JAN K. RÓŻYŁO*, HANNA KOŁODZIEJCZYK*

# APPLICATION OF TLC METHOD TO INVESTIGATING SEPARATION CONDITIONS OF SOME ISOMERIC NAPHTHALENE DERIVATIVES

The possibilities of separation of synthetic mixtures of 1,4- and 1,5-naphthalene derivatives by adsorption thin-layer chromatography (TLC) have been demonstrated. These substances have been synthesized in the Department of Organic Chemistry at Maria Curie-Skłodowska University. Due to TLC process on $SiO_2$ layer we can obtain some information about purity of final products. The possibilities of application a thermodynamic optimization theory to prediction of optimal conditions of mixture separation in the case of binary mobile phases have been also investigated. Knowledge of behaviour of these substances during chromatographic process and prediction of retention data theoretically may be useful in purification of industrial effluents.

## 1. INTRODUCTION

Diacetoxymethylnaphthalene (AMN), dimercaptomethylnaphthalene (MMN) and dihydroxymethylnaphthalene (HMN) have been synthesized for the first time in the Department of Organic Chemistry at our University.

Basic substrate used for synthesis of 1,4-MMN, 1,5-MMN and their mixture is the mixture of 1-chloromethylnaphthalene, 1,4-dichloromethylnaphthalene and 1,5-dichlorodimethylnaphthalene prepared by chloromethylation of naphthalene using paraformaldehyde and concentrated hydrochloric acid in glacial acetic acid. When the mixture of 1,4- and 1,5-dichloromethylnaphthalenes in glacial acetic acid is treated with anhydrous sodium acetate, the mixture of 1,4- and 1,5-AMN is formed. This mixture treated next with methanolic solution of potassium hydroxide gave the mixture of 1,4- and 1,5-HMN. The substances prepared in such a way have bifunctional molecules and are used as initial monomers in synthesis of some polymolecular substances, e.g., epoxides.

* Faculty of Chemistry, Maria Curie-Skłodowska University, Pl. Curie-Skłodowskiej 3, 20-031 Lublin, Poland.

Determination of the purity degree as well as identification of individual isomers during synthesis and purification of these substances are of crucial importance. *A priori* determination of optimal conditions of mixture separation in TLC is the aim of investigations. So far this determination has been realized by trials and errors method.

Our experiments were carried out in an attempt to find a method of analytical identification and optimal choice of mobile phase which allow us to separate efficiently 1,4- and 1,5-isomers.

Experimental relations between $R_M$ values and composition of mobile phase were confirmed theoretically by thermodynamical theory of adsorption from binary solutions. Basic equation of this theory related $R_M$ values of chromatographic substance to adsorption parameters of mobile phase components as follows:

$$R_{M12} = x_1 \Delta R_{M12} + (x_1^s - x_1)(\Delta R_{M12} + A_z) + R_{M2} \qquad (1)$$

where $\Delta R_{M12} = R_{M1} - R_{M2}$; $R_{M12}$ is $R_M$ value of the substance chromatographed in binary solvent "1+2"; $R_{M1}$ and $R_{M2}$ are $R_M$ values of the substance chromatographed in pure solvents "1" and "2", respectively; $A_z$ is the value equal to logarithm of partition coefficient of the substance between molecules of solvent components and substances chromatographed; $x_1^s$ is the volume fraction of component "1" in surface phase; $x_1$ is volume fraction of component "1" in bulk phase; $(x_1^s - x_1)$ is adsorption excess of component "1" of mobile phase. This last quantity is calculated on the basis of separation function of mobile phase components:

$$x_1^s - x_1 = \frac{x_1(K_1 - 1)(1 - x_1)}{(1 + x_1)(K_1 - 1)} \qquad (2)$$

where $K_1$ is adsorption equilibrium constant of component "1" of mobile phase. For ideal and regular solvents this quantity can be expressed in the term of $\log K_1$ equal to mean value of $\Delta R_{M12}$.

