Solubility of some carrier gases in stationary liquid phases used in gas-liquid chromatography

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A simple gas chromatographic technique for the determination of the solubility of gases in low-volatile liquids was proposed. The procedure is based on the introduction of a certain volume of the liquid saturated with the gas at atmospheric pressure into a gas chromatograph. The solubility of carrier gases (helium, hydrogen, nitrogen, methane, and carbon dioxide) in various stationary liquid phases (SLP), such as pentadecane, polydimethylsiloxane PMS-100, and polyethylene glycol PEG-600, was studied. The carrier gases studied can be arranged in the following series by solubility in SLP: He $<$ H_2 $<$ N_2 $<$ CH_4 $<$ CO_2. This order coincides with the series reflecting change in the retention values in GLC for different carrier gases.

Key words: gases, solubility, gas-liquid chromatography, stationary liquid phases, carrier gas.

It has been shown in recent years (see, *e.g.*, Refs. 1—3) that the retention and selectivity of separation in capillary GLC depend on the nature and pressure of the carrier gas. It has been assumed and substantiated during the study of this phenomenon that a change in the partition constants of chromatographed compounds is mainly determined by a change in the properties of the stationary liquid phase (SLP) due to the dissolution of the carrier gas in the latter.

Studies on the determination of the solubility of carrier gases in SLP are unavailable. Therefore, it was reasonable and interesting to determine experimentally the solubility in SLP of such gases as helium, hydrogen, nitrogen, methane, and carbon dioxide and to reveal the parallelism in the series of the gas solubility and their influence on the retention values.

Since the determination of the gas solubility in real widely used SLP is associated with methodological difficulties, we chose comparatively low-viscous liquids: pentadecane, polydimethylsiloxane PMS-100, and polyethylene glycol PEG-600, which can be considered as close analogs of such widely used SLP as hydrocarbons (squalane, apiesone), polydimethylsiloxanes (SE-30 and others), polar polyethers (PEG-20M), and others.

Note that methane was included in the number of gases studied, because it is used as the carrier gas when a mass spectral detector is applied in the chemical ionization regime.

In connection with the aforesaid, the purpose of this work is the determination of the solubility of the gases indicated in pentadecane, polydimethylsiloxane PMS-100, and polyethylene glycol PEG-600.

Experimental

The known (see, *e.g.*, Refs. 4 and 5) methods of determination of the solubility of gases in liquids are usually characterized by a high accuracy; however, the apparatus and procedure of measurements are sufficiently complicated. Since, for the purpose of our study, the error of measurements of the gas solubility in model SLP can be restricted by ±10%, we proposed and used a simple method based on the gas chromatographic determination of the volume of the gas dissolved in the known volume of the liquid phase.

The gas solubility in the model SLP was determined within the 20—90 °C temperature range. Each of the SLP studied was saturated with one of the gases at atmospheric pressure using a bubbler. The gas passed through a stainless tube in the form of a coil with a length of 2 m and an inner diameter of 0.5 mm, which was immersed into the SLP to the bottom of the bubbler. To create finer bubbles, the outlet end of the tube was flattened. The second tube, whose end was above the SLP level, served for removal of the gas into the atmosphere. Small glass cylindrical 4.5-mL vessels with screwed caps and elastic upper packing, through which gas-supplying and gas-removing tubes were passed, were used as the bubblers. The gas was supplied from a cylinder through a pressure regulator under a pressure that provided the formation of fine bubbles (the

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excess pressure at the inlet of the saturation system was about 20—30 kPa, and that in the bubbler did not virtually differ from atmospheric pressure).

The SLP (2.0—2.5 mL) was poured into the bubbler, which was placed in a thermostat of an HP 5890A chromatograph where the gas was passed through the SLP at a specified temperature for 30 min. The gas-supplying tube was also placed in the thermostat in order that the gas passed through the thermostat would not change its temperature.

The solution saturated with the gas at atmospheric pressure (the volume of the sample was 5 mL) was taken from the bubbler with a Hamilton 25-μL microsyringe and introduced into a Carlo Erba HRGC 5300 gas chromatograph with an HWD 430 thermal conductivity detector. Stainless steel packed columns with a size of 100×0.3 cm filled with zeolite CaA (the size of adsorbent particles was 0.16—0.2 mm) were used for the analysis. To separate the liquid phase used in analysis from the zeolite, the first 10—12 cm from the inlet of the column was packed with Chromaton N-Super (with a particle size of 0.250—0.315 mm). This column was used for the analysis of the solubility of all gases, except for CO_2. A column with a size of 100×0.3 cm packed with Silokhrom II (with a particle size of 0.15—0.5 mm) was used for analysis of CO_2.

