The Correlations between Capacity Factors k' and R_M Values in Liquid Column and Thin-Layer Chromatography

Jan K. Rożyło[a]; Joanna Gross[a]; Małgorzata Ponieważ[a]; Roman Lodkowski[a]; Bogusław Buszewski[a]

[a] Institute of Chemistry, Maria Curie-Skłodowska University, Lublin, POLAND

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THE CORRELATIONS BETWEEN CAPACITY FACTORS k´

AND R_M VALUES IN LIQUID COLUMN AND

THIN - LAYER CHROMATOGRAPHY

Jan K.RÓŻYŁO, Joanna GROSS, Małgorzata PONIEWAŻ,
Roman LODKOWSKI and Bogusław BUSZEWSKI

Institute of Chemistry, Maria Curie-Skłodowska
University, Pl.M.Curie-Skłodowskiej 3,
20-031 Lublin, POLAND

ABSTRACT

The purpose of this studie being carried out is to
define some regularities between Thin-layer and Liquid
Column Chromatography; i.e. between experimental obtained
and theotetical calculated R_M-values and experimental
obtained logk´-values for some non-active organic substances
in mixed binary solvents systems. It was studied the kind
these correlations change with changing mobile phase
compositions. The present paper is a certain aspect of new
studies on possibilities of the use Thin-layer Chromato-
graphy as a pilot technique for Liquid Column Chromato-
graphy (1,2). In a study on the optimization of chromato-
graphic process it is necessary to define the correlations
between R_M-values which characterize the retention in TLC
and k´-values which characterize the retention in in LCC.

In the paper the changes of these correlations with
the changes of mobile phase compositions are studied.
The conformity between theoretical calculated and experimental
obtained R_M-values of chromatographed substances for
differemt mobile phase compositions are investigated. A good

agreement between theoretical and experimental data makes
possible to foresee on the basis of the correlations between
logk'- and R_M-values the retention in column chromatography.

INTRODUCTION

Considering the wide application of chromatography it is
necessary to find relations between the parameters obtain by
different chromatographic techniques. Advantages of Thin-
layer Chromatography cause that it can be used as a pilot
technique for Liquid Column Chromatography.

The possibility of theoretical calculations of R_M-values
makes possible to use these data in HPLC conditions. In this
purpose it is necessary to define the correlations between
R_M and logk'-values of chromatographed substances for
a given mobile phase system. From the study it appears
that the simple theoretical dependence R_M=logk' is not
exactly conformable to experimental data. It is caused by
different conditions of the chromatographic process on
a plate and in a chromatographic column; i.e. a presence
of a gas phase in a chamber, a different stationary phase
profil on a plate and in a column, a different mobile phase
flow-rate, etc. (3,4) .

In the paper the graphical correlations between R_M and
logk'-values for some substances in three different mobile
phase systems have been shown. The changes of these
correlations with the changes of a mobile phase type and
its composition are studied.

EXPERIMENTAL

Experimental R_M-values of investigated substances were
determined by ascending adsorption thin-layer chromatography.

Silica gel 60 (Merck) was used as an adsorbent. The layer
tickness was 0.25 mm. Plates were activated for 2h at 135°C.
Chromatograms were developed in thermostatic conditions
at 21 $\pm$ 0.5 $^{\circ}$C in saturated chambers.

As the mobile phases were used pure isooctane, hexane,
cyclohexane and chloroform, and their binary mixtures
of compositions φ_1 : 0.1 ; 0.3 ; 0.5 ; 0.7 ; 0.9 (φ_1 was
a volume fraction of a stronger mobile phase component).
As a chromatographed substances were used naphtalene and its
methyl derivatives and polycyclic aromatic hydrocarbons.
These substances were visualized on chromatograms in iodine
pairs or in UV light.

For LCC experiments was used Pay Unicam LC 20 Liquid
Chromatograph. Merck Lichrosorb Si 60 of 0.5 μm particle
diameter was used as an adsorbent. The same as in TLC
studies substances and binary mixtures were used.

