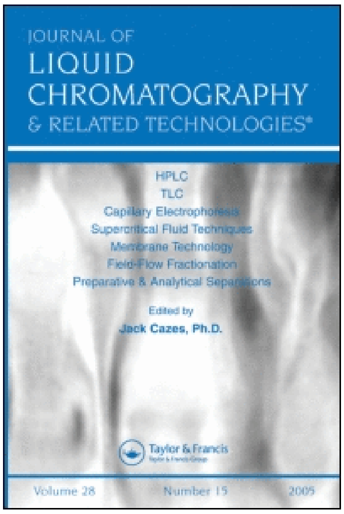

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Ościk, J. , Jaroniec, M. and Malinowska, I.(1983) 'Thermodynamic Approach to TLC with Mixed mobile Phase. Determination of Parameters Characterizing TLC Systems', Journal of Liquid Chromatography & Related Technologies, 6: 1, 81 — 93

To link to this Article: DOI: 10.1080/01483918308066872

URL: http://dx.doi.org/10.1080/01483918308066872

JOURNAL OF LIQUID CHROMATOGRAPHY, 6(2), 81-93 (1983)

THERMODYNAMIC APPROACH TO TLC WITH MIXED MOBILE PHASE. DETERMINATION OF PARAMETERS CHARACTERIZING TLC SYSTEMS

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ABSTRACT

An equation, derived in terms of the thermodynamic formulation of TLC with mixed mobile phase, has been discussed.The parameters of this equation,describing solute-solvent interactions in the mobile phase and phase-exchange equilibrium between molecules of both solvents,are determined by using its linear forms.These linear relationships have been examined by applying the TLC data for eight different binary mobile phases.

INTRODUCTION

In 1965 (1) one of the authors of this paper proposed the thermodynamic description of TLC with mixed mobile phase.This treatment has been developed theoretically (2-6) and widely examined by using the TLC data (7-10).The first theoretical considerations (1) were presented for multicomponent eluents and energetically homogeneous solid surfaces.Although,the fundamental equation resulting from this treatment has been derived for non-ideal phases, only its simplified version refering to ideal mobile and

0148-3919/83/0601-0081$3.50/0

surface phases was used for analysing the experimental TLC data. The extensions of the theoretical treatment (1) have been made for regular eluents (3) and energetically heterogeneous adsorbents (5,6).

The fundamental equation derived by Ościk (1) for TLC with binary mobile phases and energetically homogeneous adsorbents may be presented in the following form (4-6) :

$$R_M = R_{M1}x_1^s + R_{M2}x_2^s + A(x_1^s - x_1^l) \qquad (1)$$

where

$$x_1^s + x_2^s = 1 \quad ; \quad x_1^l + x_2^l = 1 \qquad (2)$$

and R_M , R_{M1} and R_{M2} are the R_M-values of a given solute chromatographed in mobile phases "1+2" , "1" and "2" ,respectively; x_i^s and x_i^l for i=1,2 are the mole fractions of the i-th solvent in the surface and mobile phases,respectively; A is a constant characterizing solute-solvent interactions in the mobile phase (2). Equation 1 contains the mole fraction x_1^s ,which may be evaluated from the excess adsorption data or may be calculated by using a theoretical equation (5,6).

In this paper we shall discuss the problems connected with evaluation of the parameters appearing in equation 1 .Moreover,we shall propose two linear forms of equation 1 ,which are very convenient for determining these parameters.The above linear forms will be examined by using the experimental TLC data.

THEORETICAL

Firstly, we consider the determination of the adsorption parameters from TLC data and the excess adsorption isotherm. Then, the mole fraction x_1^s may be evaluated by means of the well-known relationship (6) :

$$x_1^s = n_1^e/n^s + x_1^l \tag{3}$$

where n_1^e is the adsorption excess of 1-st solvent and n^s is the total number of moles of the adsorbed components in the surface phase.

