Extrathermodynamic parameters of sorption of light hydrocarbons on stationary phases prepared from tricyclononene polymers

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ABSTRACT

Enthalpy and entropy of adsorption of polar and non-polar solutes were measured by chromatographic technique for new stationary phases prepared from membrane polymers based on tricyclonones. Data obtained within temperature interval from 40 to 150 °C were used to create extrathermodynamic dependences (compensation plots, dependences of enthalpy and entropy changes on solute carbon number). Compensation plots were very similar for all the stationary phases indicating similar adsorption mechanisms. The difference between the stationary phases was elucidated using dependences of enthalpy and entropy changes on solute carbon number. Higher retentivity of the stationary phase based on polymer 1 was explained by higher both enthalpy and entropy of solute adsorption on the stationary phase.

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1. Introduction

Recently we have investigated tricyclononene polymers as stationary phases in GC [1]. These polymers belong to membrane polymers [2] and demonstrate inherent microporosity providing polymers gas separating properties. Being deposited onto inner wall of a capillary column the polymers form a porous layer thus allowing preparation of PLOT type capillary columns in much easier way than deposition of preformed porous particles onto capillary walls. Chemical structure of the tricyclononene polymers is not typical for conventional GC stationary phases providing them unusual selectivities [1]. The structure of the porous layer is also quite different from those formed by granulated porous polymers. Instead of individual porous particles fixed on the capillary walls, the membrane polymers create in the capillary a homogenous thin polymeric film like conventional liquid stationary phases but this film is porous with highly developed surface area.

Characteristics of the investigated norbornene polymers studied in membrane separations were found to be very similar [2] while significant difference between the polymers was observed in GC separations [1]. Only one of the three polymers was capable to efficient separation of light hydrocarbons and the other two polymers suffer from reduced separation efficiency though provide higher

retention capacity [3]. To elucidate the origin of different behavior of polymers in GC we studied thermodynamics of sorption of light hydrocarbons on new stationary phases and the data of the research are collected in the article.

Gas chromatography is widely applied technique for physicochemical measurements realizing methods based both on traditional techniques such as frontal analysis and displacement development [4,5], and on more sophisticated technologies such as analysis of statistical moments of the peak [6], stop-flow and reverse-flow techniques [7]. A review of applications of different chromatographic methods for evaluation of diffusion coefficients, thermodynamic quantities and kinetic constants can be found in [8].

The common thermodynamic quantities evaluated from the GC experimental data are the enthalpy of adsorption $\triangle H^o$ and the entropy of adsorption, $\triangle S^o$. They are differences in standard enthalpies (free energies or entropies) for the adsorption of a solute from the vapor phase to the stationary phase relating to the equilibrium constant of adsorption process though the known thermodynamic relationship:

$$\triangle G° = -RTlnK = \triangle H° - T\triangle S° \qquad (1)$$

where $\triangle G°$ is free energy of adsorption; R is the universal gas constant; $K = C_s/C_m$ is an equilibrium constant with C_s and C_m being solute concentrations in the stationary and the mobile phases, respectively; T is column temperature, K. Relation of the equilibrium constant to a chromatographic quantity was found by solving
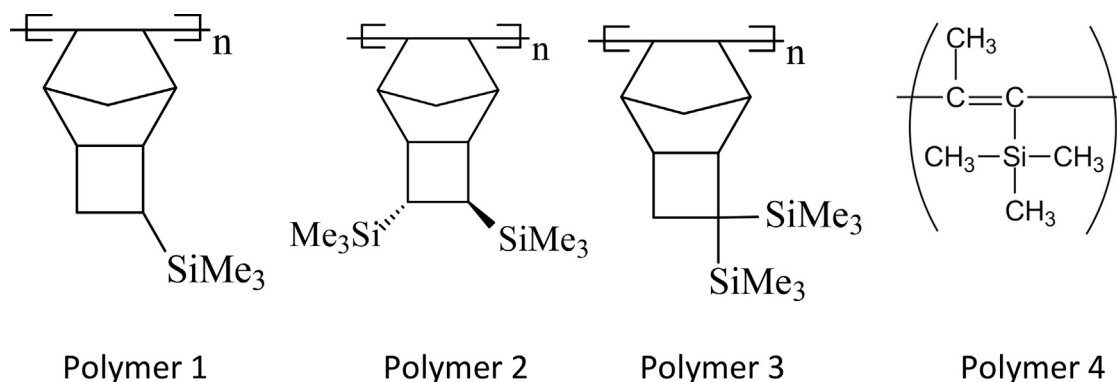
Fig. 1. Structure of monomer units of investigated polymers.

