Steam chromatography of aliphatic and aromatic amines on packed columns with aqueous potassium hydroxide as the stationary liquid phase

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Aqueous alkali was proposed as the stationary liquid phase (SLP) for separation of amines by steam chromatography. Characteristic features of retention of amines of various structures were studied. The retention of primary and secondary amines on aqueous potassium hydroxide as the SLP differs fundamentally from that observed with common organic SLP. Primary amines are eluted in the following order: *n*-pentylamine < *n*-butylamine < *n*-propylamine < *n*-hexylamine < *n*-octylamine; for secondary amines, the following sequence was established: diethylamine < dibutylamine < dimethylamine. Higher-boiling tertiary amines containing ethyl and *n*-butyl radicals are eluted ahead of diamines containing the same radicals.

Key words: steam chromatography, aqueous alkaline stationary liquid phase, selectivity, aliphatic and aromatic amines, aliphatic *n*-alcohols, retention factor, relative retention time.

We showed previously[1—3] that in the separation of aliphatic alcohols under conditions of steam chromatography (SC), aqueous solutions of inorganic salts behave as superselective stationary liquid phases (SLP) and the alcohols are eluted in the order opposite to that of increasing molecular weights and boiling points.

A similar regularity has been established for fatty acids with an acidic aqueous SLP, namely, a solution of orthophosphoric acid.[2]

Since SLP are aqueous solutions of electrolytes, it could be expected that polar organic compounds of the R—Pol type, where R is a hydrocarbon radical and Pol is a polar group, for example, an alcoholic or acidic group, would be retained in the normal order. The behavior of volatile organic compounds containing amino groups on aqueous solutions of basic inorganic electrolytes had not been studied.

The prospects of using SC for the analysis of aliphatic and aromatic amines was demonstrated in a number of papers.[4—7] The molecules of the active carrier gas, *viz.*, steam with or without ammonia or hydrazine hydrate added, block efficiently the adsorption sites on the surface of the sorbent, which is a white diatomite macroporous support not impregnated with SLP or coated with a polysiloxane polymer with vinyl groups (SKTV-1). However, under these conditions, amines come out of the column in the order of increasing boiling points.

The purpose of this work was to study the regularities of retention of the volatile aliphatic and aromatic amines on an inorganic SLP, namely, an aqueous solution of KOH, under SC conditions (N_2 saturated with water vapor was used as the mobile phase).

Experimental

Gas chromatography studies were carried out on a Biokhrom-1 chromatograph (model 21) modified for SC. Nitrogen was saturated with steam using the device described previously[8] and delivered to the packed column through a heated pipeline. The sorbent with the inorganic SLP was prepared by the usual procedure in a china cup. Chemically pure grade potassium hydroxide (6 % (w/w)) was applied onto Chromaton N-AW (0.16—0.20 mm fraction) from a solution in bidistilled water. In order to avoid the formation of potassium carbonate during drying of the sorbent in air, water was removed *in vacuo*. The sorbent was packed into a stainless-steel column (200×0.3 cm) whose ends were stopped by Teflon chips. The column was connected to an injector and a flame ionization detector, the oven temperature was 70 °C, and N_2 with steam was fed (partial pressure of steam 250 Torr). After 3 h, a solution of KOH was formed on the sorbent surface; in our experiments, this solution functioned as the alkaline aqueous SLP.

Chromatography was carried out for C_3—C_8 aliphatic amines, C_2 and C_4 di- and trialkylamines, aromatic amines (pyridine, aniline, quinoline), and C_1—C_6 nonbranched aliphatic alcohols. The sorbates were introduced both individu-

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ally and as mixtures; the sample size was 0.02—0.20 μL. The injector temperature was 220 or 350 °C, and that of the detector was 250 °C.

The relative retention time (α), retention factor (k) (taking methane to be a nonsorbed compound), and peak resolution (R_S) were determined for all of the compounds.

Results and Discussion

Primary amines. SLP containing groups able to form hydrogen bonds ensure selective GLC separation of lower alkylamines.[4] Thus, in the case of poly(ethylene glycol) SLP, ethylamine is the first to be eluted and methylamine is the second; this is followed by other members of the homologous series, eluted in the order of increasing molecular weight; with a more polar SLP based on diglycerol, retention of alkylamines increases in a different order: *n*-propylamine < methylamine < ethylamine < *n*-butylamine < *n*-pentylamine.

