Influence of a water vapor admixture in the carrier gas on capacity coefficients of polar organic compounds

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The influence of a water vapor admixture in helium, nitrogen, and carbon dioxide on capacity coefficients of C_3—C_5 alcohols and pyridine during chromatography process in capillary columns with polar (PEG-20M) and nonpolar (SE-30) stationary phases was studied. The introduction of a water admixture into the carrier gas increases the capacity coefficient of polar organic compounds on the capillary column with PEG-20M and has almost no effect on this value in the case of SE-30. The change in retention of polar organic compounds on the capillary column with the PEG-20M polar phase occurs due to a change in the properties of the stationary phase when it adsorbs water from the mobile phase.

Key words: gas liquid chromatography, capillary chromatography, capacity coefficient, retention, water-containing mobile phase, stationary phase, influence on retention.

We have shown in recent years[1—3] that the nature of the carrier gas and its concentration (pressure) in the gas phase have a noticeable effect on the relative retention values of compounds even under conditions of standard gas chromatographic experiments. Therefore, it is reasonable to consider the further use of this phenomenon to perform a purposeful action of the carrier gas on chromatographic separation. One way is to use mixed carrier gases, in which a standard carrier gas contains an added admixture that interacts specifically with components of the mixtures being separated and is well soluble in the stationary liquid phase (SLP). The aim of this work is to estimate the influence of a water admixture in the gaseous mobile phase on the retention parameters of chromatographed compounds.

It is noteworthy that we have studied previously[4] the effect of water vapor on the retention index of chromatographed polar compounds, *i.e.*, we considered the analytical aspect of the influence of the moist carrier gas on the relative retention values. In this work, we focus our attention on the physicochemical regularities related to a change in retention times when a moist carrier gas is used.

In the chromatographic system studied, water was the additive to the carrier gas. Water is capable of specific interaction with polar sorbents to form hydrogen bonds. Hydrophilic polyethylene glycol PEG-20M and hydrophobic polydimethylsiloxane SE-30 were chosen as SLP. Chromatographic measurements were carried out on capillary columns, since this type of columns is most widely used in analytical practice and makes it possible to perform measurements with the highest accuracy and with minimum effect of adsorption of chromatographed compounds on interfacial surfaces of SLP.[5]

Experimental

An LKhM-8MD (model 5) modified gas chromatograph with a flame-ionization detector (FID) (plant "Khromatograf," Moscow) was used for chromatographic measurements. Note that the FID is a detector, which is "transparent" for water vapor that is present in the mobile phase.

Retention times were measured by an I-02 modified integrator with a resolution of 0.1 s. At the minimum retention time of ~130 s, the accuracy of measurements was >0.1%. The value of mean square deviation for measuring the capacity coefficient (k) was not usually greater than $(1—5) \cdot 10^{-3}$, which corresponds to ~0.1%. Retention times were measured at different temperatures on the following quartz capillary columns: (1) 30 m × 0.25 mm, SLP was PEG-20M, the thickness of the SLP layer was 0.5 μm, the temperature of the column was 70 °C; (2) 30 m × 0.25 mm, SLP was SE-30, the thickness of the SLP layer was 1 μm, the temperature of the column was 55 °C; and (3) 25 m × 0.20 mm, SLP was SE-30, the thickness of the SLP layer was 0.11 μm, the temperature of the column was 90 °C.

Helium, helium with water vapor, carbon dioxide, carbon dioxide with water vapor, nitrogen, and nitrogen with water vapor were used as carrier gases. They can be arranged in the following series based on closeness to the ideal carrier gas: $CO_2 < N_2 <$ He. The values of the second mixed virial coefficients for benzene in helium,[6] in nitrogen,[6] and in carbon dioxide[7] can be presented as the characteristics of the "nonideal" character of these gases: 49.0±8.0, 91.0±6.0, and 257.0±6.0 cm^3, respectively.

The specified pressure of water vapor in the carrier gas was created by passage of a carrier gas flow at room temperature through a glass bubbler filled with water prior to its admission to a device for the sample inlet. The pressure of saturated water vapor at ~20 °C was ~22 Torr (~1.5%).

