



POLYMERIC STATIONARY PHASES WITH VARIABLE POLARITY FOR GC SEPARATION OF AROMATIC COMPOUNDS AND THEIR SULFUR ANALOGS

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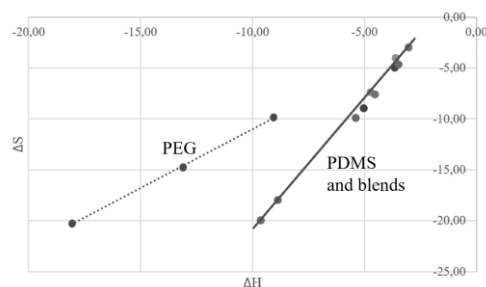
Abstract

Mixed stationary phases for **gas chromatography (GC)** were prepared by physical mixing of two polymers with different polarity: non-polar polydimethylsiloxane and polar poly(ethylene glycol). Several GC capillary columns were prepared with pure PDMS and pure PEG, and their blends in different ratios. All the polymeric mixtures were investigated using **inversed GC (IGC)**. ΔH and ΔS of the sorption for sorbates of different classes were determined for all blends and individual polymers. The efficient polarity of the prepared mixtures differed from the linear combinations of the individual ones.

Key words: polydimethylsiloxane, poly(ethylene glycol), enthalpy, entropy, compensation effect.

Introduction

The most often discussed thermodynamic functions of sorption for chromatographic systems are enthalpy ΔH and entropy ΔS of the sorption of different analytes, which serve as the tools for evaluating the properties of polymers, potentially suitable as stationary phases in GC [1]. However, the sorption system in GC separation processes is not sufficiently formalized; the phenomenon of sorption is often investigated separately from other processes, not as a part of general chemical thermodynamics of the system [2]. The present work is devoted to the evaluation of enthalpy ΔH and entropy ΔS of the sorption of analytes of different classes together with chromatographic polarity evaluation by the Rohrschneider method [3] for the newly prepared polymeric stationary phases using IGC as the comparison tool. The stationary phases were prepared by physical mixing of two polymers with different polarity: non-polar polydimethylsiloxane (SE-30) and polar poly(ethylene glycol) (PEG 20M). The polymeric stationary phases were tested for the separation of compounds of different classes, mainly focusing on the separation of aromatic compounds and their sulfur-containing analogs. The polymers were selected based on their diametral polarities and considering the necessity to maintain them at a temperature above the glass transition temperature under gas chromatographic conditions, while keeping low volatility of the material. The separation of sulfur-containing compounds and their aromatic analogs has been widely reported [4–7]. The simplest pair is benzene/thiophene. It is known that the latter is the most common impurity in benzene, which deteriorates the reagent quality. Different methods are suggested for the separation of benzene and thiophene, such as selective adsorption, solvent extraction, or extractive distillation methods [8–10], resulting in



rather low thiophene contents, which in turn demands sensitive chromatographic methods for sulfur-containing compound control. One of the current problems is the inversion of a retention time for the benzene/thiophene pair: nonpolar polymeric stationary phases demonstrate higher difference in the retention factors of the compounds of interest, but retention of thiophene is lower than those of benzene, making quantification of thiophene difficult. For polar stationary phases, the thiophene retention is higher than that for benzene; however, both retention factors are significantly lower. The solution may be either the utilization of longer chromatographic columns, leading to an increase in the analysis time, or the preparation of capillary columns with on-demand chromatographic polarity, ensuring retention owing to the non-polar polymer and selectivity owing to the polar one. This work deals with the second way.

Results and discussion

The values of differential enthalpy ΔH^0 and entropy ΔS^0 of the sorption for the saturated and aromatic hydrocarbons explored were calculated for all the stationary phases and are shown in Tables 1, 2. It was shown earlier [1] that the enthalpy-based methylene selectivity values of non-polar SE-30 and that of polar stationary phase PEG 20M differ. It was expected that the mixed stationary phase should demonstrate the properties being a linear combination of the properties of the individual polymers. To study this issue, the values of enthalpy ΔH and entropy ΔS of the sorption for the non-polar and polar sorbates (Tables 1 and 2) were determined for each individual polymer and for all the mixtures.

