3.3. Reproducibility

The precision of the method was evaluated with both within-run (twelve equal samples of a standard solution added to the traps and analysed on the same day) and between-run assays (samples of equal concentration to the traps and analysed on ten consecutive days). These results are reported in Table 2.

3.4. Detection limit

As is customary, the detection limit of the procedure was defined as the concentration derived from a signal three times the noise level. With an air sample of 20 l, the MDI derivative (DAPM) showed a detection limit of 0.7 $\mu g/m^3$, which was suitable for routine analytical work.

3.5. Storage stability

Stability permitting, it is often more practical to collect samples over a number of days and perform analysis subsequently. In the present case, storage studies indicated that samples should be desorbed within 10 days for maximum recovery when they are stored at 4°C in the dark. Losses of up to 7% can occur after 15 days. The recovery of DAPM was unchanged up to 10 days for refrigerated desorbed solutions.

3.6. Field studies

Table 3 summarizes the results of the analyses in the field. The MDI concentrations were found

Table 2
Precision of the MDI assay

n	x (nmol)	S.D. (nmol)	R.S.D. (%)
Within-run precision			
12	0.85	0.02	2.3
12	18.15	0.85	4.6
Between-run precision			
10	0.89	0.04	4.4
10	17.91	1.05	5.8

Table 3
Workplace atmosphere concentrations of MDI at various distances from production machinery

Distance (m)	Volume of air sampled (l)	Concentration ± S.D. ($\mu g/m^3$)
2	10	19.8 ± 0.79
2	20	21.4 ± 0.91
6	10	7.0 ± 0.29
6	20	5.9 ± 0.30
10	10	1.8 ± 0.02
10	20	2.1 ± 0.02

to vary between 2.1 and 21.4 $\mu g/m^3$. As expected, lower concentrations were observed at a greater distance from the machinery and the concentrations found with a longer collection time were the same as those found with a shorter collection time. The concentrations found are all below the threshold limit value for MDI according to ACGIH.

4. Discussion

During the last few decades, considerable efforts have been channelled into developing increasingly sensitive chromatography-based methods for the determination of atmospheric isocyanate monomer concentrations. As a result, spectrophotometric methods have generally been discarded or overlooked. However, the principal advantage of this method is its considerably reduced sample handling prior to the chromatographic step. The simplicity of the method is the result of the very rapid and complete one-step sample preparation and the fact that unreacted H_3PO_4 does not interfere with the subsequent chromatography. The column remains unaltered over 1000 injections. Our method is linear up to at least 3 nmol, which is 100 times above the detection limit. Complete determination, including sample preparation and analysis, can be performed in less than 30 min. This procedure is a very efficient method of collecting MDI in industrial environments, even when measuring trace concentrations. The equipment required is

relatively inexpensive and readily available. This enables on-site analysis to be carried out by most factories.

Since DAPM is also present in the environment, it can be trapped in the silica gel and consequently simulate the presence of MDI. In order to determine the environmental level of MDI only, we took advantage of the fact that MDI does not collect on silica gel without acid. This was done by preparing two types of traps: one containing acid which collected both MDI and DAPM and another without acid which collected only DAPM.

Other amines (hexamethylendiamine, 2,4-toluendiamine, 2,6-toluendiamine) do not interfere since they have different retention times and 2,4-toluene diisocyanate and 2,6-toluene diisocyanate do not interfere since they cannot be determined by gas chromatography, probably because of their polymerization.

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Thermodynamic background of selectivity shifts in temperature-programmed, constant-density supercritical fluid chromatography

Michal Roth

Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, 61142 Brno, Czech Republic

Abstract

Theoretical principles of the temperature-driven selectivity shifts in capillary supercritical fluid chromatography (SFC) at a constant density of the mobile phase fluid are outlined. Sensitivity of the separate thermodynamic properties involved in the shifts in the intensity of a particular pairwise interaction between components of the solute–stationary polymer–supercritical fluid system is discussed. Thermodynamic analysis confirms the expected significance of dissolution of the mobile phase fluid in the stationary polymer ("swelling") for this kind of selectivity shift. With a single exception, all the thermodynamic derivatives involved in the shifts are either directly related to or at least partly influenced by swelling. The selectivity shifts do not involve any property that would depend only on interaction between a solute and a pure stationary polymer. This finding shows that swelling of the stationary phase can hardly be ignored in the theoretical interpretation of selectivity in SFC.

