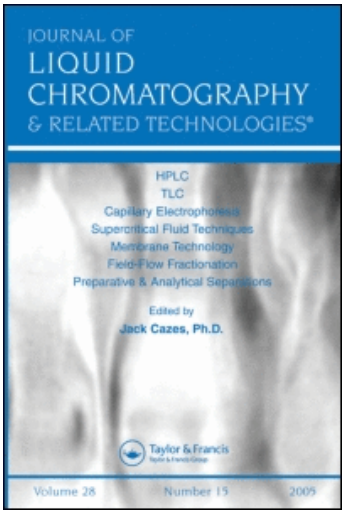

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Influence of Intramolecular Interactions on Some Parameters in Adsorption Thin-Layer Chromatography

G. Chojnacka[a]; J. Ościk[a]; R. Kusak[a]
[a] Institute of Chemistry M. Curie-Sklowdowska University, Lublin, Poland

To cite this Article Chojnacka, G. , Ościk, J. and Kusak, R.(1987) 'Influence of Intramolecular Interactions on Some Parameters in Adsorption Thin-Layer Chromatography', Journal of Liquid Chromatography & Related Technologies, 10: 16, 3547 — 3556
To link to this Article: DOI: 10.1080/01483918708077812
URL: http://dx.doi.org/10.1080/01483918708077812

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(16), 3547-3556 (1987)

INFLUENCE OF INTRAMOLECULAR INTERACTIONS ON SOME PARAMETERS IN ADSORPTION THIN-LAYER CHROMATOGRAPHY

G. Chojnacka, J. Ościk, and R. Kusak
Institute of Chemistry
M. Curie-Skłowdowska University
20-031 Lublin, Poland

ABSTRACT

Using the equation connecting the R_M values with the appropriate data of the adsorption process from solutions the values of the parameters characterizing substance↔mobile phase interactions have been calculated for the systems: silica gel—benzene+acetone and silica gel—acetone+methanol. Quinoline, aniline, nitrobenzene, phenol and their derivatives were the chromatographed substances. An influence of the structure of the substance on the parameter values has been examined, special attention being paid to intramolecular effects, mainly those of hydrogen bonds.

INTRODUCTION

Liquid adsorption chromatography is well-known as a typical analytical method generally used to separate mixtures of various types. However, good separation can be obtained when proper selectivity is characteristic of the chromatographic system. Although a lot of experi-

ments, dealing with this problem, were made a selection of the best system is still very difficult. On the one hand, it is caused by a complex mechanism of the chromatographic process, and on the other, by practitioners' little interest in the theories of liquid adsorption chromatography.

Perry (1) showed without any doubt that a lot of important conclusions for practice can be derived from theories given by Snyder (2) and Soczewiński (3). Previous investigations (4-9) show that in optimization of the chromatographic systems one can apply the equation derived by Ościk (10,11), as well. This equation connects the R_M values with the appropriate data of the adsorption process from solution. For an ideal or regular binary mobile phase, this equation has the following form

$$R_{M_{12}} = X_1 \Delta R_{M_{1,2}} + \left(X_1^s - X_1\right)\left(\Delta R_{M_{1,2}} + A_{12}\right) + R_{M_2} \qquad (1)$$

where

$R_{M_{12}}$ is the R_M values of a given substance when using the binary mobile phase 1+2;

$\Delta R_{M_{1,2}} = R_{M_1} - R_{M_2}$ expressing the difference of the R_M values for a substance when using the pure solvents 1 and 2 as the mobile phases;

X_1^s and X_1 are the mole fractions of component 1 of the binary mobile phase in the surface phase and the bulk phase, respectively;

A_{12} is the parameter characterizing substance solvent interactions. It is connected with the hypothetical rational partition coefficient for substance between the 1 and 2 components of the binary mobile phase 1+2.

Equation (1) was used to estimate the influence of such factors as properties of the mobile phases, adsor-

bents or substances on the processes taking place in the surface layers. Less attention was paid to the bulk phase. It is true that the processes taking place in this phase are of secondary importance but, if not taken into consideration, they often make the optimization of the separation process difficult in the adsorption liquid chromatography. For this reason, in the paper the authors concentrate upon calculating the parameters A_{12} of equation (1), connected with the intermolecular interactions in the bulk phase. As model substances aromatic compounds were used to make possible testing the influence of the intramolecular interactions on the A_{12} values.

