Retention of organic compounds in capillary gas chromatography using humid carrier gases

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The influence of humid carrier gases (nitrogen and carbon dioxide) on the retention of polar compounds in a capillary column with polypropylcyanophenylsiloxane stationary liquid phase OV-225 was studied. It is noted that when humid carbon dioxide is used as the carrier gas, the retention of primary amines sharply increases.

Key words: humid carrier gas, retention factor, selectivity.

Previously,[1–5] it has been shown that the relative retention of compounds subjected to chromatographic analysis depends substantially on the nature of the mobile phase used. This effect becomes especially pronounced on passing from dry to humid gases; it can be observed even at a low moisture content at the partial pressure $p_{H_2O} \approx 20$ Torr.[6] When humid carbon dioxide is used, an additional very sharp increase in the retention of organic compounds with basic properties (primary and secondary amines) can be observed due to the acid—base reactions occurring between the carrier gas and the sorbate in the stationary liquid phase.[7] As a consequence, both the distribution constant and the retention time increase. However, under conditions of conventional capillary chromatography, this new effect was observed only for one polar stationary liquid phase (SLP), poly(ethylene glycol) PEG-20M, whereas for polydimethylsiloxane SE-30, no effect of the nature of the carrier gas was found.

Therefore, it has been of interest to study the specific features of gas chromatography of polar organic compounds with humid carrier gases in capillary columns with polar polysiloxane OV-225, which contains 25% phenyl, 25% cyanopropil, and 1% vinyl side groups.

Experimental

Chromatographic retention was measured on an LKhM-8MD chromatograph (version 5) modernized for work with capillary columns using the following carrier gases: (1) nitrogen; (2) nitrogen saturated with water vapor at room temperature; (3) carbon dioxide; and (4) carbon dioxide saturated with water vapor at room temperature. To prepare a humid carrier gas, the setup was equipped with an additional column filled with a solid packing with some amount of water added. The relative retention values were determined by subjecting to chromatographic analysis a model mixture of sorbates, which contained amines, naphthalene, octan-1-ol, and other organic compounds with boiling points between 100 and 250 °C (Table 1).

The dependence of retention of the nature of the carrier gas was studied using a high-performance quartz capillary column (18 m × 0.2 mm) with a cross-linked film of polypropylcyanophenylsiloxane phase (OV-225) of thickness $d_f = 0.4$ μm at 120 and 145 °C. The specific efficiency of the column with respect to 2,6-dimethylphenol at 140 °C was 2900 tp m^{-1} (the number of theoretical plates per meter of column length) at $k = 5.3$ (k is the retention factor).

The relative retention times of sorbates were calculated using octan-1-ol as the standard. The volume of liquid samples introduced into the gas chromatograph was 0.1—0.4 μL. The temperature of the column thermostat was maintained with an accuracy of ±0.5 °C. The root-mean square uncertainty of retention values was 0.056 for dry and humid nitrogen and 0.099 and 0.056 for dry and humid carbon dioxide, respectively.

Results and Discussion

Tables 2 and 3 present the retention factors k and the relative retention values α,[8] obtained for a fused silica capillary column with OV-225 at 120 and 145 °C.

Table 1. Charactereistics of the compounds subjected to chromatography

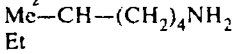
Name	Formula	B.p./°C
n-Amylamine	$AllNH_2$	104.0
n-Hexylamine	$GeNH_2$	131.0
Dibutylamine	Bu_2NH	161.0
2-Ethylhexylamine	 $\underset{Et}{Me{-}CH}{-}(CH_2)_4NH_2$	169.0
n-Octylamine	$C_8H_{17}NH_2$	178.9
Octan-1-ol	$Me(CH_2)_7OH$	194.5
Di-*n*-hexylamine	Ge_2NH	236.5
Naphthalene	$C_{10}H_8$	218.0
2,6-Dimethylaniline	$PhNMe_2$	214.0
2,6-Dimethylphenol	$C_8H_{10}O$	212.0
Di-*n*-octylamine	$[Me(CH_2)_7]_2NH$	297.8

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Table 2. Change in the retention factor (k) for various mobile phases in a capillary column with the polypropylcyanophenylsiloxane phase (OV-225) at 120 °C

