, are reflected in the values of the partition coefficient, determined by using an indirect method, and in the differences between A_{12p} and $A_{12\Delta}$ values. A_{12} values listed in Table 4 confirm this suggestion. In the Table 4 $A_{12\Delta}$ values were obtained by fitting them to equation (1), while A_{12} values were calculated from equation (1) and $(\phi_1^S - \phi_1)$ values from experimentally determined excess adsorption isotherm, A_{12G} values were obtained from equation (5) and A_{12p} values were calculated from experimentally determined partition coefficients in the trichloroethylene-water and benzene-water systems. From the comparison of the parameters values, it can be observed that in the system containing benzene+trichloroethylene as the mobile phase and silica gel as the adsorbent, $A_{12\Delta}$, A_{12} and A_{12G} parameters slightly differ, while the differences between the values of the above parameters and A_{12p} parameter are significantly high.

TABLE 4

A_{12} values calculated by different way.

Solute	$A_{12\Delta}$	A_{12}	A_{12G}	A_{12p}
Quinoline	0.0356	0.0442	0.0338	0.0569
6-Methylquinoline	0.2300	0.2281	0.2650	0.0170
8-Methylquinoline	-0.1500	-0.1770	-0.1513	-0.2291
8-Hydroxyquinoline	-0.0762	-0.0254	-0.0752	-0.1523
8-Nitroquinoline	0.1400	0.1129	0.1347	0.6149
Acridine	-0.0950	-0.0182	-0.1097	0.1987
Aniline	0.7810	0.7747	0.7731	0.4914
1-Naphthol	0.1350	0.1290	0.1122	0.1673

The analysis of the data listed in Tables 3 and 4 indicates that $A_{12\Delta}$ has usually higher values than those of A_{12p} . In this connection, the question arises whether the differences between $A_{12\Delta}$ and A_{12p} values permit the use of the experimentally determined partition coefficients in the chromatographic systems optimization.

A comparison of R_M values of chromatographed substances calculated from equation (1) and A_{12p} values with the parallel experimental values shows a good agreement between them. $R_M = f(\phi_1)$ for 8-hydroxyquinoline and isoquinolines shown on Fig. 3 is an example of the agreement. Thus it can be assumed that hypothetical partition coefficients A_{12p} of the chromatographed substances, determined by indirect method, may be successfully used for calculating $\Delta R_{M1,2}^{i,j}$ values.

Figure 4 presents the relationships $\Delta R_{M1,2}^{i,j} = f(\phi_1)$ for substance mixtures 1-naphthol+8-methylquinoline and 1-naphthol+aniline calculated by equation (7) as well as the relationships $R_{M12} = f(\phi_1)$ for pure component of the mixtures. A comparison of the parallel relation-

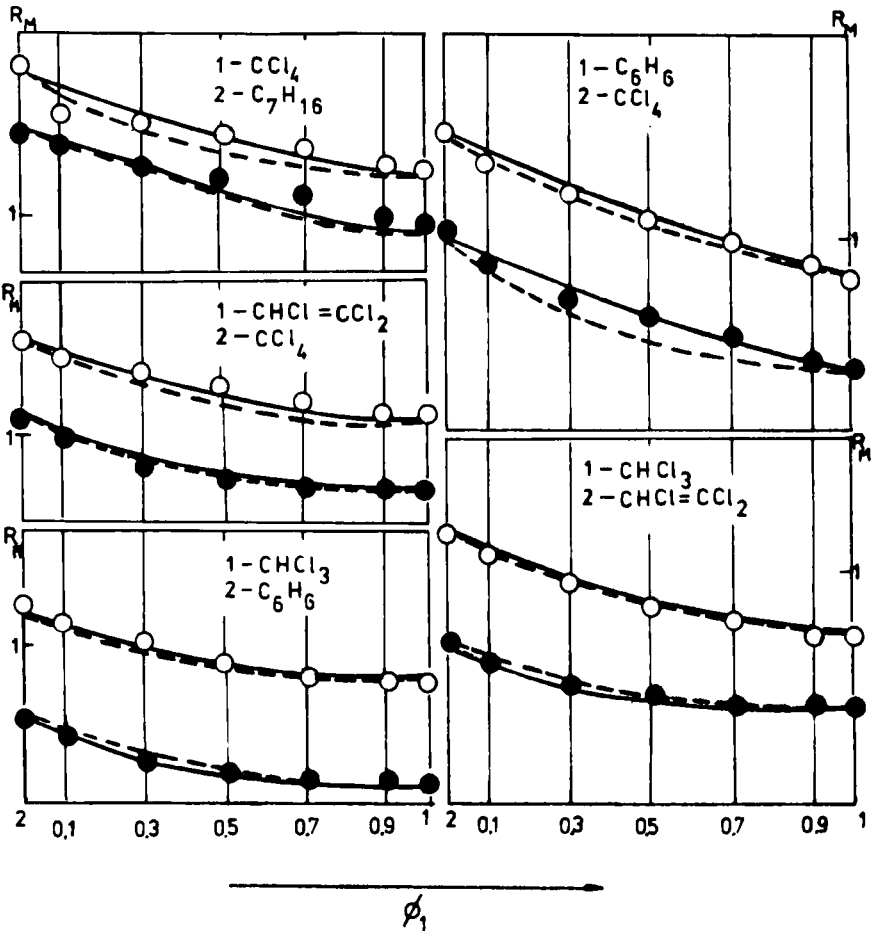


FIGURE 3

Experimental dots and calculated from equation (1) (from $A_{12\Delta}$ - solid lines and from A_{12p} --- dashed lines) relationships between the R_M values of isoquinoline - \circ and 8-hydroxyquinoline - \bullet and the volume fraction of the binary mobile phase on silica gel.

