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System constants of synthesized poly(methyl-3,3,3-trifluoropropyl) siloxanes

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Abstract

The method of solvation model has been applied to five poly (methyl-trifluoropropyl) siloxanes (TFPSXX) prepared in our laboratories, at five trifluoropropyl (TFP) group contents, XX = 0, 11.5, 26.3, 35.5 and 50.0%, at 80, 100, 120 and 140 °C. Previously, specific retention volumes of 60-odd solutes of varied polarities were measured upon each of these stationary phases within the above temperature range. Constant *s* prevails over all other constants, TFPSXX stationary phases showing strong dipole/induced dipole forces with the solutes, moderate acidity and no basicity at all. Constant *e* is zero in the stationary phase without TFP groups, but has negative low-medium values for the other fluorine contents, XX from 11.5 to 50.0%, hinting at repulsive forces, as expected. Normal values for constant *l*, decreasing from the less cohesive TFPS00 to the more cohesive TFPS50, were found. For each TFP content constants *s*, *a* and *l* show a negative temperature dependence, while constant *e* increases as temperature increases. Constant *c* also decreases with increasing temperature. At each temperature, constants *s* and *a* increase with increasing %TFP (or increasing stationary phase polarity), whereas constants *e* and *l* show the opposite trend, diminishing with increasing polarity of the stationary phase. Principal component analysis shows that the five stationary phases presented in this work conform a group with other earlier synthesized trifluoropropyl siloxanes and other fluorinated stationary phases taken from literature: VB-210, QF-1, DB-200, DB-210 and PFS6, showing the same selectivity which only the fluorine atom confers. A dendrogram of 38 stationary phases supports these results.

Keywords: Gas chromatographic capillary columns; Solvation parameter model; Specific retention volumes; Trifluoropropyl siloxane stationary phases; System constants

1. Introduction

The solvation parameter model based on the studies of Kamlet and coworkers [1,2] was promoted in 1980s by Abraham et al. [3,4], Carr and coworkers [5,6], and Poole and coworkers [7,8]. It describes with effectiveness and solvency the interactions between solutes and stationary phases, assuming that only retention plays a role in the chromatographic phenomenon at a given temperature, in which adsorption has been minimized as much as possible. Earlier, most columns used were packed or glassy columns [9], but, at present, fused-silica capillary columns are preferred owing to their many advantages [10]. Recently, already in this century, an appreciable number of studies by Poole and coworkers [11–22] have fructified in the building of a very consistent database of system constants.

Trifluoropropyl siloxanes (TFPSXX) are very interesting stationary phases of moderate polarity [23], especially suitable for the chromatography of alcohols and ketones. The stationary phase with 50% trifluoropropyl group has been the preferred among trifluoropropyl siloxanes by scientists [24] and column manufacturers, but other TFPSXX of low polarity or with XX < 50% were never considered. Dai [25] synthesized trifluoropropyl siloxanes with 0–26% trifluoropropyl group (TFP) in 1995. The constants of these polymers were determined and published in 1998 [26]. In this paper we describe the application of the solvation parameter model to the synthesized trifluoropropyl siloxanes with 0, 11.5, 26.3, 35.5 and 50.0%, and some remarkable improvements in the determination of the experi-

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mental retention magnitude (a new equation for evaluating the specific retention volumes and a new, more accurate hold-up time determination).

The aim of this paper is the characterization of the above trifluoropropyl siloxanes of compositions 0 < %TFP < 50 over the 80–140 °C temperature range by applying the solvation model. The variations of the properties of these polymers with column temperature and %TFP content are investigated. To do this, multivariate procedures as multiple linear regression analysis (MLRA), principal component analysis (PCA) and cluster analysis (CA) are used. The more recent way to present the solvation model is as follows [27]:

$$\log \mathrm{SP} = c + lL + eE + sS + aA + bB \qquad (1)$$

where L, E, S, A and B are the descriptors of the solutes with the stationary phase, and the same low case letter symbols, l, e, s, a and b, stand for the mutual specific constants that describe the interactions of the stationary phase with the solutes. c is the regression constant, arising from the application MLRA to the measured retention data (SP, the retention magnitude, can be specific retention volume, V_g; retention time, t_R; retention factor, k; distribution coefficient, K_L, etc.). The c-value depends on the retention magnitude chosen. Related with the stationary phase ratio β, it is considered unimportant but necessary for retention magnitude prediction.

l represents the cavity formation and dispersion contributions taking part between the stationary phase and the solutes; e the ability of the stationary phase to interact with n or π electron pairs; s the capacity of the stationary phase to interact with solute dipoles; a, the ability of the stationary phase to behave as a base in the donor–acceptor interaction through hydrogen bonds with acid solutes; b, the tendency of the stationary phase to interact as an acid with basic solutes through acceptor/donor hydrogen bonds.

