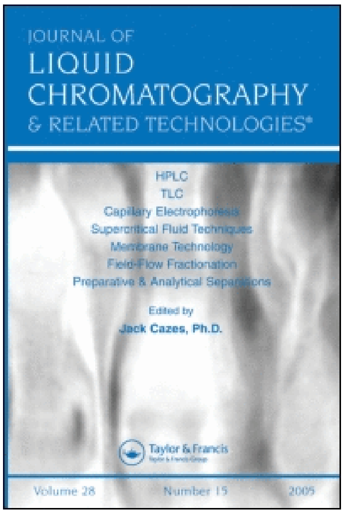

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J. K. Rózyło[a]; H. Kołodziejczyk[a]; J. A. Jaroniec[a]; M. Jaroniec[a]
[a] Institute of Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

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CHARACTERIZATION OF CHROMATOGRAPHIC SYSTEMS WITH TERNARY MOBILE PHASE

J.K.Różyło, H.Kołodziejczyk,
J.A.Jaroniec and M.Jaroniec
Institute of Chemistry,
Maria Curie-Skłodowska University,
20031 Lublin , Poland

ABSTRACT

A new equation for description of the R_M values obtained by adsorption TLC with ternary mobile phase is examined for naphthalene isomers in tetrachloride carbon-chloroform-methanol and tetrachloride carbon-chloroform-acetone solvents mixtures on silica gel at 24°C. This equation creates a possibility to calculate the R_M values for a given substance in ternary solvent mixture by means of the R_M values for this substance in the single solvents and so-called heterogeneity parameter m .

INTRODUCTION

Theoretical and experimental studies of the chromatographic systems with ternary mobile phase are difficult and timeconsuming. Only Ościk's thermodynamic approach to liquid adsorption chromatography creates a possibility to characterize the chromatographic systems with multicomponent mobile phases (1). This approach was examined for ternary mobile phases in the paper (2). In (3) it was compared with the Snyder's treatment of adsorption LC . In result of this comparison the Snyder's approach has been generalized to adsorption LC with multicomponent mobile phases.

In this paper we shall investigate the possibility of application of the Snyder's generalized equation to characterize the chromatographic systems with ternary mobile phases.

THEORETICAL

Following the paper (3) we can write the Snyder's generalized equation in the following form :

$$R_{M(n)} = - \log \left(\sum_{i=1}^{n} x_i \, 10^{-R_{M,i}} \right) \qquad (1)$$

where x_i is the mole fraction of the i-th component in the bulk phase, $R_{M(n)}$ is the R_M value for a given substance in n-component mobile phase, and $R_{M,i}$ is the R_M value for this substance in the i-th pure solvent.In(4) equation 1 has been modified to adsorption LC on energetically heterogeneous adsorbents.The modified form of equation 1 is following :

$$R_{M(n)} = - \frac{1}{m} \log \left(\sum_{i=1}^{n} x_i^{\,m} \, 10^{-m R_{M,i}} \right) \qquad (2)$$

where m is the heterogeneity parameter which characterizes the energetic heterogeneity of the adsorbent surface with regard to adsorbing molecules.The parameter m is assumed to be characteristic for a given mobile phase, adsorbent and chromatographed substance.

Let us consider a ternary mobile phase.Then equation 2 may be rewritten in a slightly different form :

$$10^{-m\,R_{M(3)}} = \sum_{i=1}^{3} x_i^{\,m}\, 10^{-m\,R_{M,i}} \qquad (3)$$

The TLC data for three-component solvent mixtures are frequently measured at constant value of x_1/x_2 . Then equation 3 may be transformed to the linear form :

$$(x_1\, 10^{R_{M(3)}})^{-m} = a\,(x_3/x_1)^m + b \qquad (4)$$

where

$$a = 10^{-m\,R_{M,3}} \qquad (5)$$

and

$$b = 10^{-m\,R_{M,1}} + (x_2/x_1)^m\, 10^{-m\,R_{M,2}} \qquad (6)$$

Equation 4 may be used to determine the parameters m , a and b from TLC data measured for ternary mobile phases.

