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Temperature and pressure effects on solubility in supercritical carbon dioxide and retention in supercritical fluid chromatography

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Abstract

Solubilities of some polycyclic aromatic hydrocarbons (PAHs) in supercritical carbon dioxide were measured with a procedure based on a direct on-line combination of a saturation cell to a flame ionization detector. Acenaphthene, anthracene and chrysene were selected as the test solutes. A method was developed and evaluated which enables the measurement of the contribution of solute vapor pressure to the overall solubility. The effects of temperature and pressure on solubility in supercritical carbon dioxide were investigated and discussed in detail. The trends of solubility changes in supercritical carbon dioxide and the variations in observed retention in supercritical fluid chromatography (SFC) were correlated. Equations were derived to estimate the effects of temperature on the solute's affinity for the stationary phase in SFC. © 1997 Elsevier Science B.V.

Keywords: Temperature effects; Solubility parameters; Supercritical fluids; Vapor pressure; Retention behaviour; Polynuclear aromatic hydrocarbons

1. Introduction

In method development for supercritical fluid chromatography (SFC) and supercritical fluid extraction (SFE), one of the most important parameters to be considered is the solubility of the target compounds in the supercritical fluid. The solubility of a component in a supercritical fluid is generally assumed to be controlled by two parameters: the vapor pressure of the component and its interaction with the supercritical fluid. Many research groups have investigated the effects of various parameters on overall solubilities in supercritical fluids [1–8].

As mentioned above, the solubility data reported in literature are the sum of the contributions of the vapor pressure of the component and its interaction

with the supercritical fluid. It is evident that these data are very important for method development in both SFC and SFE. However, to obtain a detailed insight into the effects of temperature and pressure on solubility, it is also very important to distinguish these two different contributions to the overall solubility. Unfortunately, however, no reports on the differentiation between these two contributions have been published so far. The explanations of the effects of experimental parameters on solubilities in supercritical fluids and retention in SFC are very often found to be incomplete at best. For example, in SFC at a constant pressure, curves representing the effect of temperature on retention can generally be divided into two different regions. The ascending–descending shape of the curves are normally explained by two competing effects. Under conditions where the solute vapor pressure is not a dominant consideration, increasing temperature will lead to an increase

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in retention due to a reduced supercritical fluid density. If the solute has significant vapor pressure then increasing temperature will result in lower retention factors [9]. However, as will be shown later in this report, this widely accepted explanation of the influence of temperature on retention is over simplified and in some cases even incorrect. For a more appropriate explanation, the contributions of (i) the vapor pressure and (ii) molecular interactions with the supercritical fluid to the overall solubility at different experimental conditions should be distinguished and assessed. In addition to this, for a thorough understanding of retention in SFC, the effects of temperature on the solute's affinity for the stationary phase should also be considered. Again, no reports on the influence of temperature on the affinity of a solute for a stationary phase have been published so far.

In this article, overall solubilities of some polycyclic aromatic hydrocarbons (PAHs) in supercritical carbon dioxide were determined over a wide range of temperatures and pressures. A method to measure the contribution of vapor pressure to the overall solubility was proposed and evaluated. The effects of temperature and pressure on solubilities in supercritical carbon dioxide were investigated and discussed in detail. Furthermore, the effects of experimental conditions on retention in SFC were studied and discussed. Finally, equations were derived to estimate the effects of temperature on affinity of the solute for the stationary phase in SFC.

2. Experimental

All experiments were carried out on a Carlo Erba SFC 3000 instrument (Carlo Erba, Milan, Italy) equipped with flame ionization detection (FID). A 3-ml stainless steel SFE extraction cell (Suprex Pittsburg, PA, USA) with hand-tight connectors (Suprex) was used as the saturation cell. Prior to be packed into the saturation cell, the solute to be investigated was admixed with clean sand at approximately 5% (w/w). Stainless steel frits (3 μm) were located at either end of the saturation cell. Pressurized carbon dioxide was introduced into the saturation cell through a 1-meter preheating coil made of stainless steel tubing (1/16 in. \times 0.03 in.; 1

in.=2.54 cm). A piece of fused-silica capillary (50 cm \times 200 μm I.D.) with one end carefully tapered was used as the restrictor to maintain supercritical conditions inside the saturation cell. The carbon dioxide flow-rate was measured as gaseous flow exiting from the FID system (with the FID gases off and FID temperature at 420°C). In order to prevent entrainment of the solutes by the supercritical fluid flow and to avoid incomplete vaporization in the FID system, as well as to provide enough time for saturation, the carbon dioxide flow-rate was adjusted to relatively low values (approximately 12 ml/min gaseous flow at 350 bar). For the determination of the contribution of vapor pressure to the overall solubility, similar experiments were repeated by using helium as the carrier fluid instead of supercritical carbon dioxide.

