Aqueous solution of phosphoric acid as the stationary liquid phase for selective separation of fatty acids under conditions of steam chromatography

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An aqueous solution of phosphoric acid was used as a selective stationary liquid phase for the separation of volatile fatty acids under conditions of steam chromatography. Organic acids C_2—C_8 are eluted from the column as symmetric peaks, and the order of their elution is reverse to that observed commonly on other phases.

Key words: selective stationary liquid phase; aqueous solution of phosphoric acid as stationary liquid phase; gas chromatography of fatty acids C_2—C_8; steam chromatography.

Separation of fatty acids is an important analytical task. Compounds of this type are characterized by a high polarity and adsorption capability, which makes their chromatographic determination difficult. Acids from formic to dodecanoic have been first separated as early as in 1952 in the first work on gas liquid chromatography.[1] A nonpolar phase along with stearic acid were deposited on a solid support to obtain symmetric peaks of acids. The use of nonpolar Apiezon L at high temperature (276 °C) made it possible to separate high-boilng acids C_{12-18}.[2] However, the chromatographic zones were nonsymmetric. A substantially better separation of acids C_{4-22} was obtained on pentaerythritol with addition of phosphoric acid (2% of the weight of the solid support).[3]

Further, instead of direct determination of lower acids, in the majority of cases, they were analyzed in the form of esters,[4] on the phases containing nonvolatile organic or inorganic acids (modifying agents)[5,6], or on the phases with high polarity (for example, Nukol[7]).

The purpose of the present work is to search for and study superselective phases for separation of volatile organic acids using a new approach suggested previously[8] which is based on the use of aqueous solutions of inorganic salts (selective under conditions of steam chromatography) as the stationary liquid phase (SLP).[9,10] Unlike the studies mentioned,[1—7] in the present work, an aqueous solution of phosphoric acid was used as SLP, and the separation of organic acids was studied on this phase.

Experimental

The studies were performed on a chromatograph with two independent thermostats (for a steam generator and for columns) using a procedure described previously.[9] Steel columns 2 m×3 mm were used, and SLP (H_3PO_4 (87%)) was deposited on a Chromaton solid support in amounts of 15% and 20% of the weight of the support. The rate of a carrier gas (water vapor) was 30 mL min^{-1}.

Results and Discussion

As can be seen from Fig. 1, all lower acids are selectively separated on an aqueous solution of H_3PO_4, and the order of elution is reverse as compared to the normal order[11] (Fig. 2). Thus, the phase studied is superselective.

The temperature of separation exerts a strong effect on the selectivity of separation and its duration.[12] The temperature effect upon separation of fatty acids on polar phases is described in Refs. 13 and 14. In our work, an increase in the selectivity of separation of acids

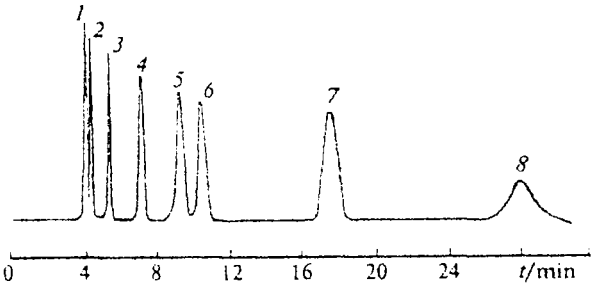

Fig. 1. Chromatogram of separation of fatty acids C_2—C_8 on a column with 20% H_3PO_4 at 115 °C. Acids: *1*, caprylic; *2*, enanthic; *3*, caproic; *4*, valeric; *5*, isobutyric; *6*, butyric; *7*, propionic; *8*, acetic.