As can be seen from Tables 1 and 2, the efficient polarities of the prepared mixtures differ from the linear combinations of

Table 1. Enthalpy of the sorption of the test solutes on the investigated polymeric stationary phases

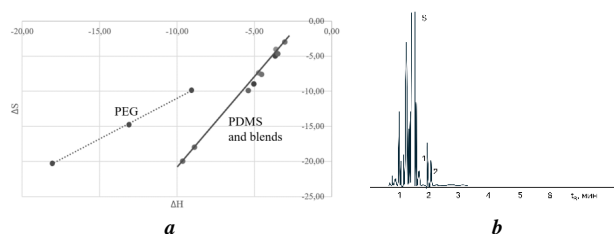
Sorbate	ΔH for the corresponding polymer blend, kJ/mol					
	PEG	80 PEG	60 PEG	40 PEG	20 PEG	0 PEG
Hexane	-8.89	-3.60	-3.65	-3.04	-3.48	-8.86
Heptane	-9.73	-4.73	-5.04	-4.54	-5.38	-9.62
Ethanol	-7.45	-4.92	-6.09	-3.75	-4.11	-9.31

Table 2. Entropy of the sorption of the test solutes on the investigated polymeric stationary phases

Sorbate	ΔS for the corresponding polymer blend, J/mol·K					
	PEG	80 PEG	60 PEG	40 PEG	20 PEG	0 PEG
Hexane	-18.09	-4.06	-5.00	-2.92	-4.62	-17.99
Heptane	-20.33	-7.37	-8.91	-7.60	-9.93	-20.00
Ethanol	-15.37	-7.92	-11.87	-5.34	-6.43	-20.65

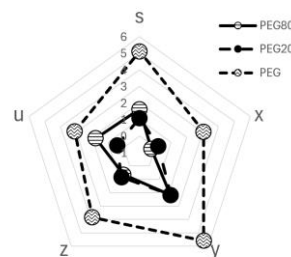
the individual values: the properties of the mixed stationary phases go through the minimum. An optimal three-parameter regression basis can be constructed in the future, reflecting the properties of permutation symmetry and considering the specifics of the isotherms of polymer mixtures, and an optimal algorithm for calculating the regression parameters of sorption isotherms for the polymer mixtures can be proposed.

The compensation temperatures were also calculated for comparison of the sorption mechanism of sorbates in all the polymeric mixtures (Fig. 1a) using the relation $\Delta H = \beta \Delta S + \alpha$, where β is the compensation temperature (K). It is interesting to note that the values of compensation temperatures were the same for all the blends containing PDMS, making it to determine the separation mechanism.

**Figure 1.** Properties of the prepared columns: compensation plots for PEG (1) and PDMS and all the blends (2) (a), separation of the test mixture on the column 40% PDMS + 60% PEG (b). S—solvent (hexane), 1—benzene, 2—thiophene.

To clarify the mechanism of the sorbate–stationary phase interaction, the Rohrschneider constants were calculated for the investigated mixed sorbents using equations shown in Table S1 in the Electronic supplementary information (ESI). Figure 2 compares the values of the Rohrschneider constants for three stationary phases, containing 20% and 80% of PEG in the polymeric mixture, and for the pure PEG sorbent. As one can see from this figure, the greatest contribution to the retention in both mixtures and for PEG itself was by hydrogen bonding with the electron-donor groups of the polymer (model compound—ethanol, coefficient y), which is rather expectable. The weight of orientational interactions also grows with an increase in the PEG percentage (model compound—nitrobenzene, coefficient u). However, the addition of the polar polymer to the sorbent results in a dramatic decrease in all the Rohrschneider constants,

demonstrating a multiple reduction in all the polar interactions even at a small proportion of the non-polar polymer in the mixture, confirming the differences in the compensation temperatures for the polymer blends and PEG.