RESULTS AND DISCUSSION

Experimental R_M-values of chromatographed substances
were obtained from TLC studies. Ościk's thermodynamic theory
of adsorption from multicomponent systems was used as the basis
of our investigations (5-7). The equation resulting from it
makes us possible to calculate theoretical R_M-values for
studied substances :

$$R_{M1,2} = \varphi_1 \Delta R_{M1,2} + \left(\varphi_1^s - \varphi_1\right)\left(\Delta R_{M1,2} + A_z\right) + R_{M2} + Y \qquad (1)$$

where $R_{M1,2}$, R_{M1}, R_{M2} are R_M-values of a given solute
in a mixed mobile phase "1+2" and in pure solvents "1" and
"2" respectively; $\Delta R_{M1,2} = R_{M1} - R_{M2}$ is the difference

of the R_M-values of a solute in pure solvents "1" and "2";
φ_1 is a volume fraction of a stronger "1" component
of a mobile phase; the value A_z represents molecular inter-
actions between molecules of the chromatographed substance
and these of the components of a solvent ; Y represents
the influence of the kind of the chromatographed substance
and components of a binary mobile phase on the parameters
discussed. In the case of ideal solvents this value is
equal to zero or it is negligible small in the case
of non-ideal solvents.

From experimental data logk'-values of chromatographed
substances were calculated.

Fig.1a,b shows the graphical relations between theoretical
calculated on the base of eq.1 and experimental obtained
R_M-values for chosen substances for given mobile phase
compositions for two different mixed phases. In all cases
a good agreement of theoretical and experimental values
of function $R_M = f(\varphi_1)$ has been obtained. Eq.1 describes
satisfactory experimental data for mixed phases c6mposed
of type N or A solvents and for type N(B) substances(8).
This results from the fact that systems of this type are
conformable to the theoretical assumptions of this equation,
e.g. insignificant and non-specific interactions between
solvent and solute molecules.

In the case of type N + N solvents, e.g. isooctane-
hexane or hexane-cyclohexane, the plots of $R_M = f(\varphi_1)$
relationships have flat shapes (Fig.1a). That means that
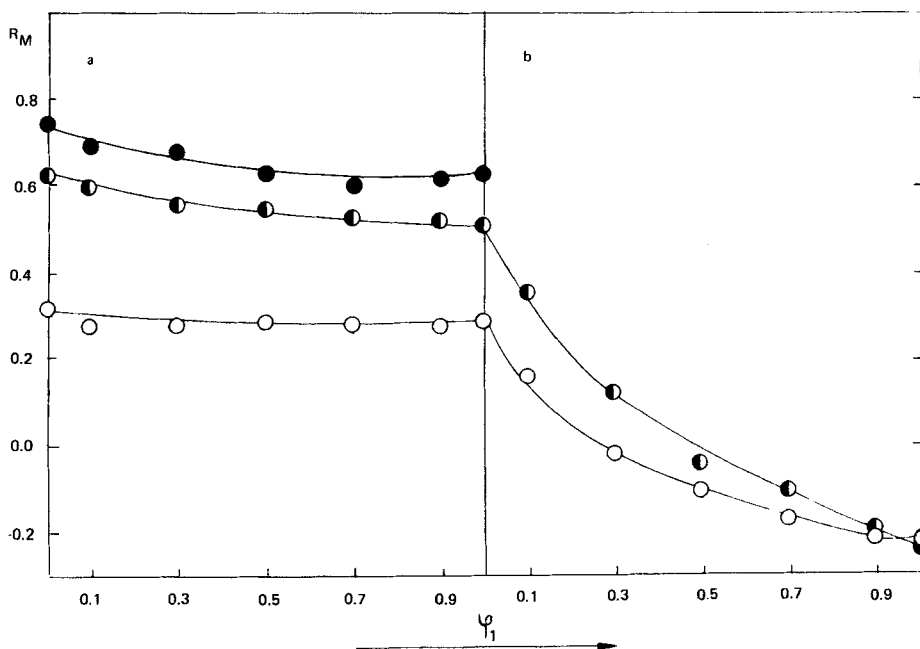the increase of φ_1-value not influences considerably on

Fig.1

The graphical relationships between theoretical (lines)
and experimental (circles) R$_M$-values and the composition
of the mobile binary solvents phase;

(a) the mobile phase: isooctane - hexane,

(b) the mobile phase: hexane - chloroform,

○ 1,5-dimethylnaphtalene,

◑ phenantrene,

● fluoranthene.

the retention of chromatographed substances in this kind
of mobile phase systems. Both of these mobile phases
are mixtures of non-active solvents which non-specific
interact with investigated substances, and that the increase
of R_M-value not changes the elution strenght of a given
mobile phase.