Sorbate	$k(N_2)$	$k(N_2+H_2O)$	$\Delta k(N_2+H_2O, N_2)$	$\Delta k_r(N_2+H_2O, N_2)$ (%)	$k(CO_2+H_2O)$	$\Delta k(CO_2+H_2O, N_2+H_2O)$	$\Delta k_r(CO_2+H_2O, N_2+H_2O)$ (%)
n-Amylamine	0.24	0.26	0.02	7.7	0.39	0.13	33
n-Hexylamine	0.46	0.54	0.08	15.0	0.71	0.17	24
2-Ethylhexylamine	1.06	1.08	0.02	1.8	1.49	0.41	28
n-Octylamine	1.33	1.46	0.13	8.9	2.01	0.55	27
Octan-1-ol	2.66	2.75	0.09	3.3	3.37	0.62	18
Di-*n*-hexylamine	4.46	4.57	0.11	2.4	4.76	0.19	4

Note. $\Delta k(G_1,G_2) = k(G_1) - k(G_2)$, where G_1 and G_2 are carrier gases 1 and 2, respectively; $\Delta k_r(G_1,G_2) = [\Delta k(G_1,G_2)/k(G_2)] \cdot 100 = \{[k(G_1) - k(G_2)] \cdot 100\}/k(G_2)$.

Table 3. Change in the relative retention (α) for various mobile phases in a capillary column with the polypropylcyanophenylsiloxane phase OV-225 (octan-1-ol as the standard) at 120 °C

Sorbate	$\alpha(N_2)$	$\alpha(N_2+H_2O)$	$\Delta\alpha(N_2+H_2O, N_2)$	$\Delta\alpha_r(N_2+H_2O, N_2)$ (%)	$\alpha(CO_2+H_2O)$	$\Delta\alpha(CO_2+H_2O, N_2+H_2O)$	$\Delta\alpha_r(CO_2+H_2O, N_2+H_2O)$ (%)
n-Amylamine	0.09	0.095	0.005	5.3	0.11	0.015	14.0
n-Hexylamine	0.17	0.20	0.03	15.0	0.21	0.01	4.8
2-Ethylhexylamine	0.40	0.39	0.01	2.5	0.44	0.05	11.0
n-Octylamine	0.50	0.53	0.03	5.7	0.59	0.06	10.1
Di-*n*-hexylamine	1.67	1.66	0.01	0.6	1.41	0.25	15.0

Note. $\Delta\alpha(G_1,G_2) = \alpha(G_1) - \alpha(G_2)$; $\Delta\alpha_r(G_1,G_2) = [\Delta\alpha(G_1,G_2)/\alpha(G_2)] \cdot 100$ (%).

The use of humid nitrogen as a carrier gas results in a larger retention of primary amines, which is apparently due to the increase in the polarity of the OV-225 phase following the dissolution of water vapor in it, *i.e.*, its moistening. The retention of octan-1-ol and secondary amines increases to a lesser extent, probably due to the fact that these compounds form weaker hydrogen bonds with the water-containing OV-225 phase.

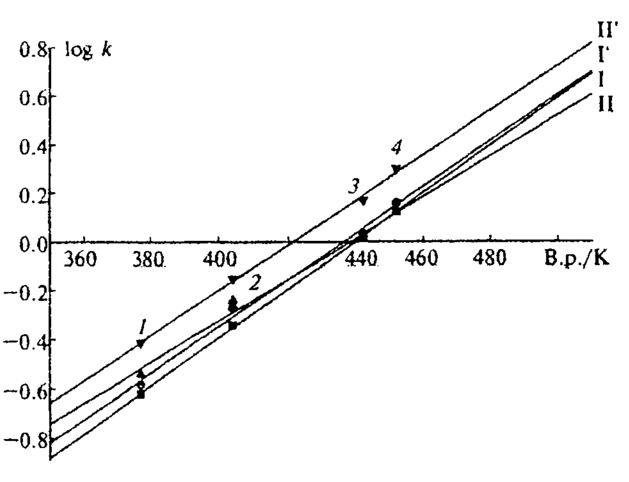

Fig. 1. Dependence of log$k$ on the boiling points (b.p.) of primary amines (*1*, *n*-amylamine; *2*, *n*-hexylamine; *3*, 2-ethylhexylamine; *4*, *n*-octylamine) with dry nitrogen (I), humid nitrogen (I'), dry carbon dioxide (II), and humid carbon dioxide (II') as carrier gases.