corresponding mass-balance equations in LC [9] and GC [10,11]. In both cases the concentration equilibrium constant $K_c = C_s/C_m$ was used in derivation procedure and a simple relationship was obtained:

$$k = K_c/\beta \qquad (2)$$

where $\beta = V_m/V_s$ is the phase ratio, i.e. the ratio of the mobile phase volume V_m in the column to those of stationary phase V_s, and $k = (t_R - t_o)/t_o$ is the retention factor with t_R and t_o being solute retention time and column hold-up time, correspondingly. Combining Eqs. (1) and (2) one gets a relationship allowing evaluation of thermodynamic quantities from correlation between lnk and 1/T:

$$\ln k = -\triangle H°/RT + \triangle S°/R - \ln\beta \qquad (3)$$

This relationship was widely used in LC [12–14] but rarely in GC [15] where the specific corrected retention volume V_x (x means that it can be weight, volume or surface specific volume) is more popular parameter than retention factor k [16–18]. Unfortunately, usage of different parameters means different definitions of equilibrium constant K and, consequently, different values of enthalpy and entropy. For example, there are two different correlations described in the literature for V_x: the isosteric heat of adsorption $\triangle H_{is}$ is evaluated from a linear correlation between $\ln(V_x/T)$ and 1/T, while the differential heat of adsorption $\triangle H_{ad}$ is estimated from a linear correlation between $\ln(V_x)$ and 1/T [19,20]. The isosteric enthalpy H_{is} and the differential enthalpy H_{ad} related to each other as [21]:

$$\triangle H°_{ad} = \triangle H°_{is} - RT \qquad (4)$$

However, calculating any of enthalpies and entropies, the parameters are assumed to be temperature independent. Therefore, the same must be true for their difference! Regrettably, not only properties but even terms are muddled in the literature and sometimes the differential enthalpy of adsorption is designated as isosteric enthalpy, sometimes vice-versa, and sometimes even as isosteric differential enthalpy (see e.g. [21]). Accounting for such unpleasant situation the molar differential enthalpy and entropy of adsorption in this publication were estimated using Eq. (3) [15,17] from linear dependence of lnk on 1/T. The advantages of the solute retention factor k in GC were mentioned by Everett [22] more than 50 years ago. These advantages became particularly important nowadays accounting for the discussion on the physical meaning of the corrected retention volume taking place in the literature [23,24].

2. Experimental

2.1. Chemicals

All reagents used in the study were of chemical pure grade, were purchased from Sigma-Aldrich LLC (St. Louis, MO, USA) and were used without additional purification. The carrier gas helium had purity of 99.99% and was obtained from local supplier, and was additionally dried to remove water by passing through a molecular-sieve-cartridge.

2.2. Synthesis of polymers

Polymers 1–3 were synthesized by additive polymerization in the presence of a palladium-containing catalytic system [25]. Polymer 4 was obtained by the procedure described in [26] using a niobium catalyst. The structures of monomer units of the resulting polymers are shown in Fig. 1 and their molecular mass characteristics are listed in Table 1.

2.3. Column preparation

The capillary columns were prepared by the dynamic coating method [26]. All columns were prepared from quartz capillary of I.D. 0.21 mm (d_c) and have stationary phase thickness d_f 0.25 μm. Columns with stationary phase based on polymers 1 and 3 were of 16 m length, with polymer 2–13 m; and column with polymer 4 was of 25 m length. Phase ratio for the columns was calculated according to known relationship [27]:

$$\beta \sim \frac{d_c}{4d_f} \qquad (5)$$

2.4. Chromatographic measurements

All gas chromatographic measurements were performed on a gas chromatograph GC 2010 (Shimadzu LLC, Japan). The split ratio was 1:50 and detection was performed by means of FID. The measurements were carried out in the range of temperatures from 40 to 120 °C. A mixture of C1–C4 light hydrocarbons was used as solute test-mixture. Another test-solutes (benzene, methylethylketone, ethanol, n-hexane) were injected individually. Solute retention times were acquired using software package GC-solution (Shimadzu LLC, Japan) with data rate of 0.1 s per point and r.s.d. better than 0.3%. The data were further processed by a personal computer using the Origin (version 8.5) software.