Equations 1 and 3 give :

$$R_M = D\,x_1^l + R_{M2} + (C/n^s)n_1^e \tag{4}$$

where

$$D = R_{M1} - R_{M2} \tag{5}$$

and

$$C = A + D \tag{6}$$

The constant D is the difference of the R_M-values of a given solute chromatographed in 1-st and 2-nd solvents, and it is known from experiment. Thus, equation 4 may be transformed to the following linear form :

$$R_M - D\,x_1^l = R_{M2} + (C/n^s)n_1^e \tag{7}$$

The constant C/n^s may be calculated from the slope of the linear dependence $(R_M - D\,x_1^l)$ vs. n_1^e. Since the value of n^s may be evaluated from the excess adsorption isotherm n_1^e vs. x_1^l (11), the relationship 7 leads for evaluating the constant C .However,the constant A may be calculated by means of equation 6 .Concluding these considerations, we can draw that equation 4,correlating the chromatographic and adsorption data,makes possible the determination of the parameters A and n^s .

The parameter A may be determined directly from the chromatographic data.For this purpose the mole fraction x_1^s is evaluated by means of the following equation:

$$x_1^s = K_{12}x_1^l/(x_2^l + K_{12}x_1^l) \qquad (8)$$

where K_{12} is the equilibrium constant defining the phase-exchange reaction between molecules of 1-st and 2-nd solvents.Equation 8 is the well-known relationship (4) defining the mole fraction x_1^s for the adsorption model involving ideality of both phases, energetic homogeneity of the adsorbent surface and equality of molecular sizes of both solvents.

The constant K_{12} may be approximated by :

$$K_{12} = 10^{-\bar{D}} \qquad (9)$$

where $\bar{D}$ is the arithmetical average of the D-values for different chromatographed substances.Applying the approximate equation 9 for calculating K_{12} ,equation 1 contains only one unknown parameter; it is A .This parameter may be easily calculated from TLC data (7-10). This method for calculating the parameters K_{12} and A from TLC data was used up-to-date (7-10).

In this paper, two linear forms of equations 1 and 8 are proposed for determining the parameters K_{12} and A . Combining equations 1 and 8 we have :

$$G(x_1^l) = \frac{x_1^l\,(1 - x_1^l)}{R_M - Dx_1^l - R_{M2}} = [C(K_{12}-1)]^{-1} + C^{-1}\,x_1^l \qquad (10)$$

$$G'(x_1^l/x_2^l) = \frac{x_1^l}{R_M - Dx_1^l - R_{M2}} = \frac{1}{C(K_{12}-1)} + \frac{K_{12}}{C(K_{12}-1)} \cdot \frac{x_1^l}{x_2^l} \qquad (11)$$

Equations 10 and 11 make possible the calculation of K_{12} and A directly from the experimental dependence R_M vs. x_1^l .In the next section of this paper we shall examine these equations by using TLC data.

RESULTS AND DISCUSSION

For the purpose of examination of equations 10 and 11 the TLC data for the selected chromatographic systems were taken from the literature (8-11).These data were measured for different substances chromatographed in eight different binary eluents on silica gel and aluminium oxide at 297 K.The other details concerning the TLC measurements are given in the references (8-11).

The TLC data for some methyl derivatives of naphthalene and polycyclic hydrocarbons chromatographed in dichloroethylene/carbon tetrachloride and dichloroethylene/n-heptane on silica gel were analysed by means of equations 10 and 11.The numerical values of the parameters K_{12} and

TABLE I

The parameters K_{12} and A for solutes chromatographed in binary eluents on silica gel at 297 K.

Substance	Equation 10		Equation 11	
	K_{12}	A	K_{12}	A
Mobile phase : dichloroethylene/carbon tetrachloride				
pyrene	3.70	-0.17	3.81	-0.16
3,4-benzopyrene	3.62	-0.23	5.61	-0.12
naphthalene	3.99	-0.11	3.33	-0.16
2,3-dimethylnaphthalene	3.91	-0.28	3.87	-0.29
2,3,5-trimethylnaphthalene	3.46	-0.44	2.50	-0.65
Mobile phase : dichloroethylene/n-heptane				
pyrene	1.95	-1.16	1.18	-1.69
anthracene	1.68	-0.60	1.49	-0.93
naphthalene	1.84	-1.33	1.56	-1.98
1-methylnaphthalene	1.63	-1.66	2.00	-1.06
2-methylnaphthalene	1.96	-0.85	1.57	-1.50