METHODS

Using adsorption TLC R_F values were measured for a number of aromatic compounds (derivatives of quinoline, nitrobenzene, aniline and phenol). Silica gel 60 H with the specific surface area of 420 $m^2 \cdot g^{-1}$, produced by Merck, was used as the adsorbent. Binary solutions: benzene+acetone and acetone+methanol were used as the mobile phases. The chromatographic process was carried out by ascending technique on adsorbent layers of 0.3mm in thickness in glass chambers saturated with mixed solvent vapours. All the measurements were carried out under thermostated conditions at 298°K. The detection of the substances was carried out by reaction with iodine. The obtained R_F values were converted into R_M according to the Bate-Smith and Westall equation.

The excess adsorption isotherms of acetone from benzene and methanol from acetone were determined at 298°K using the static method. Adsorbent was silica gel previously used in adsorption TLC. The solution concentrations after equilibration were analyzed by gas—liquid chromatography. The individual adsorption (X_1^s val-

ues) was calculated on the basis of the ideal model of adsorption given by Everett (12).

RESULTS AND DISCUSSION

The A_{12} values derived from equation (1) calculated from the experimental R_M values and experimental data of the excess adsorption were shown in Table 1. They are in most cases, averages of the A_{12} values calculated for four mobile phases with various concentrations. A good criterion of the assumed values of parameter A_{12} is the agreement of the relationships $R_M = f(X_1)$ of the individual substances derived from above equation with the respective relationships found during the experiment. Some relationships are shown in Figs. 1 and 2. The solid lines represents the relationships calculated from equation (1) with the help of the A_{12} values given in Table 1, circles represent the experimental R_M values.

The examination of the "ortho effects on the values of parameter A_{12} of the substances was required to calculate the values of the parameters both for ortho- and for meta- and para-isomers of chromatographed substances. It was also necessary to calculate the values of A_{12} parameters of the subscances the derivatives of which were the compounds i.e. aniline, nitrobenzene, phenol,2-naphthol and quinoline.The calculation of A_{12} values was impossible for para- and meta-isomers of dihydroxybenzene and phenylenediamine in the systems with the mobile phase benzene+acetone as their R_F values were close to zero, if the mobile phase was pure benzene. Thus,in above examinations,the model substance were both the compounds with the one functional group as well as the substance having few functional groups (chiefly two).

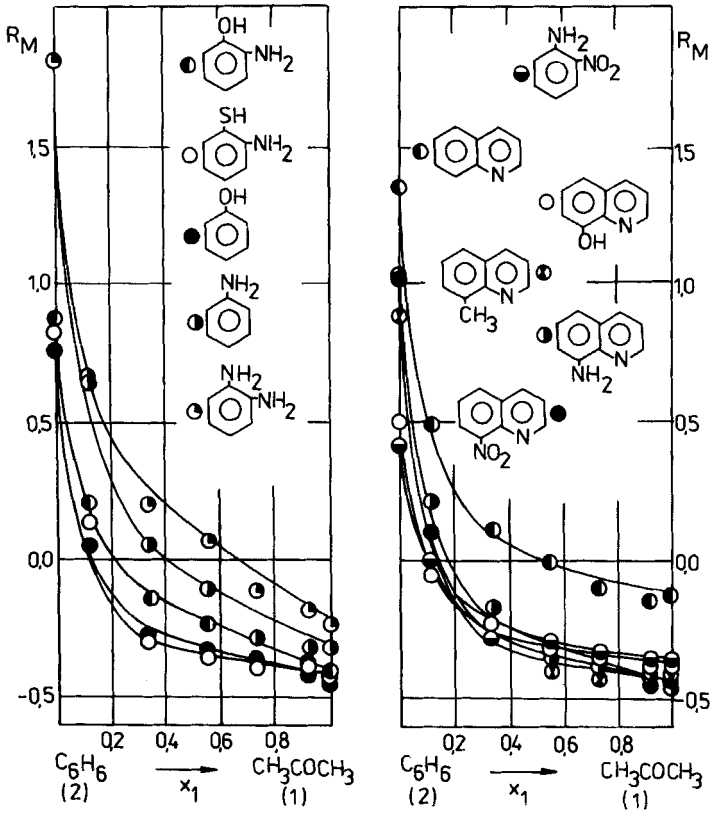

FIGURE 1

Relationships between calculated from equation (1) with the help of A_{12} values given in Table 1 (lines) and experimental (circles) R_M values and the composition of the binary mobile phase benzene + acetone.