The main purpose of this paper is to investigate the separation of the mixture of isomeric naphthalene derivatives as well as to examine the theoretical determination of $R_M$ values of these substances, depending on mobile phase composition.


## 2. EXPERIMENTAL

Thin-layer adsorption chromatographic measurements were carried out for isomers of 1,4- and 1,5-diacetoxymethylnaphthalenes (AMN), 1,4- and 1,5-dimercaptomethylnaphthalenes (MMN) as well as 1,4- and 1,5-dihydroxymethylnaphthalenes (HMN) on silica gel $HF_{254}$ Merck at temperature of 20°C using adsorbent layers of 0.3 mm thickness, activated through 2 h at temperature of 135°C. The mixtures of these substances were separated in the following binary mobile phases: carbon tetrachloride–chloroform, acetic acid–benzene, acetic acid–ethyl-methyl ketone. The solvents were selected according to Pimentel and McClellan classification because

we aimed for the greatest possible differentiation of activity of mixed solvents in respect of ability to hydrogen bonds formation. Experimental results are presented in the form of graphical relationships between $R_M$ values and mobile phase composition. $R_M$ values were calculated also from equation (1). Parameters of this equation are listed in the table.

Table

$A_z$ and $K_1$ parameters calculated from equation (1) on the basis of chromatographic data

| Substances | Mobile phase | | | | | |
| | $CCl_4$–$CHCl_3$ | | $CH_3COOH$–$C_6H_6$ | | $CH_3COOH$–EMK | |
| | $K_1$ | $A_z$ | $K_1$ | $A_z$ | $K_1$ | $A_z$ |
|---|---|---|---|---|---|---|
| 1,4-MMN | 1.16 | −1.39 | 1.12 | −17.2 | 5.56 | 3.01 |
| 1,5-MMN | 1.16 | −1.60 | 1.12 | −18.8 | 5.56 | 2.16 |
| 1,4-AMN | 1.16 | −6.70 | 1.12 | −16.7 | 5.56 | 1.58 |
| 1,5-AMN | 1.16 | −2.10 | 1.12 | −16.2 | 5.56 | 2.05 |
| 1,4-HMN | 1.16 | −2.70 | 1.12 | −20.1 | 5.56 | 1.10 |
| 1,5-HMN | 1.16 | −1.80 | 1.12 | −20.1 | 5.56 | 0.61 |

## 3. DISCUSSION

From analytical viewpoint the most efficient separation was stated in the acetic acid–benzene system in the range of the benzene volume fraction of 0.5–0.7. Effect of substituent and its position in aromatic ring on mixture separation were observed, because $R_M$ values of 1,5-derivatives were lower than those of 1,4-derivatives, and in such systems isolation of individual isomers was possible. In each system, independently of the mobile phase applied, the $R_M$ value in the case of mercaptomethylnaphthalenes, acetoxymethylnaphthalenes and hydroxymethylnaphthalenes are smallest, medium and the highest, respectively (fig. 1). In the acetic acid–ethyl-methyl ketone system the highest separation efficiency was obtained at the concentration of acetic acid ranging from 0.7 to 0.9 volume fraction. The dependence of $R_M$ value on $x_1$ has not a significant minimum and the diffrences between $R_M$ values of pure solvents are small (fig. 2).

In the carbon tetrachloride–chloroform system, small differences between $R_M$ values for 1,4- and 1,5-isomers were observed in spite of great differences in $R_M$ values of these isomers in pure solvents (fig. 3).