Nitrogen was used as the carrier gas for the gas chromatographic determination of the solubility of helium and hydrogen in SLP, whereas helium was used for the analysis of nitrogen, methane, and carbon dioxide. The regime of analysis was isothermic, the oven temperature was 70 °C, and those of the detector and injector were 100 °C. The signal from the detector was detected on an HP 3396A integrator. The amount of the dissolved gas was determined from the surface area of the peak.

For calibration, the graduation plots for pure gases were obtained. The volume of the sample introduced into the injector was 2—20 μL. For all gases used, the graduation plots in the sample volume (μL)—peak surface area (μV s) coordinates were a straight line passing through the origin. This made it possible to calculate the gas concentration in the sample using a simple linear interpolation. Every day the calibration was checked by the introduction of 5 μL of the gas into the chromatograph. The error of determination was found using the average value of the gas solubility from five analyses.

Comparison of the results obtained by the introduction of different columns of the same sample of SLP showed that an increase in the volume of the injected sample from 5 to 20 μL has almost no effect on the results of determination of the concentrations (the relative standard deviation did not exceed 4—5%). Hereinafter, the volume of the injected sample was 5 μL. This provided a sufficient accuracy of determination of the gas solubility in SLP and favored the elongation of the working life of the column. The concentration of the gas in SLP reduced to standard conditions was calculated from the equation

$$C = S_{\text{liq}} \cdot V_{\text{g}} \cdot 1000 \cdot 273.2B/[V_{\text{liq}} \cdot S_{\text{g}} \cdot 760 \cdot (273.2 + T)],$$

where C/mL L^{-1} is the gas concentration in SLP; S_{liq} is the surface area of the peak of the gas dissolved in the SLP sample with a volume of V_{liq}; S_{g} is the surface area of the peak of the pure gas with a volume of V_{g}; B/Torr is the barometric pressure; and T/°C is the temperature at which the SLP was saturated with the gas.

Table 1. Solubility of gases (C/mL L^{-1}) in pentadecane, PMS-100, and PEG-600 at 20 (A), 60 (B), and 90 °C (C)

Carrier gas	Pentadecane			PMS-100			PEG-600		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
He	29.5	45.0	55.9	35.6	56.6	70.8	6.44	10.8	15.8
H_2	68.7	87.3	97.8	118	137	145	17.5	29.6	36.0
N_2	125	131	136	154	162	166	26.6	29.7	32.0
CH_4	700*	583	542	587	394	329	103*	1120	118
CO_2	1490	1160	726	2050	1360	886	1630	1160	768

* The data were obtained at 40 °C.

Results and Discussion

The results of measuring the solubility of the carrier gases in SLP are presented in Table 1. These data show that, as expected, the solubility of the carrier gases in the SLP studied differ sharply. For example, the solubility of permanent gases (H_2, He, and N_2) is the lowest in PEG-600 and the highest in PMS-100 (the difference is 5—6 times). The situation is almost the same for methane (the solubility of methane in pentadecane is somewhat higher than that in PMS-100). At the same time, the solubilities of the heaviest carrier gas (carbon dioxide) in all SLP are close.

The solubility of the gases in the SLP used increases in the following series: He < H_2 < N_2 < CH_4 < CO_2, and the solubility of carbon dioxide is 50—90 times higher than that of helium. The presented series of increasing solubility of the gases under study is identical to the series of the same gases for their increasing influence on the retention values of the chromatographed compounds.[1–3,6] This confirms the validity of the concept suggested previously for the effect of the carrier gas and SLP on the retention values in GLC.

It is of interest to consider the temperature dependences of the solubility of the gases in SLP. The solubility in SLP of the permanent gases increases somewhat (by 1.1—2.0 times) when the temperature increases from 20 (40) to 90 °C, and for polyatomic gases (CH_4 and CO_2), it decreases by 2.0—2.5 times.

When the temperature increases to 90 °C, the maximum difference in the gas solubility decreases by approximately 4 times for pentadecane and PMS-100 and by 2 times for PEG-600.

Thus, we proposed a simple gas chromatographic procedure for the determination of the gas solubility in low-volatile liquids based on the introduction of a certain volume of the liquid saturated with the gas at atmospheric pressure into a gas chromatograph. The solubility of the gases in some SLP was found. By the solubility in SLP (pentadecane, PMS-100, and PEG-600), the gases studied are arranged in the series He < H_2 < N_2 < CH_4 < CO_2, which coincides with the series of the changing retention values in GLC with different carrier gases.

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