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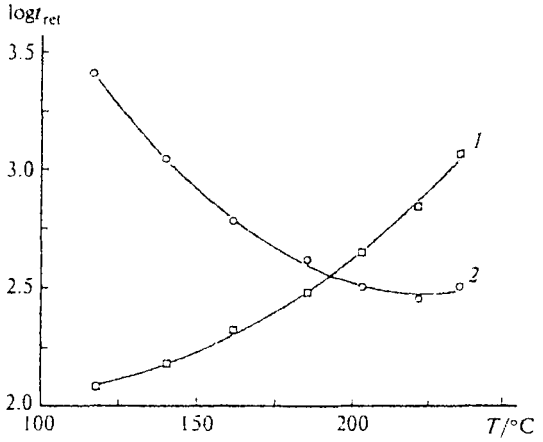

Fig. 2. Correlation dependence of the retention time of fatty acids C_2—C_8 on their boiling points on polar phases: *1*, "trimeric acid"[12] and *2*, water—H_3PO_4.

was observed as the temperature increased, which differed from the known SLP (Table 1). For example, as the temperature increased from 115 to 120 °C, the value of the relative retention of acetic acid (succinic acid as the standard) increased from 2.6 to 5.2, respectively. The unusually strong temperature effect observed is caused by two factors: 1) the role of hydrogen bonds, whose contribution depends sharply on the temperature; 2) an additional change in the phase composition (the content of water in the stationary phase decreases simultaneously as the temperature increases, and a certain concentration of acid in a solution of SLP corresponds to each temperature).

As can be seen from Table 2, the content of the acidic SLP on the solid support has a substantial effect on the retention parameters, especially for the first representatives of the homological series. This is likely the result of a change in the contribution of the adsorption to the retention values.[15] The selectivity of separation decreases as the molecular weight of acidic sorbates increases. This is especially pronounced for the phase containing a great amount of acid. The degree of separation of normal and isobutyric acids is sufficiently high

Table 1. Temperature effect on retention of fatty acids on an aqueous solution of phosphoric acid

Acid	Temperature of column			
	115 °C		120 °C	
	k	α	k	α
Acetic	46.3	2.6	42	5.2
Propionic	28.9	1.6	17.7	2.2
Butyric	17.9	1	7.3	1
Caproic	11.1	0.6	10.3	1.4
Caprylic	7.5	0.4	13.7	1.8

k is the capacity coefficient, α is the coefficient of relative retention.

Table 2. Effect of the content of acid in the sorbent on retention of fatty acids at 120 °C

Acid	Content of H_3PO_4 on support			
	15%		20%	
	k	α	k	α
Acetic	48.3	3.8	54.7	4.2
Propionic	23.7	1.9	25.7	2.0
Butyric	12	1	12.3	1
Isobutyric	8.3	0.7	9	0.75
Valeric	6.8	0.6	8.3	0.7
Enanthic	8	0.7	5.3	0.5
Caprylic	9.7	0.8	6	0.5

k is the capacity coefficient, α is relative retention.

Table 3. Retention of some cyclic and higher acids at 120 °C on H_3PO_4

Acid	k	α
Margaric	20.6	1
Stearic	39.7	1.9
Oleic	27.3	1.3
Salicylic	35	1.7
Benzoic	25.1	1.2

k is the capacity coefficient, α is the coefficient of relative retention.

and increases as the content of SLP on the solid support increases.

Our experiments showed that the chromatographic separation of acids C_{17-18}, as well as benzoic and salicylic acids, depends strongly on the molecular weight (Table 3). However, for higher acids the order of elution of saturated and unsaturated compounds is the same as that on inorganic salts with water vapor as the carrier gas.[8] A stronger retention of an acid with a higher polarity is observed in the benzoic—salicylic acid mixture.

As known,[13] the separation coefficient is mainly determined by the selectivity of SLP and efficiency of the column. The dependence of the efficiency of separation (the height equivalent to a theoretical plate (HETP)) on the pressure at the inlet of the column is presented in

Table 4. Dependence of HETP on the pressure at the inlet of the column for valeric and succinic acids

P/atm	HETP	
	Valeric acid	Succinic acid
1.28	3.8	3.2
1.37	3.3	2.8
1.46	4.7	3.1
1.56	5.4	3.9
1.69	5.5	5.1

Table 4. It can be seen that the smallest HETP is observed when the pressure at the inlet (P) is equal to 1.37 atm, which corresponds to the linear rate of the steam flow (V) of 12 cm s^{-1}.

Thus, based on the data obtained, it can be concluded that the use of steam chromatography and application of acidic SLP makes it possible to separate saturated and unsaturated acids in the free form and to perform chromatographic elution of fatty acids in the reverse order compared to other phases.

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