If neutral nitrogen in the gas—water vapor binary mixture, acting as the carrier gas, is replaced by carbon dioxide, retention of primary amines sharply increases with respect to that observed for humid nitrogen, whereas retention of secondary amines increases to a substantially lesser extent.

The observed sharp increase in the retention of basic amines with acidic carbon dioxide can be explained by assuming that the acid—base equilibrium in the SLP shifts toward ionization of the amine and this increases the distribution constant of the amine between the SLP and the gaseous phase. Previously we have found a similar effect when polar poly(ethylene glycol) PEG-20M was used as the SLP.[7] In the case of a humid carrier gas and a polar SLP, fast reversible dissociation of basic sorbate B occurs in the stationary phase

$$B_l + H_2O \rightleftharpoons BH^+ + OH^-. \qquad (1)$$

If an acidic carrier gas (*e.g.*, CO_2) is employed, it reacts in the SLP with water to increase the hydrogen ion concentration in this phase

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+. \qquad (2)$$

The interaction of hydrogen ions with hydroxyl ions shifts equilibrium in reaction (1) to the right; consequently, the overall distribution constant of sorbate B between the SLP and the gaseous phase increases

$$K_{B_{eff}} = [BH^+ + B_l]/B_g. \qquad (3)$$

Table 4. Change in the retention factor (*k*) for various mobile phases in a fused silica capillary column with the polar OV-225 at 145 °C

Sorbate	$k(N_2)$	$k(N_2+H_2O)$	$\Delta k(N_2+H_2O, N_2)$	$\Delta k_r(N_2+H_2O, N_2)$ (%)	$k(CO_2+H_2O)$	$\Delta k(CO_2+H_2O, N_2+H_2O)$	$\Delta k_r(CO_2+H_2O, N_2+H_2O)$ (%)
n-Hexylamine	0.23	0.27	0.04	15	0.30	0.00	6.7
n-Octylamine	0.64	0.73	0.09	12	0.68	0.05	6.8
Octan-1-ol	1.09	1.22	0.13	11	1.29	0.07	5.4
Di-*n*-hexylamine	1.90	1.92	0.02	1.04	1.88	0.04	2.1
Naphthalene	2.84	3.25	0.41	13	3.39	0.12	3.5
2,6-Dimethylaniline	3.29	3.68	0.39	11	3.78	0.10	2.6
2,6-Dimethylphenol	3.77	4.28	0.51	12	4.40	0.12	2.7
Di-*n*-octylamine	11.29	11.65	0.36	3.1	11.28	0.37	3.2

Note. For designations, see Table 2.

Thus, the use of humid carbon dioxide as the carrier gas in a system with polar SLP should increase the overall distribution constant of a basic sorbate B in the SLP—carrier gas system and, hence, it should increase the retention time of sorbate B. The experimental results obtained fully coincide with the above interpretation of the increase in the retention of basic sorbates (see Table 2). The relative retention values α follow a similar trend (see Table 3).

In order to elucidate the influence of the temperature factor on the retention of amines and polar compounds in humid carrier gases both for neutral N_2 and for acidic CO_2, retention measurements were carried out at two temperatures, 120 °C (see Table 2) and 145 °C (Table 4). It can be seen from the data contained in Table 4 that at higher temperatures (145 °C), the increases in the retention factors and the relative retention times are also observed; furthermore, this is also true for compounds of classes other than amines. It should be noted that an increase in the temperature of the analysis allows one to eliminate almost completely the slight blurring of the "tails" of chromatographic zones observed for primary amines at 120 °C.

When studying various chromatographic phenomena in GLC, researchers widely use logarithmic dependences of retention on the boiling points of compounds under analysis (see, for example, Ref. 9).

Figure 1 shows the plot for the logarithms of the retention factor k_i *versus* boiling points of compounds subjected to chromatographic separation with four carrier gases: nitrogen, humid nitrogen, carbon dioxide, and humid carbon dioxide. These plots imply that moistening of the carrier gas markedly increases the retention of polar compounds and this effect is especially pronounced for primary amines when humid carbon dioxide is used.

The data reported here demonstrate that the increase in the retention factor for a polar sorbate and the polar polypropylcyanophenylsiloxane SLP (OV-225) observed when humid carrier gases are used is a general feature. A noticeable increase is observed for both the retention factor and the relative retention time. In addition, the substantial effects of the change in the relative retention of primary amines for the use of humid carrier gases, especially, carbon dioxide, must be of interest for analytical purposes.

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