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Table 1. Influence of a small water vapor additive to the carrier gas (G_j = He, CO_2) on the capacity coefficients of the chromatographed compounds $k_i(G_j)$ on the capillary column with the polar PEG-20M SLP at 70 °C

Chromatographed compound	k_i(He)	k_i(CO_2)	ρ_i(He,CO_2) (%)	k_i(He+H_2O)	ρ_i(He,He+H_2O) (%)	k_i(CO_2+H_2O)	ρ_i(CO_2,CO_2+H_2O) (%)
n-Propanol	1.818±0.002	1.768±0.002	2.7	1.896±0.002	−4.3	1.843±0.002	−4.2
Isobutyl alcohol	2.579±0.003	2.501±0.002	3.0	2.674±0.002	−3.7	2.591±0.003	−3.6
n-Butanol	3.740±0.005	3.618±0.003	3.3	3.885±0.002	−3.9	3.756±0.004	−3.8
Pyridine	5.042±0.007	4.857±0.003	3.7	5.164±0.003	−2.4	4.973±0.005	−2.4
n-Pentanol	7.680±0.009	7.390±0.004	3.8	7.937±0.005	−3.3	7.646±0.003	−3.5

Table 2. Influence of a small water vapor additive to the carrier gas (G_j = He, CO_2) on the capacity coefficients of the chromatographed compounds $k_i(G_j)$ on the capillary column with the nonpolar SE-30 SLP at 55 °C

Chromatographed compound	k_i(He)	k_i(CO_2)	ρ_i(He,CO_2) (%)	k_i(He+H_2O)	ρ_i(He,He+H_2O) (%)	k_i(CO_2+H_2O)	ρ_i(CO_2,CO_2+H_2O) (%)
n-Propanol	1.815±0.001	0.796±0.001	2.3	0.817±0.001	−0.2	0.801±0.001	−0.6
Isobutyl alcohol	1.504±0.001	1.462±0.001	2.8	1.509±0.001	−0.3	—	—
n-Butanol	2.032±0.001	1.970±0.002	3.0	2.038±0.001	−0.2	1.984±0.002	−0.7
Pyridine	3.786±0.001	3.660±0.003	3.3	3.800±0.001	−0.4	3.687±0.003	−0.7
n-Pentanol	4.918±0.001	4.734±0.003	3.7			4.766±0.002	−0.6

The split ratio of the flow at the inlet of the capillary column was 1 : 100 and 1 : 150, and the pressure of the carrier gas at the inlet of the capillary column was 1.0 atm. Samples were introduced at 275 °C. The sensitivity of FID was $1 \cdot 10^{-11}$ A for the detector full scale deflection. The mixture analyzed contained 1—2% chromatographed compounds in hexane.

The mixture was injected into the chromatograph by a 1-μL microsyringe, and a sample contained 0.1—0.5 μL of the liquid mixture and 0.5 μL of methane. Each value of retention time was determined as the average of data of four or five experiments.

Results and Discussion

The results of the study of the influence of the carrier gas on the capacity coefficients (k_i) of the chromatographed compounds for different phases (SE-30 and PEG-20M) are presented in Tables 1—3. For the estimation of the effect of the carrier gas and additives on the capacity coefficients, we used the quantity $\rho_i(G_1,G_2)$, which is the relative change (in %) of the capacity coefficient $k_i(G)$ for the *i*th compound chromatographed in the experiment when one carrier gas (G_1) is replaced by another gas (G_2) (Eq. (1)).

$$\rho_i(G_1,G_2) = \frac{k_i(G_1) - k_i(G_2)}{k_i(G_1)} \cdot 100 \qquad (1)$$

The data presented in Table 1 suggest the following. First, on a capillary column with the polar SLP, when the helium carrier gas is replaced by carbon dioxide, the capacity coefficient decreases noticeably, and the value of its relative change increases monotonically from 2.7% (for *n*-propanol) to 3.8% (for *n*-pentanol). Note that according to our data and published data,[1—3,8—10] a decrease in the capacity coefficients of sorbates is observed on going from helium to any other carrier gas. Second, the introduction of small additives of water to both helium and carbon dioxide results not in a decrease in the capacity coefficients (as for other carrier gases), but in their increase, and the observed increase in $\rho_i(G_1,G_2)$ is rather high (by 2.4—4.3%) when the water content in the carrier gas is only ~1.5%. Note that the magnitude of the change in the capacity coefficients in the case of a water-containing carrier gas depends on the nature of the chromatographed compound.