1. Introduction

In an experimental study of temperature-programmed, capillary supercritical fluid chromatography (SFC) at a constant density of the mobile phase fluid (carbon dioxide), Chester and Innis [1] noted density- and temperature-dependent selectivity shifts for phenanthrene and anthracene with respect to alkanes. The selectivity shifts varied strongly with substituents on the siloxane backbone of the stationary polymer, increasing from poly(dimethylsiloxane) through biphenyl-substituted polysiloxane to cyanopropyl-substituted polysiloxane. Chester and Innis concluded that the selectivity shifts most likely arose because of swelling of the stationary phase by the absorbed mobile phase.

In capillary SFC, retention and/or selectivity have been correlated or predicted by employing diverse theoretical or semi-empirical treatments, e.g., those based on the mean-field lattice-gas models of statistical thermodynamics [2–4]. However, the predictions based on such treatments are always qualified and limited by the approximations embedded in the development of the particular model. Therefore, it might be useful to return to classical rather than statistical thermodynamics and, within a model-independent analysis, attempt to identify the well defined thermodynamic properties of the solute–stationary polymer–supercritical fluid system

that are responsible for the selectivity shifts mentioned above.

2. Theory

The starting point is the expression for the change in the solute capacity factor with temperature at a constant density of the mobile phase fluid [4–6]. From that expression, one obtains the following relationship for the temperature derivative of the logarithm of the separation factor, α_{ab}^{f}, of solutes a and b on a stationary phase f at a constant density, ρ_m, of the mobile phase fluid m,

$$[\partial \ln \alpha_{ab}^{f} / \partial (1/T)]_{\rho_m} =$$

$$[\Delta H_{tb}^{m \to f} - \Delta H_{ta}^{m \to f} - T\gamma_{mV}(\Delta V_{tb}^{m \to f} - \Delta V_{ta}^{m \to f})]/R$$

$$+ (T/R)[(\partial \mu_{af}^{\infty} / \partial w_{mf}) - (\partial \mu_{bf}^{\infty} / \partial w_{mf})]$$

$$\times [(\partial w_{mf} / \partial T)_{P,\sigma} + \gamma_{mV}(\partial w_{mf} / \partial P)_{T,\sigma}] \qquad (1)$$

where R is the molar gas constant, T the absolute temperature, P the pressure, γ_{mV} the thermal pressure coefficient of the mobile phase fluid, w_{mf} the mass fraction of the mobile phase fluid m in the stationary phase f and the subscript σ denotes saturation of the stationary phase with the absorbed mobile phase fluid. It has been assumed in Eq. 1 that bulk dissolution is the only mechanism of solute retention, that the solute concentrations in both phases are close to infinite dilution and that the temperature and pressure in the column are well removed from the mobile phase critical point so that the presence of a small amount of solute does not disturb the equilibrium mass fraction of the mobile phase fluid in the stationary phase. The derivatives of the infinite-dilution chemical potentials, μ_{af}^{∞} and μ_{bf}^{∞}, of the two solutes in the stationary phase with respect to w_{mf} are those at constant temperature, pressure and amount of the stationary polymer. The ΔHs and ΔVs denote the transfer properties of the indicated solute, e.g., $\Delta H_{ta}^{m \to f}$ is the molar enthalpy of transfer of solute a from the mobile phase m to the stationary phase f:

$$\Delta H_{ta}^{m \to f} = \bar{h}_{af}^{\infty} - \bar{h}_{am}^{\infty} \qquad (2)$$

where $\bar{h}_{am}^{\infty}$ and $\bar{h}_{af}^{\infty}$ are the infinite-dilution partial molar enthalpies of the solute in the two phases, respectively. Throughout this paper, the term "stationary phase" includes the absorbed mobile phase fluid, e.g., the stationary phase f is an equilibrium mixture of a stationary polymer φ with the dissolved mobile phase fluid m. Employing general thermodynamic identities, one may recast the last bracketed term in Eq. 1 as

$$(\partial w_{mf} / \partial T)_{P,\sigma} + \gamma_{mV}(\partial w_{mf} / \partial P)_{T,\sigma}$$

$$= [\gamma_{mV} - \Delta S_{tm}^{m \to f} / \Delta V_{tm}^{m \to f}](\partial w_{mf} / \partial P)_{T,\sigma} \qquad (3)$$

where $\Delta S_{tm}^{m \to f}$ and $\Delta V_{tm}^{m \to f}$ denote, respectively, the molar entropy and molar volume of transfer of the mobile phase fluid m from the pure mobile phase into the stationary phase f, i.e.