The retention of a substance in the partition version of SC is determined, as in traditional GLC, by interaction of the substance with SLP and depends on the partition ratio between the mobile phase and the SLP.[9] The relative retention values of aliphatic amines in the aqueous alkaline SLP obtained in our study are presented in Table 1. It follows from these data that the relative retention values depend on the type of radical and the number of alkyl groups in the amine molecule. Primary alkylamines subjected to chromatography come out of the column in the following order: *iso*-butylamine < *n*-pentylamine < *n*-butylamine < *n*-propylamine < *n*-hexylamine < *n*-octylamine.

Table 1. Relative retention time (α) of polar organic compounds on KOH—H_2O as the stationary liquid phase

Compound	B.p./°C	α
Aliphatic amines		
n-Propylamine	49.0	0.07
n-Butylamine	77.8	0.06
iso-Butylamine	68.9	0.03
n-Pentylamine	117.0	0.05
n-Hexylamine	169.0	0.16
n-Octylamine	214.0	0.04
Dimethylamine	7.4	0.15
Diethylamine	55.5	0.03
Di-*n*-butylamine	159.0	0.05
Di-*n*-hexylamine	331.0	1.00
Triethylamine	89.4	0.04
Tri-*n*-butylamine	216.5	0.04
Aromatic amines		
Pyridine	115.6	0.05
Aniline	184.4	0.19
Quinoline	237.0	0.40
Aliphatic alcohols		
Methanol	64.7	0.72
Ethanol	78.4	0.21
n-Propyl alcohol	97.4	0.07
n-Butyl alcohol	117.0	0.07
n-Pentyl alcohol	138.4	0.06
n-Hexyl alcohol	157.5	0.16

Secondary amines. Dialkylamines subjected to chromatography on the aqueous alkaline SLP were eluted in the following order: diethylamine < dibutylamine < dimethylamine. The retention of low-boiling dimethylamine was somewhat longer than that of diethylamine and dibutylamine. The α parameter of dimethylamine was close to that of *n*-hexylamine, whose boiling point is ~20 times higher, and diethylamine and *n*-butylamine were retained equally. The selective properties of inorganic SLP ensure complete separation of dibutylamine and *n*-hexylamine (R_S = 2.0), whereas on an organic SLP, this pair of compounds is separated incompletely even in a capillary column.[10]

Tertiary amines. The molecules of tertiary amines, unlike primary and secondary amines, cannot form hydrogen bonds with one another or with SLP. It follows from the data of Table 1 that triethylamine emerges

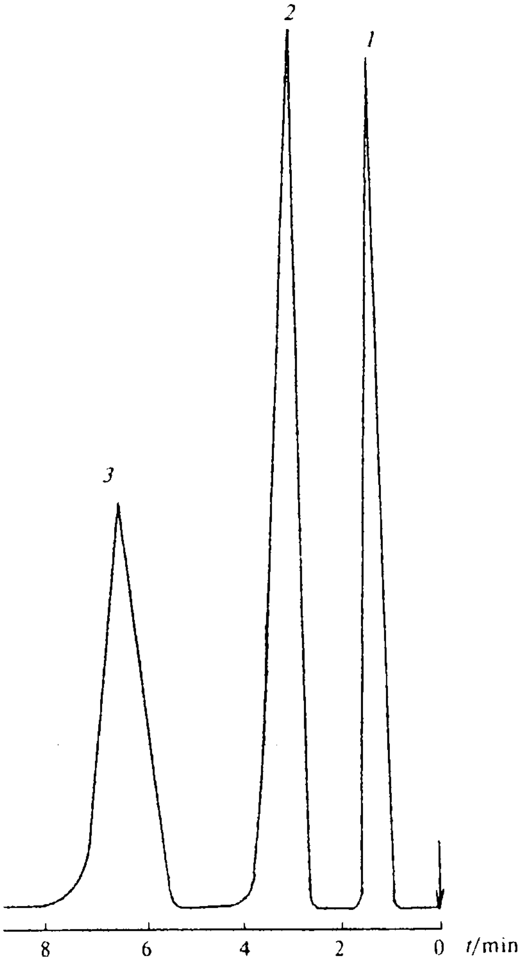

Fig. 1. Chromatogram of a mixture of aromatic amines obtained by the VPC method on a sorbent with aqueous alkaline stationary phase: (*1*) pyridine, (*2*) aniline, (*3*) quinoline.