The different situation is in the case of hexane-
chloroform mobile phase (type N +A). The curves illustrated
R_M = $f(\varphi_1)$ relationships for this system have steep shapes
(Fig.1b). It is comprehensible when we notice that the more
active component of a mobile phase (chloroform) is able
to arise stronger intermolecular interactions with regard
to its electron-acceptor properities. The increase
of chloroform amount in a mobile phase from φ_1 = 0.0 to 0.3
influences considerably on R_M-values of chromatographed
substances. The R_M-values not change so considerably with
a further increase of φ_1-values.
In the range of low φ_1-values (0.0 - 0.3) there are
a continuous increase of chloroform amount in an adsorption
phase and that effects on the retention of chromatographed
substances (9).

On the base of experimental obtained logk'-values
and experimental obtained and theoretical calculated R_M-values
of studied substances the correlations logk' = $f(R_M)$ are
illustrated graphical for given mobile phase compositions.
From the theoretical equation logk' = R_M it seems that these
plots ought to be straight-lines with slopes equal to unity
and that they are independent on the kind and the composition

of a mobile phase. From experimental data it arises that
though these graphical relationships are straight-lines
the slopes of them are not only different from unity
but are different for various mobile phase compositions as well.

Fig.2 and 3 show the graphical relationships between
experimental logk'-values and theoretical and experimental
R$_M$-values for chromatographed substances for hexane -
cyclohexane and isooctane - hexane systems and for given
mobile phase compositions. These correlations are straight-
lines of near unity slopes. From the comparison of graphical
calculated slopes it seems that they change insignificantly
with mobile phase compositions. In practice they receive
similar values in a narrow range for both mobile phases.
The oscilations of slope values result rather from
experimental errors then from changes in mobile phase
properities resulting from the changes in its composition.

The analisis of the plots on Fig.2 and 3 shows that
R$_M$-values for naphtalene and its methyl derivatives are
near the same in both mixed mobile phases irrespective
of the site of the substituting groups in the naphtalene
molecule. This results from small values of the adsorption
energies of these groups on silica gel (10).

In the case of polycyclic aromatic hydrocarbons
the differences in R$_M$-values result from the fact that
interactions between solvent and solute molecules are
negligible and a higher influence of the structural
effects of these molecules can be observed.

It can be noticed from Fig.2 and 3 that the correlations
logk' = $f(R_M)$ are different for two groups of chromatographed
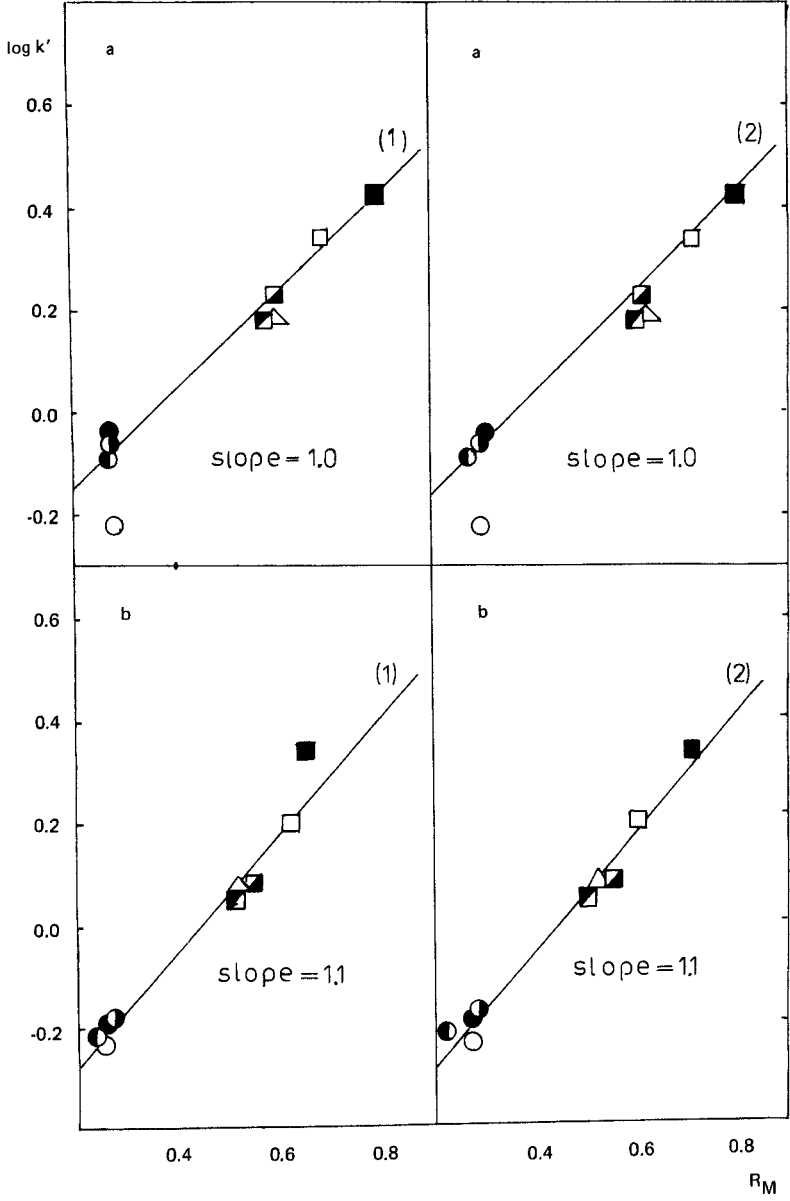
substances; i.e. for naphtalene and its methyl derivatives
and for polycyclic aromatic hydrocarbons. The distribution
of these correlations can be explained by structural
effects of these organic compounds. To study this problem
more precisely is necessary to gather much more experimental
data.