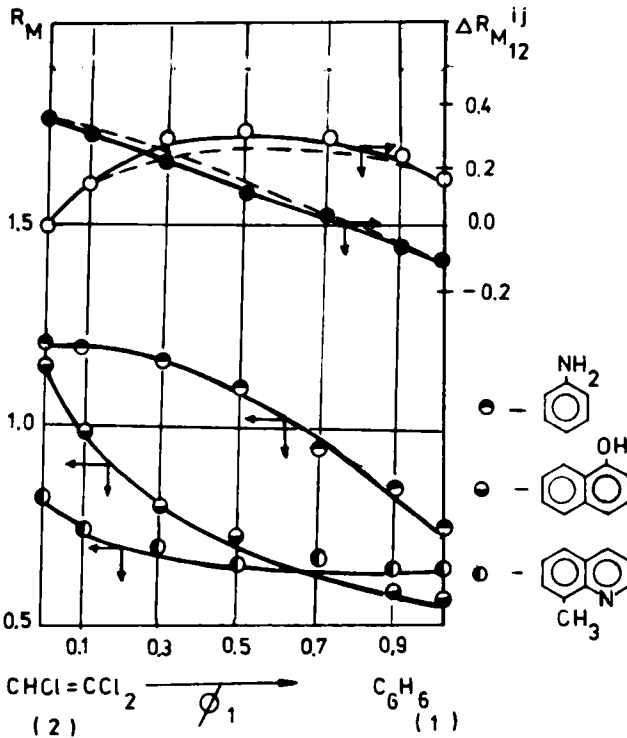


FIGURE 4

Experimental (points) and calculated from eq. (7) on the basis of $A_{12\Delta}$ (solid lines) and A_{12p} (dashed lines) relationships between $\Delta R_{M1,2}^{1,j}$ values and composition of mobile phase for 1-naphthol+aniline and 1-naphthol+8-methylquinoline mixtures and their $R_{M12} = f(\phi_1)$ relationships. Adsorbent: silica gel G.

ships show that maximum of $\Delta R_{M1,2}^{i,j} = f(\phi_1)$ points out to the optimum composition of the binary mobile phase giving the best separation of the mixture components. Maximum on the $\Delta R_{M1,2}^{i,j} = f(\phi_1)$ curve corresponds to optimal composition of a binary mobile phase with permits to obtain a best chromatographic separation of the components of the chromatographed mixture.

Apart from binary mobile phases, ternary mobile phases are also often used. An addition of the third component to a binary mobile phase permits improve sig-

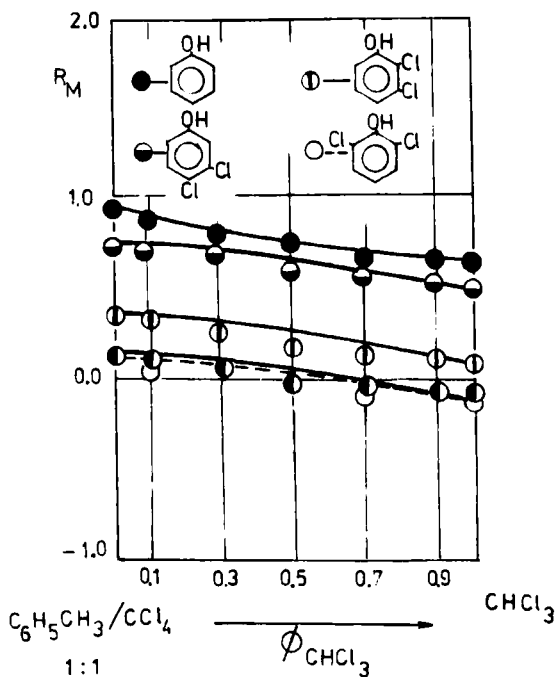


FIGURE 5

Relationship between the theoretical (eq. (8) (lines)) and experimental (circles) R_M values and the composition of the ternary mobile phase.

nificantly the separation of the mixture components. It has been stated, that Ošcik's equation can also be helpful in the optimization of the chromatographic systems containing such mobile phases [28] because it permits to predict the course of the dependence of R_M values of the substances separated from the mobile phase composition on the basis of the data obtained by using unary and binary mobile phases.