EXPERIMENTAL

The TLC measurements were made under thermostatic conditions at 24°C. Silica gel (type 60) ,obtained from

E.Merck, Darmstadt,G.F.R., was the adsorbent,whereas , tetrachloride carbon (1) - chloroform (2) - methanol (3), and tetrachloride carbon (2)-chloroform (2)-acetone (3) liquid mixtures were used as the mobile phases.The above compounds (puriss.grade) were obtained from Polskie Odczynniki Chemiczne, Gliwice, Poland.

In all measurements the ratio x_1/x_2 was equal to unity ; the subscripts "1" and "2" refer to the numbers written at the names of components of the mobile phases used. The naphthalene isomers,prepared in Department of Organic Chemistry at M.Curie-Skłodowska University (Lublin , Poland)(5) ; they are : 1,4- and 1,5-di(mercaptomethyl)-naphthalene, 1,4- and 1,5-di(acetylmethyl)naphthalenes and 1,4- and 1,5-di(hydroxymethyl)naphthalenes.For these substances we shall use the following codes : DMN for di(mercaptomethyl)naphthalenes, DAN for di(acetylmethyl)-naphthalenes and DHN for di(hydroxymethyl)naphthalenes. At the isomers 1,4- and 1,5- we shall write the numbers 4 and 5 ,respectively ; for example : DMN4 , DMN5, etc.

RESULTS AND DISCUSSION

The experimental data $R_{M(3)}$ measured at $x_1/x_2 = 1$ for different values of x_3 were approximated by means of equation 3 . This equation contains one best-fit parameter ,i.e., the parameter m .The parameters $R_{M,1}$, $R_{M,2}$ and $R_{M,3}$ are R_M values for a given substance measured in pure solvents "1" , "2" and "3" ,respectively.

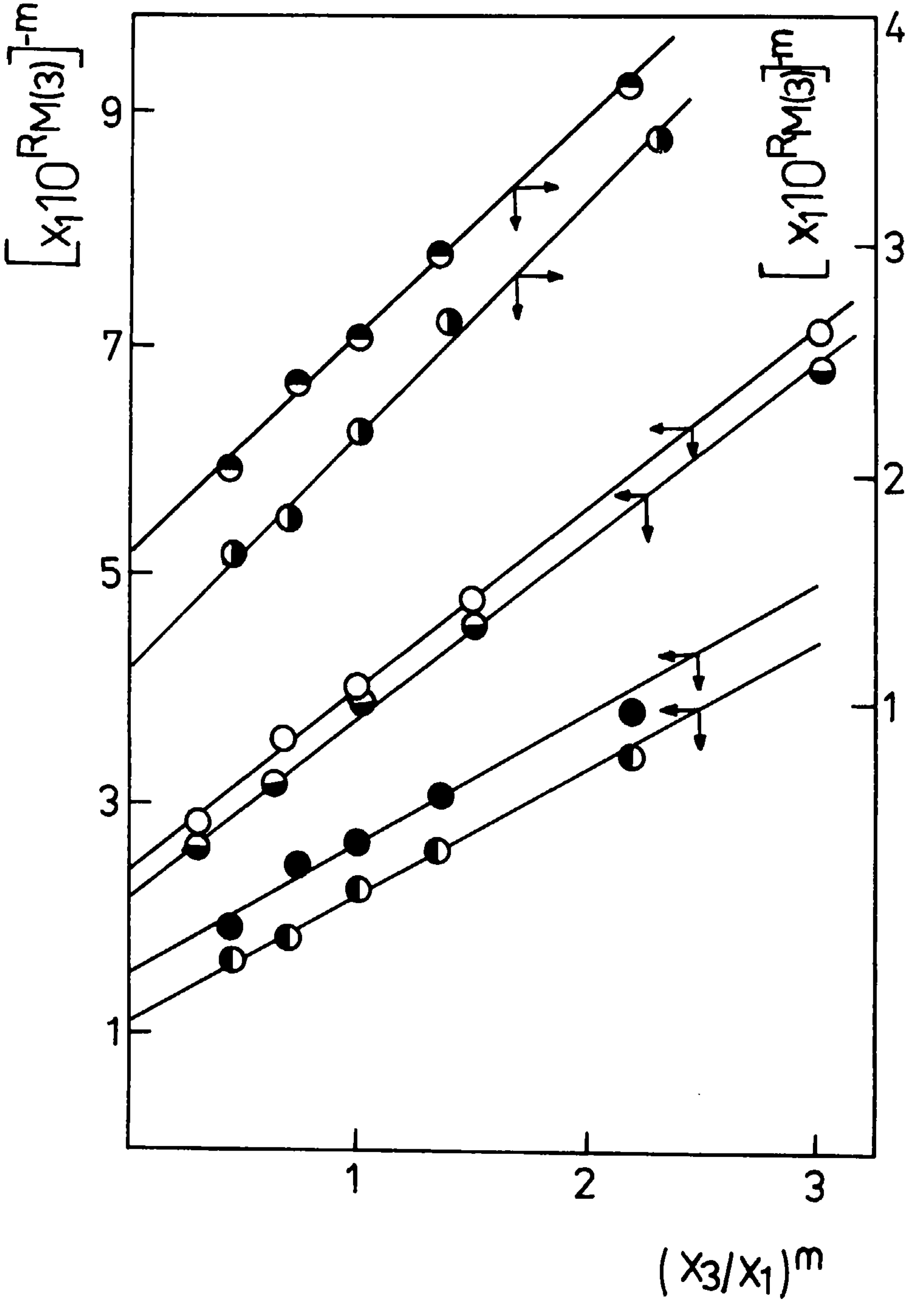
In Table 1 the parameters $R_{M,1}$, $R_{M,2}$, $R_{M,3}$, m and the standard deviations (SD) are summarized.