In addition, the solute descriptors compiled mostly by Abraham [28], which are complementary to the stationary phase constants, have the following meanings: L, earlier denoted as $\log L^{16}$, is the distribution coefficient of *n*-hexadecane at 298 K; E, earlier denoted as R_2, is the excess molar refraction of the solute; S, earlier denoted as π_2^H, is the effective dipolarity/dipolarizability of the solutes; A, earlier denoted as $\sum\alpha_2^\mathrm{H}$, is the effective hydrogen bond acidity of the solute, and B, earlier referred to as $\sum\beta_2^\mathrm{H}$, the effective hydrogen bond basicity of the solute.

The different product terms lL, eE, sS, aA and bB quantify the different stationary phase–solute interactions operating in the retention, if adsorption is disregarded. The four last binomials are polar interactions, while the first one represents non-polar interactions, dispersive forces and the cavity formation. So, the sum $(c + lL)$ adequately describes the interactions of non-polar solutes as *n*-alkanes on non-polar stationary phases.

2. Experimental

2.1. Instrumentation

Gas chromatographs HP5890 A (Hewlett-Packard) equipped with a flame ionization detector (FID), injection system split/splitless and "back pressure" regulator, and Varian 3300 with split/splitless injection system, FID and conventional pressure regulator were used.

Electronic integrators SP-4270 (Spectraphysics) were used for data acquisition.

Microsyringes of 1 μl from Hamilton (serie 7001) were used for sampling.

Nitrogen used as carrier gas (99.999% pure) was produced by a NITROX (Domnick Hunter) gas generator. Hydrogen of 99.995% purity (Air Liquid) and air produced by a conventional compressor were used for the FID.

2.2. Probes

Hydrocarbons: methane (from natural gas), *n*-alkanes (from C5 to C17), aromatics (benzene, toluene, ethylbenzene, *n*-propylbenzene and *n*-butylbenzene), cyclohexane and *cis*-hydrindane; ketones (2-ketones from propanone to 2-undecanone) and cyclohexanone; alcohols (*n*-alkanols from *n*-propanol to *n*-decanol and cyclohexanol); esters (methyl, ethyl, *n*-propyl and *n*-butyl acetates); amines (*n*-propylamine, *n*-butylamine, *n*-pentylamine, *n*-hexylamine, *n*-heptylamine, and aniline); nitriles (*n*-butanenitrile, *n*-

Table 1
Characteristics of the chromatographic columns used in this work

Parameter	TFPS00	TFPS12	TFPS26	TFPS35	TFPS50
L (m)	30.1	24.7	25.3	25.3	25.7
d_c (mm)	0.225	0.211	0.214	0.214	0.216
d_f (μm)	0.300	0.300	0.300	0.300	0.300
c_s (g cm^{-3})	0.00520	0.00607	0.00661	0.00692	0.00732
%TFP group	0	11.5	26.3	35.5	50.0
R_p[a], retention polarity	6.39	15.22	26.77	35.1	49.13
$\Delta G_\mathrm{s}^\circ(\mathrm{CH_2})$[b] (kJ mol^{-1})	−1.884	−1.830	−1.737	−1.667	−1.552

[a] $R_\mathrm{p} = 20\sum_{i=1}^{5}(I(\mathrm{TFPSXX})/I(\mathrm{squalane}) - 100$ [32]. I are the retention Kovats indices [33] of the first five McReynold's probes (benzene, *n*-butanol, 2-pentanone, 1-nitropropane and pyridine) on the trifluoropropyl siloxanes and squalane.

[b] $\Delta G_\mathrm{s}^\circ(\mathrm{CH_2}) = -2.303RT \times$ slope. $R = 8.313\ \mathrm{J\ mol^{-1}\ K^{-1}}$; T, column temperature = 393 K; slope is the slope of the $\log(V_{\mathrm{g},Z})$ of then-alkanes vs. their carbon number Z plot [42].