Considering the values obtained from equation (1), it can be seen that for carbon tetrachloride–chloroform and acetic acid–benzene systems $A_z$ values are negative. Negative $A_z$ values may be related to relatively strong adsorption of more polar component of mobile phase. For 1,5-AMN and 1,4-, 1,5-HMN, $A_z$ values show

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a great similarity. 1,4- and 1,5-MMN are characterized by slightly lower $A_z$ values, whereas $A_z$ values for 1,4-AMN differ significantly from the other. For the systems considered here the differences in $K_1$ values are small.
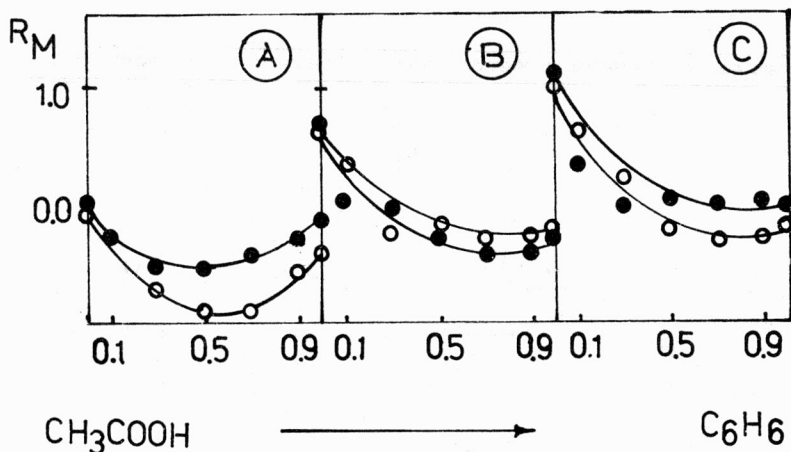


Fig. 1. Dependences of $R_M$ values on mobile phase composition for

A — ● 1,4-dimercaptomethylnaphthalene (MMN),
○ 1,5-dimercaptomethylnaphthalene (MMN)
B — ● 1,4-dihydroxymethylnaphthalene (HMN),
○ 1,5-dihydroxymethylnaphthalene (HMN)
C — ● 1.4-diactoxymethylnaphthalene (AMN),
○ 1.5-diactoxymethylnaphthalene (AMN)

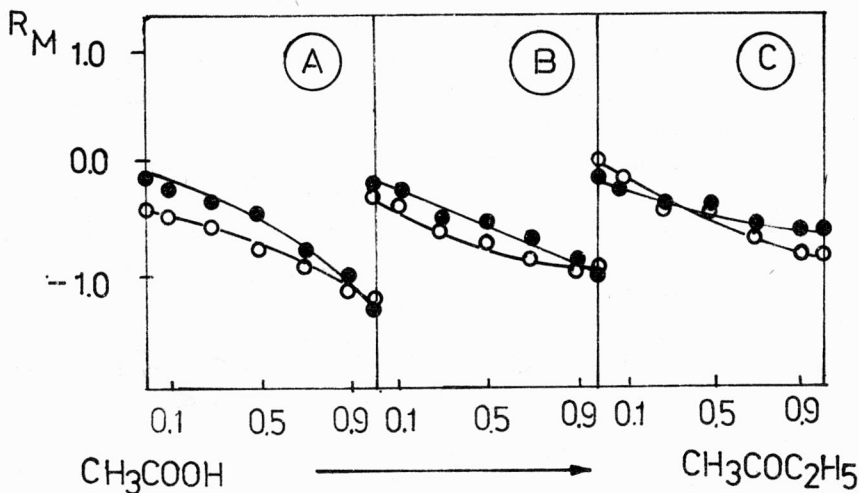Circle — experimental data, lines — theoretical data. Mobile phase: acetic acid–benzene