$$\Delta S_{tm}^{m \to f} = \bar{s}_{mf} - s_m^0 \qquad (4)$$

$$\Delta V_{tm}^{m \to f} = \bar{v}_{mf} - v_m^0 \qquad (5)$$

where s_m^0 and v_m^0 are the molar entropy and molar volume of the pure mobile phase fluid and $\bar{s}_{mf}$ and $\bar{v}_{mf}$ are the partial molar entropy and partial molar volume of the mobile phase fluid dissolved in the stationary phase. The two terms in brackets on the right-hand side of Eq. 3 have the same physical dimension, since

$$\gamma_{mV} \equiv (\partial P / \partial T)_{\rho_m} = (\partial s_m^0 / \partial v_m^0)_T \qquad (6)$$

For discussion of the selectivity shifts mentioned above [1], the relevant quantity is the difference between the rates of temperature change in selectivity for solutes a and b on stationary phases f and g at a constant density of the mobile phase fluid. It follows from Eqs. 1–3 that

$$[\partial \ln \alpha_{ab}^{f} / \partial (1/T)]_{\rho_m} - [\partial \ln \alpha_{ab}^{g} / \partial (1/T)]_{\rho_m}$$

$$= [\Delta H_{tb}^{f \to g} - \Delta H_{ta}^{f \to g} - T\gamma_{mV}(\Delta V_{tb}^{f \to g} - \Delta V_{ta}^{f \to g})]/R$$

$$+ (T/R)\left[\left(\frac{\partial \mu_{af}^{\infty}}{\partial w_{mf}}\right) - \left(\frac{\partial \mu_{bf}^{\infty}}{\partial w_{mf}}\right)\right]\left[\gamma_{mV} - \frac{\Delta S_{tm}^{m \to f}}{\Delta V_{tm}^{m \to f}}\right]$$

$$\times \left(\frac{\partial w_{mf}}{\partial P}\right)_{T,\sigma} - (T/R)\left[\left(\frac{\partial \mu_{ag}^{\infty}}{\partial w_{mg}}\right) - \left(\frac{\partial \mu_{bg}^{\infty}}{\partial w_{mg}}\right)\right]$$

$$\times \left[\gamma_{mV} - \frac{\Delta S^{m \to g}_{tm}}{\Delta V^{m \to g}_{tm}} \right] \left(\frac{\partial w_{mg}}{\partial P} \right)_{T,\sigma} \qquad (7)$$

The mobile phase fluid and its density are the same for both stationary phases. Therefore, the solute properties in the mobile phase are absent from Eq. 7, and the ΔHs and ΔVs in the first bracket on the right-hand side refer to solute transfer from the stationary phase f to the stationary phase g. The molar volume of transfer of solute a, for example, is

$$\Delta V^{f \to g}_{ta} = \bar{v}^{\infty}_{ag} - \bar{v}^{\infty}_{af} \qquad (8)$$

where $\bar{v}^{\infty}_{af}$ and $\bar{v}^{\infty}_{ag}$ are the infinite-dilution partial molar volumes of the solute a in the stationary phases f and g, respectively. The stationary phase g is an equilibrium mixture of a stationary polymer γ with the dissolved mobile phase fluid m.