A are summarized in Table I.It follows from this table that both linear forms obtained from equations 1 and 8 predict similar values of the adsorption parameters .In Figure 1 the linear dependences 10 and 11 are presented for naphthalene chromatographed in dichloroethylene/carbon tetrachloride on silica gel.The experimental points plotted according

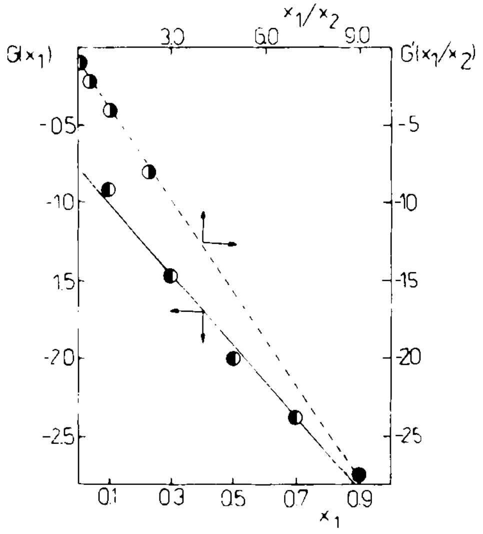

FIGURE 1 . Linear dependences 10 (the solid line) and 11 (the dashed line) for naphthalene chromatographed in dichloroethylene/carbon tetrachloride on silca gel at 297K.

to the dependence 10 are distributed proportionately on the straight line $G(x_1^1)$ vs. x_1^1 ,whereas,in the case of the dependence 11 these points are compressed at lower concentrations of x_1^1. This distribution of the experimental points on the straight lines 10 and 11 may be useful to select the suitable method for determining the parameters K_{12} and A .For instance : if we have TLC data ,in which the R_M -values for high concentrations of x_1^1 were measured with a small preciseness, the method utilizing the relationship 10 seems to be better for their interpretation than the method basing on equation 11 .

TABLE II

The parameters K_{12} and A calculated according to equation 10 for solutes chromatographed in binary eluents.

Substance	Eluent and Adsorbent	K_{12}	A
quinoline	benzene/cyclohexane	12.00	0.82
6-methylquinoline	on aluminium oxide	12.37	0.95
2,6-dimethylquinoline	at 293 K	12.00	0.83
isoquinoline		11.97	0.44
acridine		12.66	0.81
5,6-benzoquinoline		12.67	0.49
naphthalene	benzene/n-heptane	13.63	0.31
diphenyl	on silica gel at	11.98	0.38
chrysene	297 K	13.14	0.48
anthracene		12.08	0.42
acenaphthene		11.55	0.26
pyrene		12.40	0.44
diphenyl	trichloroethylene/	13.78	0.51
naphthalene	n-heptane on silica	13.61	0.36
chrysene	gel at 297 K	14.04	0.62
anthracene		13.78	0.42
pyrene		14.49	0.53
acenaphthene		14.11	0.36

In Table II the parameters K_{12} and A ,evaluated according to equation 10 , are summarized for some quinoline derivatives chromatographed in benzene/cyclohexane on aluminium oxide and for polycyclic hydrocarbons in benzene/n-heptane and trichloroethylene/n-heptane on silica gel.For these chromatographic data equation 10 gives better results than the relationship 11 .Figure 2 shows the linear relationship 11 for some substances chromatographed in benzene/cyclohexane on aluminium oxide.It follows from this figure that equation 10 gives good representation of the data measured for the systems from Table II.