Calibration of the FID system was performed by weighing approximately 5 mg of a test compound into the saturation cell followed by elution of the solute at the desired temperature and pressure. The FID response was recorded until the signal returned to baseline. Solubilities were calculated by:

$$S = \frac{A_x W_0 V_{\text{CO}_2}}{A_0 F t_x M_x} \quad (1)$$

where A_x is the area of the test compound, W_0 the amount of test solute weighed into the saturation cell (g), V_{CO_2} the molar gas volume of carbon dioxide (22.4 l/mol), A_0 the area of the calibration compound measured at an amount of W_0 , F the supercritical fluid flow-rate (l/min), t_x the width of the plateau-peak of the FID response (min) and M_x the molecular weight of the test solute (g/mol).

The SFC experiments were performed on the same Carlo Erba SFC 3000 system. The column used for the SFC experiments was a Zorbax ODS reversed-phase HPLC column (25 cm \times 4.6 mm, 5- μm particles) purchased from Rockland Technologies (Chadds Ford, PA, USA). Prior to use, the column was deactivated with *N,O*-bis(trimethylsilyl)-tri-fluoroacetamide (BSTFA) as described previously [10]. The column effluent was split into two streams. One stream was fed to the FID system via a linear fused-silica restriction capillary (45 cm \times 10 μm I.D.). The other was used to control the flow-rate through the column. For the determination of re-

tention factors, methane was used as the dead time (t_0) marker.

The PAHs (acenaphthene, anthracene and chrysene) were all purchased from Aldrich (Milwaukee, WI, USA) with the highest purity available. Carbon dioxide used in the experiments had a purity of 99.996% (Intermar, Breda, Netherlands).

3. Results and discussion

3.1. Solubility determination with on-line FID method

Supercritical carbon dioxide has the capability to dissolve numerous compounds ranging in polarity from non-polar to moderately polar. The aims of this article are threefold: (i) measure the contribution of vapor pressure to the overall solubility; (ii) investigate temperature and pressure effects on SFC retention and (iii) correlate solubilities in supercritical fluids with retention in SFC. In the present investigation, three PAHs (acenaphthene, anthracene and chrysene) were selected as the test solutes. The

method used for measuring solubility was an on-line FID method similar to that described by Miller and Hawthorne [5]. Examples of FID solubility measurements are shown in Figs. 1 and 2. Fig. 1 shows the FID response versus pressure for anthracene at 40°C. Similar curves were also recorded at other temperatures and for the other PAHs. As expected, the solubilities of PAHs in carbon dioxide at constant temperature increase dramatically with increasing pressure.

Compared to the simple effects of pressure (at constant temperature), the effects of temperature on solubility in supercritical CO₂ at constant pressure are far more complicated. Somewhat controversial results on the influence of temperature on solubility were published in literature. Zhao et al. [11] found that in the near-critical region the solubilities of some PAHs in supercritical CO₂ decrease significantly when increasing temperature at a constant pressure. In contrast to this, Miller and Hawthorne [5] reported a continuous increase in the solubility of some organic compounds in CO₂ when increasing temperature at a constant pressure, despite of the decrease in CO₂ density. In our experiments, at