The difference given by Eq. 7 exactly equals zero only in the trivial case when the two stationary phases are the same, $f = g$ ($\varphi = \gamma$). This situation is characterized by the following equalities in the types and/or intensities of the three kinds of pairwise interactions that occur within the system:

$$\left. \begin{array}{l} a-\varphi = a-\gamma \\ b-\varphi = b-\gamma \end{array} \right\} \qquad \text{solute–polymer;}$$

$$\varphi-m = \gamma-m \qquad \text{polymer–mobile phase fluid; and}$$

$$\left. \begin{array}{l} (a-m)_f = (a-m)_g \\ (b-m)_f = (b-m)_g \end{array} \right\} \qquad \begin{array}{l} \text{solute–mobile phase fluid} \\ \text{interaction within the} \\ \text{stationary phase.} \end{array}$$

Consequently, a temperature-driven selectivity shift between the stationary phases f and g results only if at least one equality within the three groups above has been broken. It is important to note that, because of generality of Eq. 7, the particular character of intermolecular interactions involved is immaterial; the interactions may range from ubiquitous dispersion, induction and orientation forces through specific interactions by hydrogen bonding or charge transfer to shape selectivity resulting from chiral discrimination or from effects of oriented

mesophases (liquid crystals). In what follows, the terms in Eq. 7 that are affected by a particular pairwise interaction between components of the chromatographic system will be identified and discussed.

2.1. Solute–stationary polymer interaction (a–φ)

Among the three kinds of pairwise interactions underlying the selectivity shifts, this one is the easiest to interpret. In Eq. 7, the only quantities influenced by the $a-\varphi$ interaction are $\Delta H^{f \to g}_{ta}$, $\Delta V^{f \to g}_{ta}$ and $(\partial \mu^{\infty}_{af}/\partial w_{mf})$. The first two quantities relate to the transfer of solute a between swollen stationary phases f and g. In the two stationary phases, the polymers φ and γ are diluted with the absorbed mobile phase fluid. For this reason, the effects of the $a-\varphi$ interaction on $\Delta H^{f \to g}_{ta}$ and $\Delta V^{f \to g}_{ta}$ will be suppressed as compared with the transfer of solute a from the state of infinite dilution in the pure polymer φ to the state of infinite dilution in the pure polymer γ.

In effect, the quantity $(\partial \mu^{\infty}_{af}/\partial w_{mf})$ measures how the solute fugacity responds to the changing molecular environment in the stationary phase. This quantity results from a complex interplay of the enthalpic and entropic effects because

$$(\partial \mu^{\infty}_{af}/\partial w_{mf}) = (\partial \bar{h}^{\infty}_{af}/\partial w_{mf}) - T(\partial \bar{s}^{\infty}_{af}/\partial w_{mf}) \qquad (9)$$

where $\bar{s}^{\infty}_{af}$ is the infinite-dilution partial molar entropy of the solute a in the stationary phase f. At a low pressure, $w_{mf} \to 0$, and a strong and/or specific $a-\varphi$ interaction will result in a value of $(\partial \mu^{\infty}_{af}/\partial w_{mf})$ that will be different from the values typical of systems dominated by dispersion forces. The trend in that value with increasing pressure and increasing w_{mf} will depend on the strength and specificity of both $a-m$ and $\varphi-m$ interactions. If these interactions are not specific, then the effect of a strong $a-\varphi$ interaction on $(\partial \mu^{\infty}_{af}/\partial w_{mf})$ will gradually be attenuated by an increasing amount of the mobile phase fluid dissolved in the stationary phase. In a model system dominated by dispersion forces, with a = naphthalene, φ = poly(dimethylsiloxane) and $m = CO_2$, previous statistical thermodynamic calculations [4] suggest that

$(\partial\mu_{af}^{\infty}/\partial w_{mf})$ is negative, ranging from -3 to -5, and that it makes an important contribution to the slope $\partial \ln k'_{af}/\partial(1/T)$ at a constant density of the mobile phase fluid. In a system with a specific $a-\varphi$ interaction, the ratio $(\partial\mu_{af}^{\infty}/\partial w_{mf})$ would be even more important. This will result in amplification of the selectivity shift for the solutes a and b between the stationary phases f and g.

2.2. Stationary polymer–mobile phase fluid interaction (φ–m)

Among the three kinds of pairwise interactions within the solute–stationary polymer–mobile phase fluid system, the φ–m interaction concerns the largest number of thermodynamic properties appearing in Eq. 7. The quantities directly affected by the φ–m interaction are $(\partial w_{mf}/\partial P)_{T,\sigma}$ and $\Delta S_{tm}^{m\to f}/\Delta V_{tm}^{m\to f}$. In addition to these first-order effects, there are a number of second-order effects involving the ratios $(\partial\mu_{af}^{\infty}/\partial w_{mf})$ and $(\partial\mu_{bf}^{\infty}/\partial w_{mf})$ as well as all the transfer properties of the solutes, $\Delta H_{ta}^{f\to g}$, $\Delta H_{tb}^{f\to g}$, $\Delta V_{ta}^{f\to g}$ and $\Delta V_{tb}^{f\to g}$.