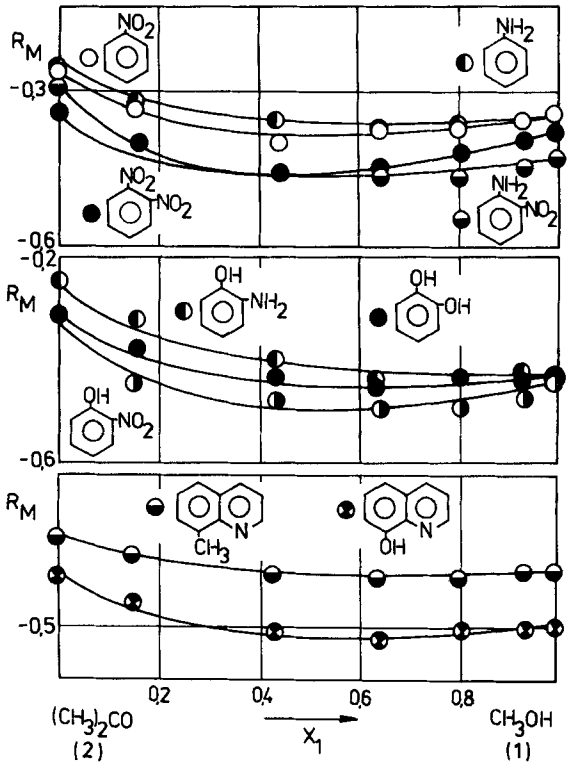

FIGURE 2

Relationships between calculated from equation (1) with the help of A_{12} values given in Table 1 (lines) and experimental (circles) R_M values and the composition of the binary mobile phase acetone + methanol.

TABLE 1

The A_{12} values calculated from equation (1) from the experimental R_M values and experimental data of the excess adsorption.

Solute \ Mobile phase	benzene + acetone	acetone + methanol
Nitrobenzene	0.054	-0.114
o-Dinitrobenzene	0.196	-0.197
m-Dinitrobenzene	0.158	-0.372
p-Dinitrobenzene	0.082	-0.422
o-Nitrophenol	0.170	-0.145
m-Nitrophenol	0.206	-0.173
p-Nitrophenol	0.236	-0.112
o-Nitroaniline	0.212	-0.112
m-Nitroaniline	0.322	-0.097
p-Nitroaniline	0.421	-0.026
2,6-Dinitroaniline	0.094	-0.220
Aniline	0.411	-0.066
o-Phenylenediamine	0.722	-0.180
o-Aminophenol	0.522	0.009
o-Aminotiophenol	0.153	-0.185
Phenol	0.234	-0.038
o-Dihydroxybenzene	0.374	-0.062
2-Naphthol	0.106	-0.191
2,3-Dihydroxynaphthalene	0.331	-0.117
Quinoline	0.283	-0.101
8-Methylquinoline	0.140	-0.074
8-Nitroquinoline	0.205	-0.195
8-Aminoquinoline	0.316	-0.128
8-Hydroxyquinoline	0.143	-0.031

As mobile phases binary solutions were used: benzene+acetone and acetone+methanol, the properties of which are decidely different. The first of them is a typical conformal solution and totally fulfills the assumption with which equation (1) was derived. Another solution being the mixture of the solvents of B and AB classes (according to Pimentel and McClellan) is characteristic due to strong hydrogen bonds of intermolecular interactions. If values A_{12} are indeed related to the interactions: substance↔components of the mobile phase, then the differences in the properties of the

phases should possibly be confirmed by the values of these parameters. The data in Table 1 confirm this assumption. Values A_{12} of the separate substances depend exactly on the kind of the mobile phase in the way that the change of the phase results not only in the change of the values of parameters A_{12} but also in that of its sign.

The analysis of A_{12} values given in Table 1,points out to the fact that among the monofunctional compounds the highest and the lowest A_{12} values have aniline and nitrobenzene, respectively.