In case of a ternary mobile phase, equation (1) can be written as follows:

$$R_{Mt} = \phi_{1t} \Delta R_{M13} + \phi_{2t} \Delta R_{M23} + (\phi_{1t}^s - \phi_{1t}) (A_{13} + \Delta R_{M13}) + (\phi_{2t}^s - \phi_{2t}) (A_{23} + \Delta R_{M23}) + R_{M3} \quad (8)$$

where

R_{Mt} is the R_M value of the chromatographed substance when a ternary mobile phase is used;

$$\Delta R_{Mi3} = R_{Mi} - R_{M3} \quad \text{for } i = 1 \text{ or } 2$$

R_{Mi} for $i=1$ or 2 or 3 , is the R_M value of the substance when pure solvent i is used as the mobile phase;

ϕ_{it}^s and ϕ_{it} are the respective volume fractions of component i of the ternary mobile phase in the surface and bulk phase for $i=1$ or 2 ;

$A_{i3} = \log k_{i3}$ for $i=1$ or 2 k_{i3} is the value of the hypothetical partition coefficient of the chromatographed substance between pure solvent i and 3 ; the A_{i3} values can be calculated from the experimental data when the binary mobile phase $i+3$ is used.

The ϕ_{it}^s values can be calculated from the following equation [12]:

$$\phi_{it}^s = \frac{K_{i3} \phi_{i3}}{1 + K_{i3} \phi_{i3} + K_{23} \phi_{23}} \quad (9)$$

where

$$\left. \begin{aligned} K_{i3} &= 10^{-\Delta R_{M_{i3}}} \\ \phi_{i3} &= \phi_{it} \phi_{3t} \end{aligned} \right\} \text{ for } i=1 \text{ or } 2$$

Figure 5 presents the theoretical relationships calculated from equation (8) and experimental ones of R_M values of phenol, 2,3-dichlorophenol, 3,4-dichlorophenol and 2,6-dichlorophenol to the composition of the ternary mobile phase. A good agreement of both relationships shows that equation (8) may be useful in the optimization of this type of chromatographic systems.

In summing up the present results one can state that they fully confirm the usefulness of equations discussed in the paper to the optimization of adsorption chromatographic systems. It relates both to binary and ternary mobile phases.

REFERENCES

1. Getz M.E., Paper and Thin-Layer Chromatographic Analysis of Environmental Toxicants, Heiden, London 1980
2. De Spiegeler B.M.J., De Moerloose P.H.M., Slegers G.A., Anal. Chem., 59, 62 (1987)
3. Różyło J.K., Malinowska I., Ponieważ M., Fresenius Z. Anal. Chem., 307 (1984)
4. Veksler M.A., Rodionova R.A., Michenkova O.A., Arzamascev A.P., Zh. Anal. Khim., 41 6, 987 (1986)
5. Ościk-Mendyk B., Różyło J.K., J. Liquid Chromatogr., 10 7, 1399 (1987)
6. Perry J.A., J. Chromatogr., 165, 117 (1979)
7. Snyder L.R., Principles of Adsorption Chromatography, M.Dekker, New York 1968
8. Soczewiński E., Anal Chem., 41, 179 (1969)

9. Ościk J., *Roczn. Chem.*, 34, 745 (1960)
10. Ościk J., Różyło J.K., *Chromatographia*, 4 516 (1971)
11. Różyło J.K., Ościk-Mendyk B., Ościk J., *Annales Universitatis M.Curie-Skłodowska*, p. 24-44, 1984/85
12. Everett D.H., *Trans. Faraday Soc.*, 1 69, 1803 (1964)
13. Różyło J.K., Gross J., Chojnacka G., Malinowska I., *J. Liquid Chromatogr.*, 3 6, 921 (1980)
14. Chojnacka G., Ościk J., Różyło J.K., *Chromatographia*, 13, 109 (1980)
15. Ościk J., Jaroniec M., Malinowska I., *J. Liquid Chromatogr.*, 6, 81 (1983)
16. Różyło J.K., Ościk-Mendyk B., *Chromatographia*, 19, 371 (1984)
17. Ościk J., Chojnacka G., Zamojska E., in "Problems of Chromatography and Other Separation Methods", p. 67-74 (in Polish)
18. Różyło J.K., Chojnacka G., Kołodziejczyk H., *J. of HRC and CC*, 5, 139 (1982)
19. Hildebrand J.H., Scott R.L., *The Solubility of Nonelectrolytes*, Dover, New York 1964
20. Karger B.L., Snyder L.R., Eon C., *J. Chromatogr.*, 125, 71 (1975)
21. Keller R.A., Snyder L.R., *J. Chromatogr. Sci.*, 9, 346 (1971)
22. Ościk-Mendyk B., Różyło J.K., *Chromatographia*, in press
23. Kusak R., private information
24. Różyło J.K., Chojnacka G., Malinowska I., *Chromatographia*, 13, 218 (1980)
25. Chojnacka G., Różyło J.K., Malinowska I., *J. of HRC and CC*, 4, 224 (1981)
26. Ościk J., Chojnacka G., *Chromatographia*, 7, 708 (1974)
27. Ościk J., Chojnacka G., *Chromatographia*, 6, 133 (1973)
28. Ościk J., Różyło J.K., Gross J., Malinowska I., Chojnacka G., *Chromatographia*, 15, 25 (1982)