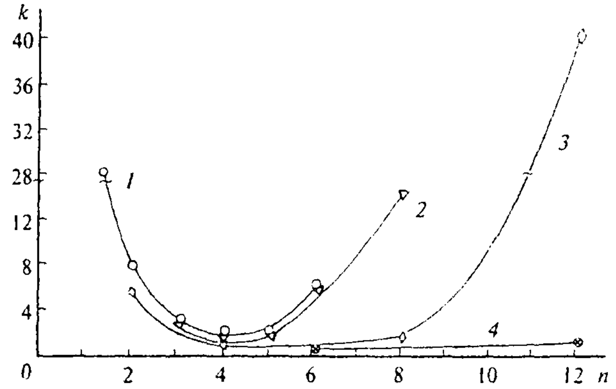

Fig. 2. Correlation dependences of the retention factor (*k*) of aliphatic alcohols (*1*) and primary (*2*), secondary (*3*), and tertiary (*4*) amines on the number of carbon atoms (*n*) in the molecule obtained on an aqueous alkaline SLP (KOH) under SC conditions.

before diethylamine, and the retention in the series of primary, secondary, and tertiary *n*-butylamines on an aqueous alkaline SLP changes in the following order: tributylamine < dibutylamine < butylamine.

Aromatic amines. A chromtogram of aromatic amines obtained under SC conditions using an aqueous alkaline SLP is shown in Fig. 1. Unlike the series of aliphatic amines, aromatic amines were eluted from the column in the order of increasing molecular weight and boiling point; high resolution was attained for pyridine/aniline (R_s = 2.0) and aniline/quinoline (R_s = 2.5) pairs. However, the relative retention times of aromatic amines and some aliphatic amines were identical, for example, those of pyridine and *n*-pentylamine, or quinoline and *n*-octylamine.

Aliphatic alcohols. The aqueous alkaline SLP ensured selective separation of a mixture of nonbranched aliphatic alcohols. The first four members of this homologous series were eluted in the order opposite to the order of increasing molecular weight and boiling point; previously this had been observed for electrolyte water—salt SLP, for example, an aqueous solution of $NaNO_3$.[1]

The following sequence of retention of the nonbranched C_1—C_6 alcohols on aqueous KOH was established: *n*-butyl alcohol < *n*-propyl alcohol < *n*-pentyl alcohol < ethanol + *n*-hexyl alcohol < methanol. Fig. 2 shows the retention factor for alcohols as a function of the number of C atoms in the molecule, which has an inversion point corresponding to *n*-pentyl alcohol. A similar variation pattern is observed for primary amines, with an inversion point corresponding to *n*-butylamine, and for secondary amines; however, in the latter case, the minimum is broader.

Thus, chromatographic data imply that specific interactions, mainly intermolecular hydrogen bonds with the aqueous alkaline SLP, play a crucial role in the separation of primary and secondary aliphatic amines and aliphatic alcohols. The regularities found for the retention of primary and secondary aliphatic amines during SC on the SLP studied here (an aqueous solution of KOH) differ fundamentally from those known for conventional organic SLP in gas and steam chromatography.

References

1. L. G. Berezkina, V. G. Berezkin, E. N. Viktorova, E. Yu. Sorokina, and T. G. Andronikashvili, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1733 [*Russ. Chem. Bull.*, 1996, **45**, 1642 (Engl. Transl.)].
2. E. N. Viktorova, V. G. Berezkin, Yu. S. Drugov, and V. N. Lipavskii, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 497 [*Russ. Chem. Bull.*, 1997, **46**, 350 (Engl. Transl.)].
3. V. G. Berezkin, E. N. Viktorova, and E. Yu. Sorokina, in *Khromatograficheskie metody v khimii, biologii i meditsine* [*Chromatographic Methods in Chemistry, Biology, and Medicine*], Minsk, 1995, p. 10 (in Russian).
4. A. A. Anderson, *Gazovaya khromatografiya aminosoedinenii* [*Gas Chromatography of Amino Compounds*], Zinatne, Riga, 1982, 374 pp. (in Russian).
5. A. Nonaka, *Anal. Chem.*, 1972, **44**, 271.
6. A. Nonaka, in *Advances of Chromatography*, Eds. J. C. Giddings and R. A. Reller, Dekker, New York, 1975, No. 12, 223.
7. B. A. Rudenko and M. A. Baidarovtseva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, 2634 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1972, **21** (Engl. Transl.)].
8. L. G. Berezkina, E. Yu. Sorokina, and G. F. Shalygin, *Zh. Fiz. Khim.*, 1996, **70**, 1124 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
9. M. S. Vigdergauz, A. V. Garusov, V. A. Ezrets, and V. L. Semkin, *Gazovaya khromatografiya s neideal'nymi elyuentami* [*Gas Chromatography with Nonideal Eluents*], Nauka, Moscow, 1980 (in Russian).

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