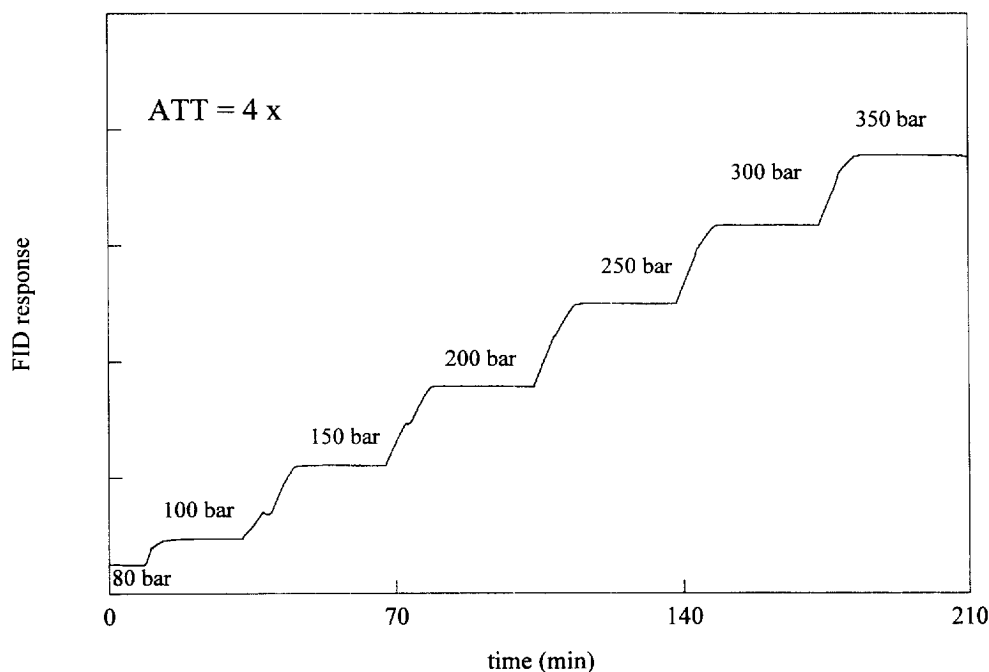


Fig. 1. FID response versus pressure for anthracene at 40°C.

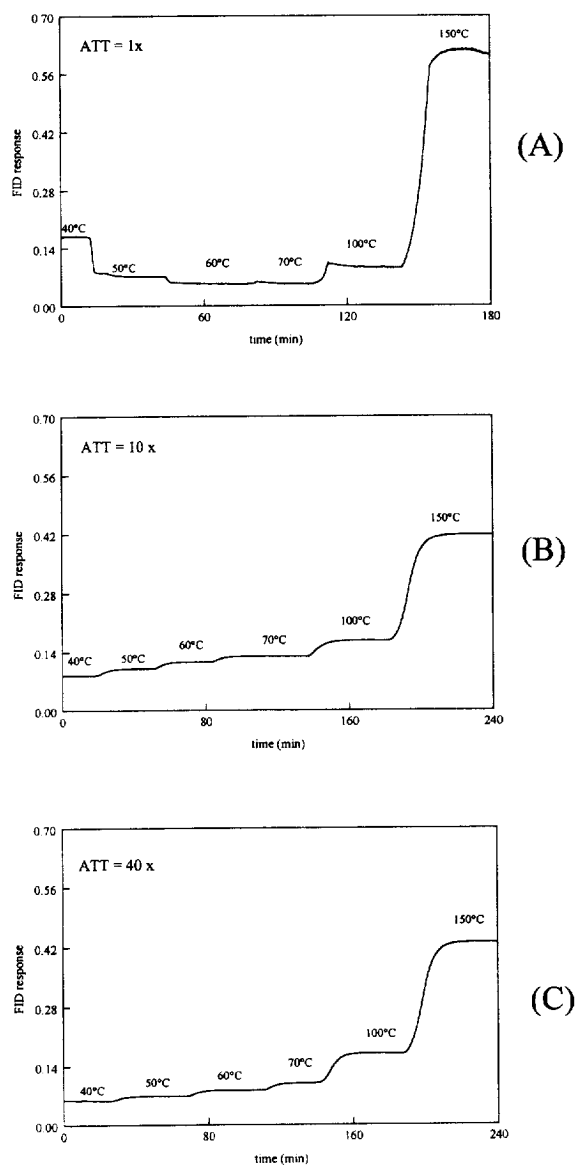


Fig. 2. FID response versus temperature for anthracene at different pressures. (A) 100 bar; (B) 200 bar; (C) 300 bar.

pressures above 200 bar, the solubility of anthracene increased continuously with increasing temperature (Fig. 2B and C), while at the pressure of 100 bar the solubility of anthracene first decreased and then increased with temperature (Fig. 2A). From these results, it can be concluded that the effects of temperature on solubility are quite complicated. Moreover, they can depend on the pressure and

temperature range in which the experiments are performed. A somewhat qualitative explanation for this observation will be discussed later in this contribution.

Table 1 lists solubility data of the PAHs measured using the on-line FID method over a wide range of temperature and pressure conditions (40–150°C and 80–350 bar). Higher temperatures and pressures were not tested because of the limitations of the polymeric seals located at the ends of the saturation cell and the maximum allowable pressure of the pump. For acenaphthene at temperatures below 100°C, an unstable FID signal was obtained at pressures above 100 bar. The reason for this is still unclear. The data listed in Table 1 are based on triplicate determinations. The relative standard deviations of all determinations were within 10%, and mostly within 5%.

