GAS CHROMATOGRAPHY OF ETHYL DERIVATIVES
OF SILICON, GERMANIUM, AND TIN

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The study of the intermolecular interactions of molecules of organic compounds with the surface of specific and nonspecific adsorbents in polar and nonpolar solvents by the method of gas chromatography [1-3] is interesting, in particular, for the experimental determination of the contributions of the individual functional groups contained in the molecules, to the total energy of the interaction [4]. The estimation of such contributions to the retainable volumes \( V_g \) and \( V_s \) and the heats of sorption \( Q_p \) and \( Q_a \) permits the prediction of the corresponding parameters for other organic compounds with monotypic functional groups. For organometallic compounds of the silicon subgroup, containing metal-metal bonds, analogous investigations have already been begun [5-7].

In this work we studied the separation and thermodynamics of dissolution and adsorption by methods of gas-liquid chromatography (GLC) and gas adsorption chromatography (GAC) of organometallic compounds containing one heteroelement: \((C_2H_5)_4M\) and \((C_2H_5)_3MH\), where \( M = Si, Ge, \) and \( Sn \).

**EXPERIMENTAL**

The investigations were conducted on Tswett-3 and Tswett-4 analytical chromatographs. Detectors: ionization-flame and katharometer. Packed columns, 100 x 0.3 cm, made from stainless steel. Silanized Chromosorb W, on which Apiezon L (20%) or Carbowax 20M (15%) was applied, was used as the carrier for GLC. For GAC, carbochrome-1 (graphitized thermal carbon black and 0.01% Apiezon L) with specific surface 8.5 m²/g, silochrome S-80, modified [8] with trimethylchlorosilane, hydroxylated and dehydroxylated [9], with a specific surface of 80 m²/g, were used as adsorbents. The column temperature was 120-250°. Carrier gas helium. Dosing was performed with a 10 µliter microsyringe.

**DISCUSSION OF RESULTS**

In molecules of compounds of the series \((C_2H_5)_4M\) there are no functional groups that would have locally concentrated electron density. Such molecules can be assigned to group A according to Kiselev's classification [10]. It is natural to assume that \((C_2H_5)_4M\) interacts with solvents or adsorbents basically nonspecifically, i.e., on account of universal dispersion forces. Compounds of the series \((C_2H_5)_3MH\) have a small negative charge on the hydrogen atom; therefore they can manifest some specificity of sorbate-sorbent interaction on specific adsorbents and solvents.

Table 1 presents the values of \( V_{Sg} \) and \( Q_{a,p} \) for the investigated compounds on various adsorbents and solvents. For GAC an increase in \( Q_a \) with increasing molecular weight is observed for both series of compounds, both nonspecific (carbochrome-1) and specific adsorbents (silochrome S-80 modified) and specific adsorbents (silochrome S-80, hydroxylated and dehydroxylated). It is known [10] that dehydroxylated silica gel interacts with molecules of group A as a nonspecific adsorbent. In accord with this, it was found that the values of \( Q_a \) on dehydroxylated silica for the compounds \((C_2H_5)_4M\) are of the same magnitude as \( Q_a \) on modified silicochrome. In addition, for the series \((C_2H_5)_3MH\), a small increase in \( Q_a \) is observed for the dehydroxylated surface in comparison with the modified surface, which can be explained by interaction of the hydrides with the partially remaining hydroxyl groups (up to 10% [10]) of the dehydroxylated silochrome. The presence of free hydroxyl groups was confirmed by the IR spectra of dehydroxylated silochrome (the band 3750 cm⁻¹ is present).

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Fig. 1. Chromatograms of separation of compounds (C₂H₅)₃MH and (C₂H₅)₄M by the method of GAC: a) on carbochrome-1 at 190°; b) on modified silochrome S-80 at 100°; c) on hydroxylated silochrome S-80 at 147°; d) on dehydroxylated silochrome S-80 at 203°.

Fig. 2. Chromatograms of separation of the compounds (C₂H₅)₃MH and (C₂H₅)₄M by the method of GLC: a) on Apiezon L at 120°; b) on Carbowax 20M at 90°.

The fact that the Qₐ of the hydrides is substantially larger for hydroxylated silochrome than for modified silochrome agrees with this explanation. Thus, with increasing number of hydroxyl groups on the surface of silochrome, the specific contribution of the interaction of hydrides of the series (C₂H₅)₃MH with the surface of the adsorbent and Qₐ to the total energy increases. In the case of GLC, during the dissolution of the organometallic compound in Apiezon L and Carbowax 20M there is a negligible increase in Q₀, both for compounds (C₂H₅)₃MH and for (C₂H₅)₄M, corresponding to the increase in their molecular weight. In this case Q₀ for a polar solvent is somewhat higher for both series. Consequently, in contrast to adsorption, no specificity of the interaction of the hydrides with the solvent is detected by the GLC method, which can be explained by the complexity of the dissolution.

Chromatograms of the separation of compounds (C₂H₅)₃MH and (C₂H₅)₄M by the methods of GAC and GLC are given in Figs. 1 and 2.