Using the parameter m from Table 1 the experimental TLC data were plotted in the system of coordinates $(x_1 \cdot 10^{R_{M(n)}})^{-m}$ vs. $(x_3/x_1)^m$ according to equation 4 . Figures 1 and 2 show the linear dependences for all sub-

Table 1

CHROMATOGRAPHIC PARAMETERS EVALUATED ACCORDING TO EQ. 3

Solute	$R_{M,1}$	$R_{M,2}$	$R_{M,3}$	m	$SD \cdot 10^2$
tetrachloride carbon(1)-chloroform(2)-methanol(3)					
DMN4	0.29	-0.35	-0.50	0.50	7.52
DMN5	0.32	-0.37	-0.39	0.50	6.71
DAN4	1.06	0.14	-0.37	0.36	13.14
DAN5	0.95	0.09	-0.35	0.36	10.23
DHN4	1.06	0.75	-0.31	0.38	8.91
DHN5	1.12	0.67	-0.35	0.36	9.49
tetrachloride carbon(1)-chloroform(2)-acetone(3)					
DMN4	0.29	-0.35	-0.60	1.26	7.18
DMN5	0.32	-0.37	-0.45	1.24	5.92
DAN4	1.06	0.14	-0.47	0.66	8.18
DAN5	0.95	0.09	-0.31	0.66	9.09
DHN4	1.06	0.75	-0.33	1.18	3.99
DHN5	1.12	0.67	-0.30	0.88	2.89


$[x_1 10^{R_{M(3)}}]^{-m}$
9
7
5
3
1
$[x_1 10^{R_{M(3)}}]^{m}$
4
3
2
1
1
2
3
$(x_3/x_1)^m$

stances investigated plotted according to equation 4 .The parameters a and b of these straight lines are given in Table 2 .These parameters may be also evaluated according to equations 5 and 6 by using the $R_{M,i}$ values from Table 1 ; in such way we calculate a^o and b^o .In Table 2 the parameters a and b are compared to that a^o and b^o. It follows from Figures 1 and 2 that equation 4 well approximates the experimental TLC data.Also the agreement of the numerical values of a and a^o , b and b^o is satisfactory (see Table 2).It means that the $R_{M(3)}$ values may be predicted by means of the $R_{M,i}$ values for i=1,2,3 and the parameter m which in the first approximation is characteristic for a given adsorbent and mobile phase.Evidently,the type of functional group in naphthalene isomers has also influence on the value of m (see Table 1).

The mobile phases used differ the third component, which is the more efficient eluting solvent.It follows from Table 1 that the kind of the more efficient eluting component has greatest influence on the value of m ;

Figure 1

Linear dependences plotted according to equation 4 for DMN4 (○),DMN5 (◒),DAN4 (◓), DAN5(●), DHN4(◑) and DHN5 (◐) substances in tetrachloride carbon(1)-chloroform(2)-methanol(3) on silica gel at 24°C .