**Figure 2.** Rohrschneider scheme for the stationary phases containing 80% of PDMS and 20% of PEG, 20% of PDMS and 80% of PEG, and 100% of PEG.

The prepared columns were evaluated for the separation of aromatic compounds and their sulfur-containing analogs and demonstrated selectivity sufficient for the basic separation of benzene and thiophene (Fig. 1b).

Experimental section

General remarks

All reagents used in this study were of reagent grade and were used without additional purification. Helium (grade A) was used as the carrier gas and was additionally dried through a molecular sieve cartridge. All GC measurements were performed on a Shimadzu GC 2010 gas chromatograph (Japan). The split ratio was 1:50, and the detection was performed with a flame ionization detector (FID). The data were acquired using the GC-solution software package (Shimadzu, Japan) and were evaluated using the Origin software (version 2018, OriginLab Corp., USA). The capillary columns were prepared using the static method. The characteristics of the prepared columns are presented in Table 3. After the column preparation and installation in the gas chromatograph, the columns were conditioned at 150 °C for 60 min prior to the measurements.

Table 3. Properties of the resulting GC columns

Stationary phase	L , m	d_c , mm	d_f , μm	β
PEG	16	0.165	0.25	165
20% PDMS 80% PEG	10	0.165	0.25	165
40% PDMS 60% PEG	10	0.165	0.25	165
60% PDMS 40% PEG	10	0.165	0.25	165
80% PDMS 20% PEG	10	0.165	0.25	165
PDMS	15	0.23	0.22	261

Calculations

The thickness of the stationary phase layer d_f and the phase ratio values β for the resulting columns were calculated according to relations (1) and (2) described in Ref. [11] and are presented in Table 3.

$$d_f = 0.5r_c \cdot \frac{C_L \cdot \rho}{100 - C_L} \quad (1),$$

$$\beta = \frac{r_c}{2d_f} = \frac{V_m}{V_s} \quad (2).$$

Here r_c is the inner capillary radius, C_L is the concentration of the polymer in the working solution (g/mL).

The thermodynamic parameters of the sorption for the analyte separation in GC were evaluated by IGC [12]. The thermodynamic parameters of the sorption, usually evaluated by IGC, are the enthalpy ΔH^0 and entropy ΔS^0 of the sorption, which are related to the partitioning coefficient (Henry constant) of the analyte K between the mobile and stationary phases.

$$\Delta G^0 = -RT \ln K = \Delta H^0 - T \Delta S^0 \quad (3)$$

where ΔG^0 is the free energy of sorption; R is the universal gas constant; $K = \frac{C_s}{C_m}$ is an equilibrium constant, C_s and C_m are the analyte concentrations in the stationary and mobile phases; T is the column temperature, K. The partitioning coefficient K correlates with the retention factor $k = \frac{t_R - t_0}{t_0}$

$$K = k \cdot \beta \quad (4)$$

A combination of equations (3) and (4) affords the relationship for evaluating the thermodynamic parameters of the sorption from the linear correlation between $\ln k$ and $1/T$

$$\ln k = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} - \ln \beta \quad (5).$$

Conclusions

The mixed stationary phases for GC were prepared by physical mixing of non-polar polydimethylsiloxane and polar poly(ethylene glycol). Based on the values of ΔH and ΔS of the sorption for the polar and nonpolar sorbates on all the stationary phases, it was demonstrated that the values of the compensation temperatures were the same for all the blends containing PDMS. This fact indicated that PDMS determines the separation mechanism in the mixed stationary phases, which is the non-polar interactions. Among the other interactions, the hydrogen bonding with the electron-donor groups of the polymer make the largest contribution. Moreover, the efficient polarity of the resulting mixtures differed from the linear combinations of the individual values: the properties of the mixed stationary phase go through the minimum, demonstrating the expected thermodynamic incompatibility of two polymers explored. The resulting columns were also tested for the separation of aromatic compounds and their sulfur-containing analogs and demonstrated the selectivity sufficient for the basic separation of benzene and thiophene.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: [the model sorbates of the Rohrschneider model](#). For ESI, see DOI: 10.32931/ioXXXXX.

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