Relationship between chromatographic properties of aromatic carboxylic acids and their structure

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Abstract

The retention of aromatic carboxylic acids and their esters in reversed-phase HPLC is proportional to the sum of their partition coefficients in octanol–water system and retention increments. This equation can be used for the identification of various side-products formed in monomer production.   © 2002 Published by Elsevier Science B.V.

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1. Introduction

Aromatic carboxylic acids are widely used in the production of thermostable polymers. These polymers are obtained by the following reactions [1]:
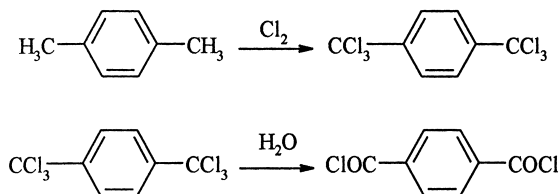
The production process is monitored by reversed-phase high-performance liquid chromatography (HPLC). The requirements for the purity of products are very strict. Even traces of impurities can drastically decrease the quality of products. Identification of impurities is very important for the process control. The task of identification of various admix-

tures formed in the process is very time-consuming and tedious.

HPLC allows quick identification of side-products which is very important for the adjustment of operation parameters in real time. This identification is achieved using retention–structure relationships based on the additive nature of the partition coefficient. This work was aimed at developing structure–retention relationship in the series of aromatic carboxylic acids and their esters. These models are based on the linear free energy relationship.

2. Experimental

2.1. Chemicals

Therephthalic, *p*-toluic and pyromellitic acids (supplier ''Khimreaktiv'', analytic grade) were used without additional purification. Methyl esters were synthesised from corresponding commercial acyl chlorides by reaction with methanol. Other compounds were obtained by preparative liquid chromatography from the reaction mixture formed in the

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oxidation of durene (1,2,4,5-tetramethylbenzene), using silica gel L (40–60 μm) treated with dimethyl-dichlorosilane. All the resulting compounds were identified by their IR and magnetic resonance spectra.

2.2. Equipment

HPLC of therephthalic acid derivatives was performed with a Milikhrom chromatograph with a UV detector from Orelnauchpribor (Orel, Russia) operated at wavelength of 240 nm with attenuation of 0.8. Samples prior to injection were dissolved in dimethylsulfoxide and injected using a manual injector. Compounds were separated on a 60 mm×2 mm I.D. KAKH-2 column (Orelnauchpribor) packed with 5 μm Silasorb C_{18} at room temperature. The mobile phase was acetonitrile–water–phosphoric acid (85%) (50:50:0.2, v/v), flow-rate was 100 μl/min under isocratic regime.

HPLC of durene (1,2,4,5-tetramethylbenzene) oxidation products was performed with a Tsvet'' Model 304 chromatograph with a UV detector from Khimavtomatica (Dzerzhinsk, Russia) operated at wavelength of 254 nm. Samples were prepared for analysis as indicated above. Compounds were separated on a 100 mm×6 mm I.D. column packed with 10 μm Silasorb C_2 at room temperature. The mobile phase was water–acetic acid (98:2, v/v), flow-rate was 1 ml/min under isocratic regime.

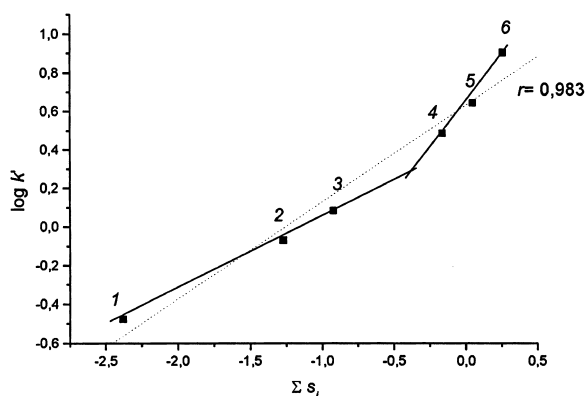The hold-up time was determined by injection of air.

Fig. 1. Dependence of retention coefficient on the sum of retention increments.