First-order effects

The ratio $(\partial w_{mf}/\partial P)_{T,\sigma}$ measures the isothermal rate of increase with pressure in the equilibrium mass fraction of the mobile phase fluid in the stationary phase. Among the polymer–supercritical fluid systems of interest in open-tubular capillary SFC, the largest amount of reliable data on swelling is available for the poly(dimethylsiloxane)–CO_2 system in the form of changes in volume [7–11] or composition [9–12] with pressure. Information on other systems is scarce [13–16]. The pressure courses of w_{mf} and of the swollen volume generally follow complex S-shaped patterns, and, in the poly(dimethylsiloxane)–CO_2 system, they have been correlated by employing diverse forms of the lattice-gas model of statistical thermodynamics [4,11,12,17,18]. A strong or specific φ–m interaction promotes both the solubility, w_{mf}, and the rate of its increase with pressure, $(\partial w_{mf}/\partial P)_{T,\sigma}$. For example, at a fixed tempera-

ture and pressure, the solubility of CO_2 in poly(methyltrifluoropropylsiloxane) [13,14] is larger than that in alkyl- or aryl-substituted polysiloxanes because of a specific interaction between an oxygen atom in CO_2 and the hydrogen atoms of the methylene group adjacent to the trifluoromethyl group in the side-chain of the polymer. It is apparent from Eq. 7 that an increase in $(\partial w_{mf}/\partial P)_{T,\sigma}$ enhances the selectivity shift between the stationary phases f and g.

The ratio $\Delta S_{tm}^{m\to f}/\Delta V_{tm}^{m\to f}$ reflects the changes in the molar entropy and molar volume of the mobile phase fluid upon its dissolution in the stationary phase. The contribution of the uptake of mobile phase fluid by the stationary polymer to the temperature-induced selectivity shifts (Eq. 7) is proportional to the difference between the thermal pressure coefficient, γ_{mV}, of the pure, supercritical, mobile phase fluid and the ratio $\Delta S_{tm}^{m\to f}/\Delta V_{tm}^{m\to f}$. Recalling Eq. 6, one finds that the difference $\gamma_{mV} - \Delta S_{tm}^{m\to f}/\Delta V_{tm}^{m\to f}$ measures how the ratio of changes in the molar entropy and molar volume of the mobile phase fluid upon its dissolution in the stationary polymer departs from the slope of an isochore of the pure mobile phase fluid. The transfer properties $\Delta S_{tm}^{m\to f}$ and $\Delta V_{tm}^{m\to f}$ will be correlated to some extent, and the correlation will tend to produce a levelling among the ratios $\Delta S_{tm}^{m\to f}/\Delta V_{tm}^{m\to f}$ in different polymer–fluid systems. However, the absolute difference $\gamma_{mV} - \Delta S_{tm}^{m\to f}/\Delta V_{tm}^{m\to f}$ will generally increase with increasing strength and/or specificity of the φ–m interactions. For example, at a given temperature and pressure, the difference is certainly larger in magnitude in the poly(methyltrifluoropropylsiloxane)–CO_2 system as compared with the poly(dimethylsiloxane)–CO_2 system, for the reasons mentioned above.

Second-order effects

The indirect effects of the φ–m interaction in Eq. 7 concern the differences between some properties of solutes a and b, namely $(\partial\mu_{af}^{\infty}/\partial w_{mf}) - (\partial\mu_{bf}^{\infty}/\partial w_{mf})$, $\Delta H_{ta}^{f\to g} - \Delta H_{tb}^{f\to g}$ and $\Delta V_{ta}^{f\to g} - \Delta V_{tb}^{f\to g}$. Therefore, if neither of the interactions $a-\varphi$, $b-\varphi$, $a-\gamma$, $b-\gamma$, $a-m$ and $b-m$ is specific or much stronger than the rest, the