A different situation is in the case of hexane -
chloroform system $\left(N + A \text{ type} \right)$. Fig.4 shows the correla-
tions between logk' and R_M-values for chosen mobile phase
concentrations for this system. The distinct changes
of the line slopes with changing the mobile phase
composition are observed. The straight-lines become more
steep while the amount of chloroform $\left(\varphi_1 \right)$ in a mobile phase
increases, e.g. the increas of the mobile phase elution
strenght influences on the shapes of the straight-lines
illustrated graphical the relationships logk' $= f\left(R_M \right) \left(9 \right)$.
For this system hexane - chloroform, $\left(N + A \text{ type} \right)$ the separa-
tion of these correlations for two groups of compounds
is not observed.

Fig.2

The correlations between experimental logk'-values and
experimental (line 1) and theoretical (line 2) R_M-values
with using isooctane - hexane as the mobile phase;
(a) φ_1 = 0.1 ; (b) φ_1 = 0.7 ;
○ naphtalene, ◑β-methylnaphtalene, ◐ 1,3-dimethylnaphtalene,
● 1.5-dimethylnaphtalene, ◪ anthracene, ◩ pyrene,
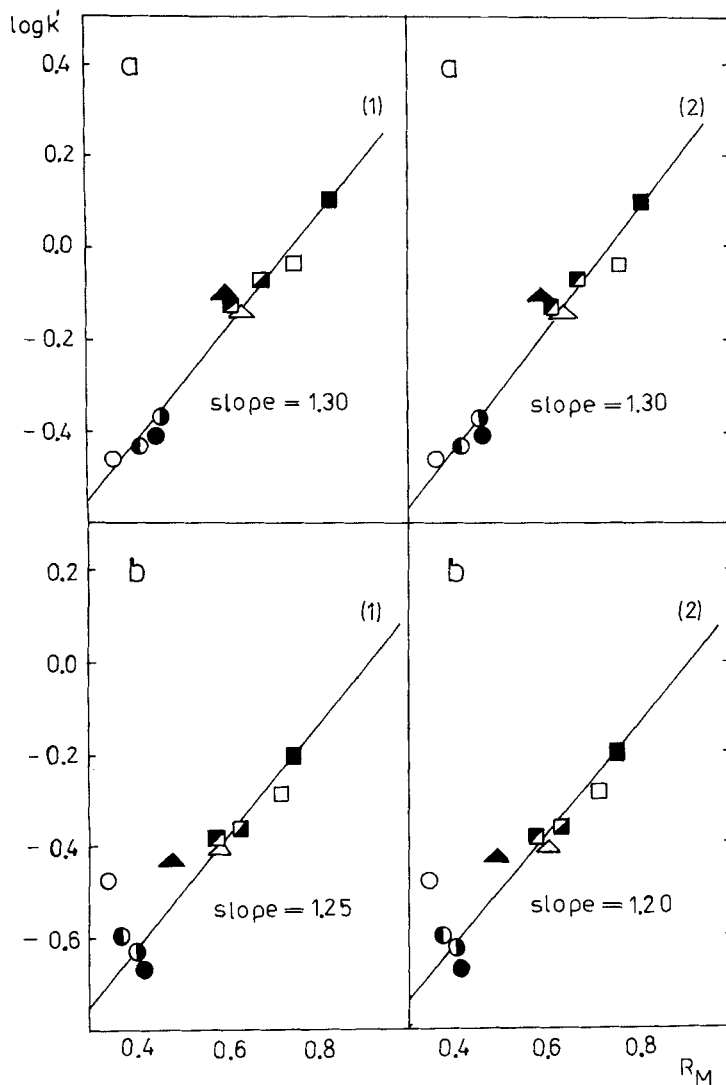■ chrysene, □ fluoranthene, △ phenantrene.