Table 3. Influence of a small water vapor additive to the carrier gas (N_2) on the capacity coefficients of the chromatographed compounds on the capillary column with the nonpolar SE-30 SLP at 90 °C

Chromatographed compound	k_i(N_2)	k_i(N_2+H_2O)	ρ_i (%)
n-Decane	1.047±0.001	1.049±0.001	0.19
n-Octanol	1.527±0.002	1.528±0.001	0.06
2,6-Dimethylphenol	1.820±0.001	1.826±0.001	0.33
n-Undecane	2.055±0.001	2.059±0.001	0.19
N,*N*-Dimethylaniline	2.605±0.001	2.608±0.001	0.12
Naphthalene	3.005±0.002	3.008±0.002	0.09
n-Dodecane	4.017±0.001	4.026±0.002	0.22

It is of interest that the change in the capacity coefficients of the sorbates when helium is replaced by carbon dioxide is lower than that when helium is replaced by moist (~1.5% H_2O) helium.

In the analysis of the aforementioned unusual properties of the moist carrier gas, it is reasonable to answer the following question: what phase (gas or liquid) does change its properties to a greater extent in the presence of a water admixture in the carrier gas? For this purpose, using two carrier gases (nitrogen and helium), we carried out similar experiments on the nonpolar hydrophobic SLP — polydimethylsiloxane SE-30 (see Tables 2 and 3), in which the solubility of water is very low. For this SLP, it is reasonable to assume that a change in the properties of SE-30 due to dissolution of water can be neglected and, hence, all observed changes in retention should be related only (or predominantly) to the gas phase. The results obtained (*cf.* Tables 1 and 2, 3) indicate that when the polar SLP is used, the effect of water vapor is approximately an order of magnitude higher than that in the case of the nonpolar SLP.

Let us consider this problem in the light of the known theoretical concepts, which are presented rather completely and critically in the monograph.[9] According to the data in this work and our recent results,[1] the dependence of the capacity coefficient k_i of the chromatographed compound on the nature and pressure of the carrier gas used (in the region of small pressures to 10—20 atm) can be described by the following equations:

$$k_i = k_{i,0} + k_{i,0} \cdot \beta_i \cdot p_{av}, \tag{2}$$

$$\beta_i = \beta_g + \beta_{liq}, \tag{3}$$

$$\beta_g = (2B_{12} - V_{liq}^{\infty})/(RT), \tag{4}$$

$$\beta_{liq} = \lambda\left[1 - \left(\frac{\partial \ln \gamma_{liq}^{\infty}}{\partial X_2}\right)_{X_2=0}\right], \tag{5}$$

$$p_{av} = p_0\left[\frac{3}{4}\cdot\frac{(p_i/p_0)^4 - 1}{(p_i/p_0)^3 - 1}\right], \tag{6}$$

where $k_{i,0}$ is the limiting (invariant) value of the capacity coefficient at the "zero" pressure of the carrier gas;[1] β_i is the net proportionality factor caused by the effect of the carrier gas on the retention values; β_g and β_{liq} are the partial proportionality factors caused by the interaction of the carrier gas and sorbate in the gas and liquid phases, respectively (Eqs. (2) and (3)); B_{12} is the second mixed virial coefficient of the carrier gas and sorbate; V_{liq}^{∞} is the partial molar volume of the sorbate when it is infinitely diluted in SLP; R is the universal gas constant; T is the absolute temperature; λ is the molar solubility of the carrier gas in SLP; γ_{liq}^{∞} is the activity coefficient of the sorbate in SLP for infinite dilution; X_2 is the molar fraction of the carrier gas dissolved in SLP; p_{av} is the average pressure of the carrier gas in the column; p_i and p_0 are the pressures of the carrier gas at the inlet and outlet of the column, respectively.