Variations in A_{12} values caused by introducing another functional group into the substance molecule are dependent on the properties and mutual position of both functional groups in this molecule. Values A_{12} of o-nitroaniline and m-nitroaniline are lower than the respective values of aniline. The same is true in case of o-nitrophenol, m-nitrophenol and phenol. However, the presence of group $-NO_2$ in the para position in relation to group $-NH_2$ or that of -OH slightly affects the value of parameter A_{12}. These regularities are true both for the mobile phases benzene + acetone as well as for the mobile phases acetone + methanol.

The data shown in Table 1 point out that A_{12} value confirm different intramolecular effects. In case of o-nitrophenol, o-aminotiophenol, 2,6-dinitroaniline and o-nitroaniline, decreased A_{12} values can be found when compared with the respective values obtained for phenol and aniline. A similar regularity can be found for A_{12} values in case of 8-methylquinoline, 8-hydroxyquinoline, 8-nitroquinoline and quinoline.

In case of o-dinitrobenzene, o-phenylenediamine and 8-aminoquinoline for the mobile phase benzene+acetone and in case 2,3-dihydroxynaphthalene and o-dihydroxybenzene for both mobile phases A_{12} values were found to be

higher than the respective values of monofunctional compounds.

Increased values A_{12} for o-dinitrobenzene in relation to those of nitrobenzene and the remaining isomeric dinitrobenzenes are possibly due to some tendency of nitrocompounds to electrostatic interactions dipol↔dipol with the components of the chromatographic systems. A higher dipole moment (6.0 D of o-dinitrobenzene while dipole moments of nitrobenzene and m-dinitrobenzene and p-dinitrobenzene are 4.24 D and 4.07 D and 0.0, respectively) is possibly due to stronger interactions with acetone.

The cause of some higher A_{12} values for o-phenylenediamine, o-dihydroxybenzene, 2,3-dihydroxynaphthalene and 8-aminoquinoline than the values for appropriate monofunctional compounds is the presence of two donor-acceptors groups in the molecules of the substances. The substances can simultaneously form intra- and inter-molecular hydrogen bonds.One may suppose that inter-molecular bonds are even stronger than those of monofunctional compounds.

Values A_{12} for o-aminophenol are also higher than those found for aniline and phenol as a result of the absence of intramolecular hydrogen bond in the molecule of this substance.It is in agreement with the works by Baker and Shulgin (13).They found out that only one sharp band of the hydroxyl group in the spectrum of o-aminophenol occurred and this fact totally excludes the presence of intramolecular hydrogen bond.

One should add that the convertion of the mobile phase benzene+acetone into that of acetone+methanol besides the above change of the sign of parameter A_{12}, causes also a decreased effect of the mutual position of the functional groups on the values of this parameter. This concerns chiefly all isomeric nitrophenols and nitroanilines.

In conclusion one can state that the analysis of the values of parameters A_{12} can be source of information concerning intramolecular interactions in the adsorption chromatographic systems.It can also point out if hydrogen bonds or other intramolecular effects occur in the molecules of the chromatographed substances and that their influence on the chromatographic process can be estimated.

REFERENCES

1. Perry J.A., J. Chromatogr. 165, 117 (1979)
2. Snyder L.R., Principles of Adsorption Chromatography M.Dekker, New York 1968
3. Soczewiński E., Anal. Chem., 41, 179 (1969)
4. Chojnacka G., Różyło J.K., Ościk J.,Chromatographia, 13, 109 (1980)
5. Różyło J.K., Gross J., Chojnacka G., Malinowska I., J. Liquid Chromatogr., 3 6 , 921 (1980)
6. Różyło J.K., Chojnacka G., Malinowska I., J. High Resolution Chromatogr., 4, 224 (1981)
7. Różyło J.K., Chojnacka G., Kołodziejczyk H., J. High Resolution Chromatogr., 5, 139 1982
8. Ościk J., Różyło J.K., Gross J., Malinowska I., Chojnacka G., Chromatographia, 15, 25 (1982)
9. Ościk J., Jaroniec M., Malinowska I., J. Liquid Chromatogr., 6, 2 , 81 (1983)
10. Ościk J., Przem. Chem., 44, 129 (1965)
11. Jaroniec M., Ościk J., J. High Resolution Chromatogr., 5, 3 (1982)
12. Everett D.H., Gas Chromatography 1964, London 1965 p. 219
13. Baker A.W., Shulgin A.T., J. Am. Chem. Soc., 80, 5358 (1958)