3. Results and discussion

The a priori calculation of retention parameters is still impossible. However, there exist a number of models linking retention with properties of the molecule. Simple additive models describe retention factor as the sum of retention increments corresponding to various structural fragments. These increments are readily available in the literature [2] and can be used for the prediction of retention parameters. We have determined retention factors of therephthalic acid and its derivatives and tried to correlate them with retention increments. The retention factors obtained are listed in Table 1. The treatment of data, using the equation $\log k' = a + b\Sigma s_i$, gave a linear dependence with correlation coefficient of 0.983 (Fig. 1). It is seen that this

Table 1
Retention data

Compound No.	Log k'	Σs_i [2]	Log P [4]	Structure
1	−0.477	−2.38	1.40	p-HOOCC$_6$H$_4$COOH
2	−0.071	−1.27	1.86	p-MeOOCC$_6$H$_4$COOH
3	0.082	−0.92	2.27	p-HOOCC$_6$H$_4$Me
4	0.485	−0.16	2.11	p-MeOOCC$_6$H$_4$COOMe
5	0.641	0.05	2.82	p-MeOOCC$_6$H$_3$ClCOOMe
6	0.900	0.26	3.53	p-MeOOCC$_6$H$_2$Cl$_2$COOMe
7	1.230	−0.12	3.08	2,4,5-Me$_3$C$_6$H$_2$COOH
8	0.190	−1.84	0.99	1,2-(HOOC)$_2$-4,5-Me$_2$C$_6$H$_2$
9	0.510	−1.84	2.75	1,4-(HOOC)$_2$-2,5-Me$_2$C$_6$H$_2$
10	0.760	−1.84	2.75	1,5-(HOOC)$_2$-2,4-Me$_2$C$_6$H$_2$
11	−0.097	−2.52	0.64	1,2,4-(HOOC)$_3$-5-MeC$_6$H$_2$
12	−0.220	−3.72	0.18	1,2,4,5-(HOOC)$_4$C$_6$H$_2$

dependence can be broken into two parts: for compounds with the carboxylic group and those without them. The corresponding correlation coefficients are equal to 0.999 and 0.990. It is known that simple, single-parameter relationships of structure property are valid only within narrow series of homologs [3]. It is also known that retention in reversed-phase systems can be calculated using partition coefficients in the octanol–water system. The necessary partition coefficients were calculated using the Leo–Hansch procedure [4]. However, the model obtained was not accurate, as it ignores the selectivity of the chromatographic system (the correlation coefficient for Eq. (1) is equal to 0.880):

$$\log k' = a + b \log P \qquad (1)$$

Nevertheless, the partition coefficients are listed for a lot of compounds and can be calculated very easily. In my opinion, the selectivity of the chromatographic system can be accounted for, using retention increments together with partition coefficients. Thus, the data were treated using the following equation:

$$\log k' = a + b \left(\log P + \sum s_i\right), \ (r = 0.990) \qquad (2)$$

This improvement of correlation obtained confirms the hypothesis that two main factors determine the retention of aromatic carboxylic acids and their esters in a reversed-phase system: interaction of the sorbate with alkyl radicals of the sorbent and its interaction with surface-solvated sorbent. The first of these factors can be described by the partition coefficient, the second one by the sum of retention increments. These factors are homogeneous, as can be seen from the equation. I treated in the same way
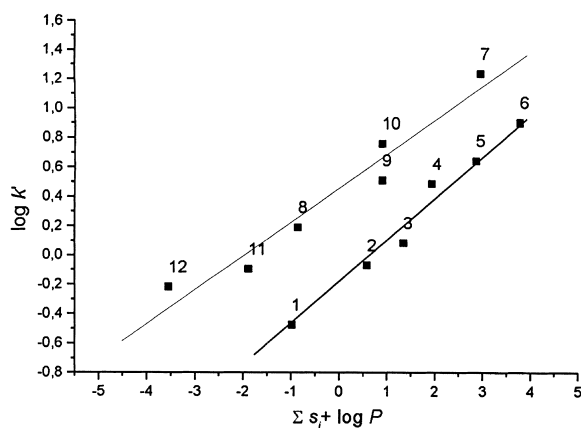

Fig. 2. Dependence of retention coefficient on the sum of partition coefficients and retention increments.

the retention data obtained for the aromatic acids formed in the durene oxidation (Fig. 2). In this case, the correlation coefficient for Eq. (1) is $r = 0.936$ and for Eq. (2) it is $r = 0.960$. The results obtained confirm the validity of my approach. It is interesting to note that both charged and uncharged species follow this relationship.

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