The equilibrium constants K_{12} ,given in Table II, are greater than those summarized in Table I.It means that differences of the elution strengths,characterizing the binary eluents from Table II,are greater than those for the eluents from Table I .Although,the constant K_{12} is evaluated

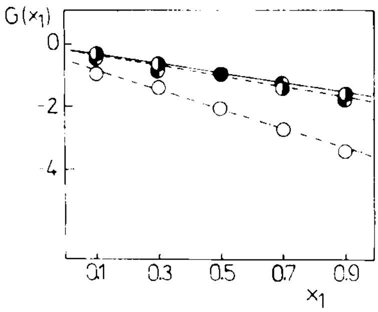

FIGURE 2. The linear dependence 10 plotted for isoquinoline (◑),acridine (◐) and 5,6-benzoquinoline (○) chromatographed in benzene/cyclohexane on aluminium oxide at 293 K.

from the TLC data measured for a given solute, its dependence on the kind of solute is rather small. This result is physically correct, because according to the theory the constant K_{12} characterizes the phase-exchange reaction between molecules of both solvents. Therefore, it is characteristic for a given binary eluent. However, the constant A characterizes interactions of a given solute with solvents in the mobile phase, and it depends on the nature of solute and solvents.

TABLE III

The parameters K_{12} and A calculated according to equation 11 for solutes in binary eluents on silica gel at 297 K.

Substance	Eluent	K_{12}	A
phenol	chloroform/carbon	1.35	-0.57
2,4-dichlorophenol	tetrachloride	1.65	-0.60
2,6-dichlorophenol		1.64	-0.52
3,4-dichlorophenol		1.22	-0.53
pyrene	chloroform/n-heptane	2.68	-0.61
anthracene		2.16	-0.42
chrysene		2.36	-0.96
3,4-dichlorophenol		2.15	-1.43
naphthalene	trichloroethylene/	2.10	-0.06
2,3-dimethylnaphthalene	carbon tetrachlo-	2.70	-0.36
2,4-dichlorophenol	ride	2.63	-0.22
2,6-dichlorophenol		2.06	-0.16

In Table III the parameters K_{12} and A ,evaluated according to equation 11, are summarized for solutes chromatographed in chloroform/carbon tetrachloride, chloroform/n-heptane and trichloroethylene/carbon tetrachloride on silica gel at 297 K.

For systems summarized in Table III equation 11 gives slightly better results than equation 10. The values of K_{12} for chloroform/carbon tetrachloride, chloroform/n-heptane and trichloroethylene/carbon tetrachloride on silica gel are analogous to those characterizing dichloroethylene/carbon tetrachloride and dichloroethylene/n-heptane on this same adsorbent (c.f.,Tables I and III).

In Table IV the average values of K_{12} are compared for the systems summarized in Tables I-III.The first column of this table contains the average values of K_{12} calculated according to equation 9 .The second and third columns of this table contain the $\bar{K}_{12}$ -values obtained by averaging the K_{12}-values for different solutes chromatographed in a given eluent/adsorbent system.It follows from Table IV that the differences in the values of $\bar{K}_{12}$,predicted by equations 9 and 10 or 11 ,are greatest for binary eluents containing a solvent of very small elution strength,for instance : n-heptane.Then,the measurements of R_M-values in the pure eluent with a greater preciseness is very difficult. Application of inaccurate R_M-values ,measured for different solutes in a pure solvent, in equation 9 predicts an inaccurate value of $\bar{K}_{12}$ .Therefore,this $\bar{K}_{12}$-value differs from those evaluated by means of equations 10 and 11 .

TABLE IV

The average values $\bar{K}_{12}$ evaluated according to equations 9 , 10 and 11 for the chromatographic systems studied.

System	$\bar{K}_{12}$ (eqn 9)	$\bar{K}_{12}$(eqn 10 and eqn 11)	
dichloroethylene/ CCl_4	2.48	3.74	3.82
dichloroethylene/n-heptane	4.33	1.81	1.56
benzene/cyclohexane	12.60	12.28	-
benzene/n-heptane	6.74	12.46	-
trichloroethylene/n-heptane	5.24	13.97	-
chloroform/CCl_4	1.98	-	1.47
chloroform/n-heptane	5.17	-	2.34
trichloroethylene/CCl_4	1.86	-	2.37

Concluding,we can draw that equations 10 and 11 seem to be more suitable for evaluating the $\bar{K}_{12}$ -value than equation 9, because they utilize the R_M-values measured at different compositions of the binary eluent.

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