Fig. 2. Dependences of $R_M$ values on mobile phase composition for substances tested. Mobile phase: acetic acid-ethyl–methyl ketone
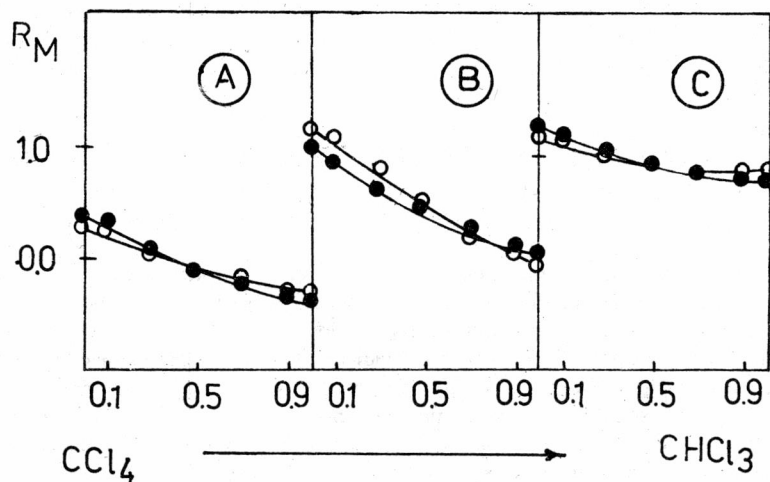
For explanation see fig. 1

Fig. 3. Dependences of $R_M$ values on mobile phase composition for tested chromatographed substances. Mobile phase: carbon tetrachloride–chloroform

For explanation see fig. 1.

In the acetic acid–ethyl-methyl ketone system, adsorption equilibrium constant $K_1$ is significantly greater than that in the other systems, whereas $A_z$ values are positive. It can be seen that for 1,4-isomers, $A_z$ values are nearly 1.5 times greater than for 1,5-isomers. A change of $A_z$ sign from negative to positive is caused by reduced interactions between molecules of the mobile phase and molecules of substances chromatographed. On the other hand, this fact indicates that there exist strong interactions between both components of mobile phase: ethyl-methyl ketone–acetic acid, which owing to their polarity can form associated molecules. Thus interactions between molecules of components of mobile phase are stronger than those between molecules of mobile phase components and molecules of the substances chromatographed. Similarly, $K_1$ value increases as a result of polarity of mobile phase components.

The results of our experiments found their confirmation in theoretical data which indicates that there exists real possibility of satisfactory chromatographic separation of isomeric mixture with application of mobile phase of selected polarity.

ZASTOSOWANIE CHROMATOGRAFII CIENKOWARSTWOWEJ
DO BADANIA WARUNKÓW ROZDZIAŁU IZOMERYCZNYCH POCHODNYCH NAFTALENU

Przedstawiono możliwości rozdziału mieszanin 1,4- i 1,5-syntetycznych pochodnych naftalenu za pomocą adsorpcyjnej chromatografii cienkowarstwowej. Substancje te po raz pierwszy zostały otrzymane w Zakładzie Chemii Organicznej UMCS w Lublinie. Chromatografia cienkowarstwowa na warstwach żelu krzemionkowego umożliwia określenie czystości końcowych produktów syntezy. Przedstawiono także teoretyczne możliwości przewidywania optymalnych warunków rozdziału badanych mieszanin

izomerycznych naftalenów stosując teorię optymalizacji procesu chromatograficznego. Znajomość zachowania się tych substancji podczas procesu chromatograficznego i teoretyczne przewidywanie danych retencyjnych może być użyteczne w procesie oczyszczania ścieków przemysłowych.

## ПРИМЕНЕНИЕ ТОНКОСЛОИСТОЙ ХРОМАТОГРАФИИ ДЛЯ ИССЛЕДОВАНИЯ УСЛОВИЙ РАЗДЕЛЕНИЯ ИЗОМЕРНЫХ ПРОИЗВОДНЫХ НАФТАЛИНА

Представлены возможности разделения 1,4- и 1,5-синтетических смесей производных нафталина при помощи адсорбционной тонкослоистой хроматографии. Эти вещества впервые были получены в кафедре Органической Химии УМКС в Люблине. Тонкослоистая хроматография на слоях силикогеля дает возможность определения чистоты конечных продуктов синтеза. Представлены также теоретические возможности прогнозирования оптимальных условий разделения исследуемых изомерных смесей нафталинов при употреблении теории оптимализации хроматографического процесса. Знание поведения этих веществ во время хроматографического процесса и теоретическое прогнозирование ретенционных данных могут быть полезными в процессе очистки промышленных сточных вод.