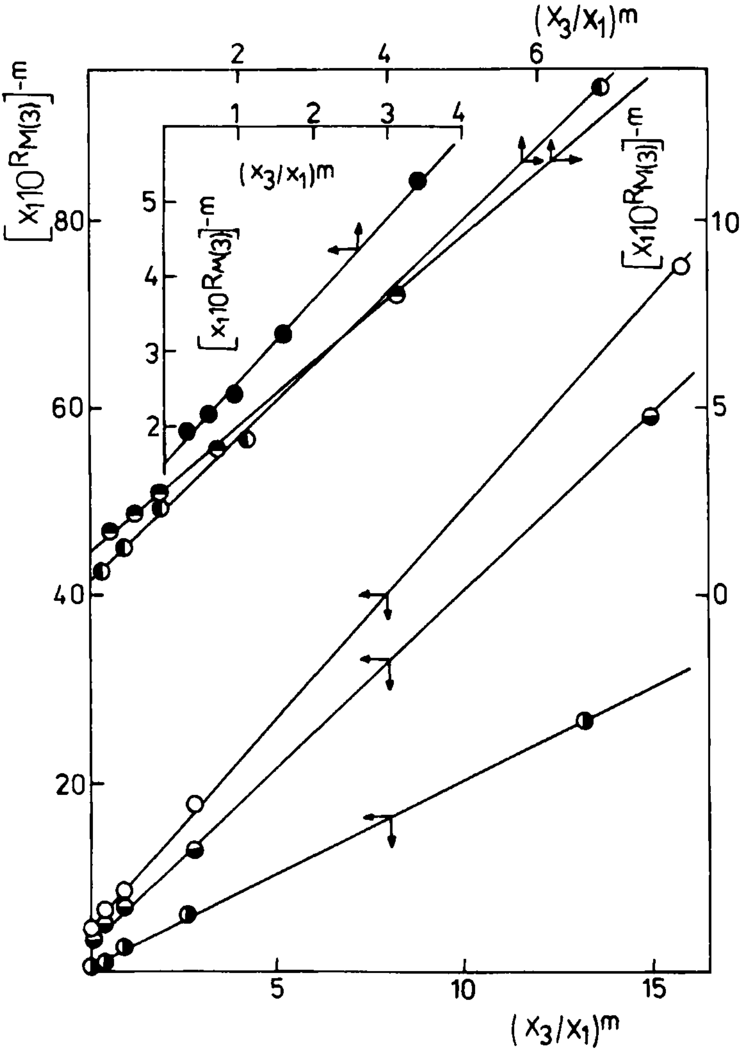


Figure 2

Linear dependences plotted according to equation 4 for naphthalene isomers in tetrachloride carbon(1)-chloroform(2)-acetone(3) on silica gel at 24°C .The labelling is as in Figure 1.

Table 2

PARAMETERS OF THE STRAIGHT LINES PRESENTED IN FIGS. 1 - 2

Solute	a	b	a^o	b^o
tetrachloride carbon(1)-chloroform(2)-methanol(3)				
DMN4	1.65	2.40	1.79	2.21
DMN5	1.65	2.20	1.57	2.22
DAN4	0.98	1.65	1.36	1.30
DAN5	1.22	1.50	1.37	1.38
DHN4	1.05	1.15	1.31	0.91
DHN5	1.22	1.05	1.37	0.97
tetrachloride carbon(1)-chloroform(2)-acetone(3)				
DMN4	4.48	4.40	5.70	3.17
DMN5	3.60	3.05	3.61	3.26
DAN4	1.95	1.11	2.04	1.01
DAN5	1.22	1.39	1.49	1.19
DHN4	2.10	0.35	2.45	0.19
DHN5	1.90	0.40	1.84	0.36

for mobile phase with methanol the average value of m is equal to 0.41 ,whereas,for mobile phase with acetone the average value of m is equal to 0.87 .The theoretical considerations show that m=1 relates to a homogeneous adsorbent surface,whereas, an decrease of m from unity to zero is connected with increasing the energetic heterogeneity of the adsorbent surface with regard to a given liquid mixture.The comparison of the parameter m for both solvent mixtures shows that the behaviour of these mixtures on the surface is different. The adsorbent surface shows a more energetic heterogeneity with regard to the solvent mixture with methanol than to that with acetone.Since the interactions of methanol molecules with the adsorbent surface are strong ,the influence of the substance chromatographed on m values is rather small.This influence is greater for the mobile phase with acetone.

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