Fig.3

The correlations between experimental logk'-values and
experimental (line 1) and theoretical (line 2) R_M-values
with using hexane - cyclohexane as the mobile phase ;
(a) $\varphi_1 = 0.1$; (b) $\varphi_1 = 0.3$;
○ naphtalene, ◐ β-methylnaphtalene, ◑ 1,3-dimethylnaphtalene,
● 1,5-dimethylnaphtalene, ◨ anthracene, ◪ pyrene,
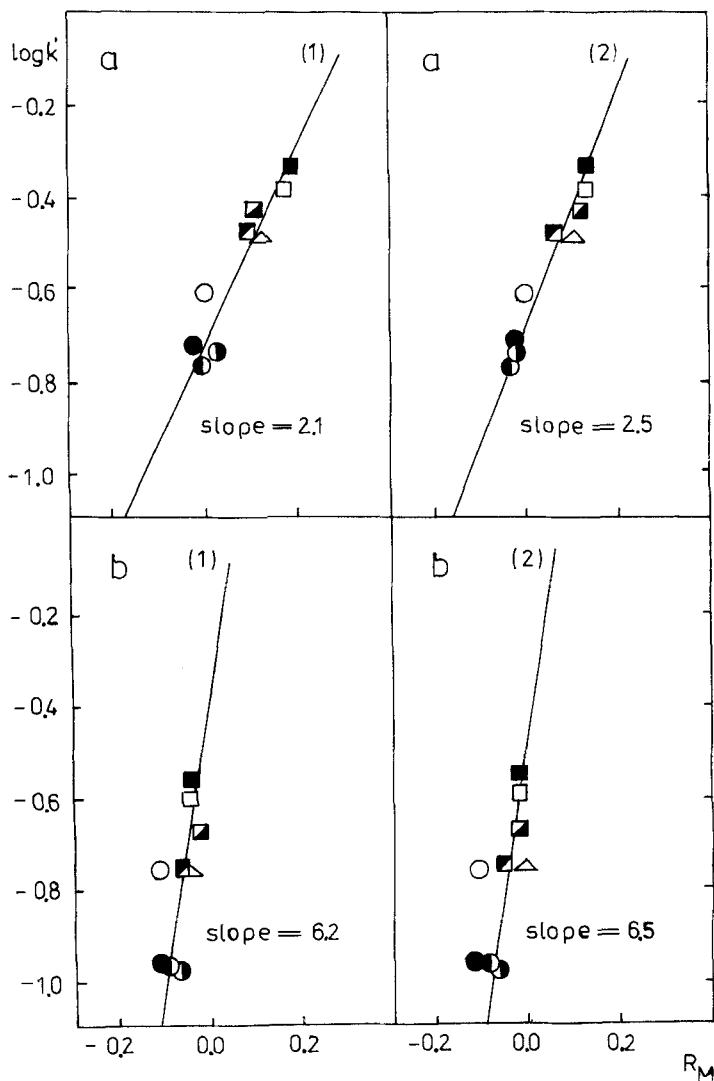■ chrysene, □ fluoranthene, △ phenantrene, ▲ fluorene.

Fig.4

The correlations between experimental logk'-values and experimental (line 1) and theoretical (line 2) R_M-values with using hexane - chloroform as the mobile phase ;

(a) $\varphi_1 = 0.3$; (b) $\varphi_1 = 0.5$;

the remaining explanations as above

From the data presented in this paper it appears that the correlations between logk' and R_M-values for chromatographed substances are straight-lines and, as it was noticed, their shapes depend on the kind and the composition of a mobile phase.

The above considerations sygnalizes the possibility of the use TLC-data, experimental obtained or theoretical calculated on the base of the eq.1, in more complex and time- wasting chromatographic technique as Liquid Column Chromatography, and that TLC can be used as a pilot technique for more precise studies.

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