Note that, according to the common viewpoint, the processes associated with dissolution of the carrier gas in SLP can be neglected. For example, in the opinion of the authors of the monograph,[9] for standard carrier gases used in gas liquid chromatography, such as helium, hydrogen, nitrogen, argon, and oxygen, the error caused by the assumption that they are insoluble at room temperature is negligible ($<5 \cdot 10^3$ mm^3 mol^{-1}). It is also shown[7] that at 80 °C for the carbon dioxide—*n*-octadecane system, the error related to the solubility of the carrier gas in SLP is sufficiently low. Therefore, in the estimation and interpretation of experimental data on the influence of the carrier gas on retention, many researchers (see, *e.g.*, Ref. 11) assume *a priori* that $\beta \approx \beta_g$, *i.e.*, they take into account only processes occurring in the gas phase.

In this work, to reveal the role of the gas and liquid phases, we suggested a new approach: the active component (water) is almost insoluble in one of the phases (hence, the role of SLP in the processed discussed can be neglected), whereas water is soluble in the second polar phase (PEG-20M), and the influence of water dissolved in SLP should be taken into account.

It was of interest to estimate the relative contribution of the chromatographic processes occurring in the gas phase and polar SLP. For this purpose, we used the fact (see, *e.g.*, Ref. 12) that the β value for the helium carrier gas is low, and it can be approximately assumed that $k_i(\mathrm{He}) = k_{i,0}(\mathrm{He})$. In this case,

$$\rho_{i,p} = \frac{k_{i,p}(\mathrm{He}) - k_{i,p}(\mathrm{He+H_2O})}{k_{i,p}(\mathrm{He})}\cdot 100 = \\ = -\beta_{i,p}(\mathrm{He+H_2O}) \cdot p_{av} \cdot 100, \tag{7}$$

$$\rho_{i,n} = \frac{k_{i,n}(\mathrm{He}) - k_{i,n}(\mathrm{He+H_2O})}{k_{i,n}(\mathrm{He})}\cdot 100 = \\ = -\beta_{i,n}(\mathrm{He+H_2O}) \cdot p_{av} \cdot 100, \tag{8}$$

where the indices "p" and "n" mean that this value was measured on the polar (PEG-20) and nonpolar SLP, respectively; the mobile phase is indicated in parentheses. Since $\beta_{i,n} = \beta_{i,g}$ and $\beta_{i,p} = \beta_{i,g} + \beta_{i,liq}$, we can write

$$\gamma = \frac{\beta_{i,liq}}{\beta_{i,g}} \approx \frac{\beta_{i,p} - \beta_{i,g}}{\beta_{i,g}} \approx \frac{\rho_{i,p} - \rho_{i,n}}{\rho_{i,n}}. \tag{9}$$

Using the data in Tables 1 and 2, we can estimate the γ value. So, $\rho_{i,p}(\mathrm{He,He+H_2O}) \approx 3.5\%$, $\rho_{i,n}(\mathrm{He,He+H_2O}) \approx 0.27\%$, and hence, $\gamma \approx 12$.

Thus, in the case of the $(\mathrm{H_2O}$+gas)/PEG-20M system considered, the main contribution to the retention is related to a change in the properties of SLP due to the dissolution of the polar component ($\mathrm{H_2O}$) in SLP, and the effect of the nature of the carrier gas on the retention values (unlike those described previously[9,11] for other systems) is almost completely the result of a change in the properties of SLP.

Note that the relative changes in the capacity coefficients of the chromatographed compounds when the dry carrier gas is replaced by the moist gas are several percent and almost independent of the nature of the gases used (see Table 1), although helium and carbon dioxide differ substantially in their physicochemical parameters.

Undoubtedly, the effect considered is of interest for analytical purposes. The use of admixtures, which interact specifically with the components of the mixture separated and (or) modify SLP, in carrier gases provides additional possibilities for controlling chromatographic separation.

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