3.2. Fundamental study of temperature and pressure effects on solubility

The solubility data obtained in the previous section can be modeled as the sum of the contributions of the vapor pressure of the component and of its interaction with the supercritical fluid. Although this might be an oversimplification of the actual physico-chemical back-grounds of the dissolution process, this way of looking at solubility in supercritical fluids is now widely accepted. For a more thorough investigation of temperature and pressure effects on solubility, the two different contributions to the overall solubility should be differentiated. The contribution of vapor pressure at different experimental conditions was measured by using helium as the carrier fluid instead of supercritical carbon dioxide. Helium, even at high pressures, is an ideal gas that exhibits no interaction with the solute molecules. Hence, transport of the solute out of the saturation cell is solely due to its vapor pressure. The data of these experiments are presented in Table 1. Evidently, the contribution of vapor pressure strongly depends on temperature and the properties of the solute. For volatile compounds at high temperatures the contribution of vapor pressure to the overall solubility can be significant. For the semi-volatile PAHs investigated, however, the contribution of vapor pressure is very much limited (see Table 1).

Table 1

Solubility of acenaphthene, anthracene and chrysene ($\text{mol/mol} \times 10^5$) in carbon dioxide at different temperatures and pressures measured by the on-line FID method

<i>P</i> (bar)	<i>T</i> (°C)					
	40	50	60	70	80	100
<i>Acenaphthene</i>						
75	2.94	2.79	3.81	5.66	9.18	17.0
80	5.61	4.12	5.07	7.75	11.0	19.0
85	12.7	7.37	6.91	11.4	14.6	23.3
90	NT ^a	11.1	9.42	13.4	16.4	24.8
100	NT	33.4	23.4	NT	NT	41.3
150	NT	NT	NT	NT	NT	237.0
He ^b	0.0038	0.013	0.031	0.07	0.14	0.52
<i>T</i> (°C)						
	40	50	60	70	100	150
<i>Chrysene</i>						
80	0.242	0.168	NT	NT	NT	NT
100	1.54	0.45	0.253	NT	0.733	7.16
150	4.98	4.62	NT	NT	3.97	NT
200	5.92	7.43	9.19	10.6	13.4	40.3
300	8.23	11.6	15.9	21.2	43.2	126.0
350	8.53	13.3	NT	NT	57.6	NT
He	ND ^c	ND	ND	ND	0.032	0.977
<i>T</i> (°C)						
	40	50	70	100	120	150
<i>Chrysene</i>						
80	0.0397	0.0204	NT	0.0422	NT	NT
100	0.0452	0.0265	NT	0.077	NT	NT
150	0.396	0.347	NT	0.367	NT	NT
200	0.483	0.619	0.826	1.08	1.54	2.85
300	0.755	1.09	2.14	4.72	7.57	14.8
350	0.800	1.19	NT	6.13	NT	NT
He	ND	ND	ND	ND	ND	0.0032

^a Not tested.

^b Contribution of vapor pressure tested by using helium as the carrier fluid.

^c Not detectable.

For example, for anthracene the vapor pressure contribution at the highest temperature tested (150°C) at 100 bar and 300 bar was only 13% and 0.8%, respectively. For the less volatile chrysene, only about 0.02% of the solubility was caused by volatility at 300 bar and 150°C. At lower temperatures, the contribution of vapor pressure to the overall solubility will be even less. No measurable contribution of volatility was found for anthracene and chrysene at temperatures below 70°C and 100°C, respectively. From this it can be concluded that the contribution of vapor pressure to the solubilities of

the PAHs is very much limited, even at relatively high temperatures. In literature, the contribution of vapor pressure to the overall solubility is often overestimated, especially for semi-volatile or non-volatile compounds. Increased solubilities at elevated temperatures are mainly due to the variations of physicochemical properties of the solutes and the supercritical fluid. This phenomenon will be addressed in more detail below.

By using the solubility parameter theory [12], the effects of temperature and density (or pressure) on solubility in supercritical fluids can be explained

qualitatively. The basis of this theory is that a higher solubility is achieved when the solubility parameters of the solute and solvent are closer to each other. The solubility parameter of a given solute is mainly controlled by its properties and temperature. It generally decreases monotonically with temperature [13]. For a supercritical fluid the solubility parameter can be calculated from [14]

$$\delta_{SF} = 1.25P_c^{1/2} \left(\frac{\rho_{r,SF}}{\rho_{r,L}} \right) \quad (2)$$

where δ_{SF} is the solubility parameter of the supercritical fluid, P_c the fluid critical pressure, $\rho_{r,SF}$ the reduced density of the fluid and $\rho_{r,L}$ the reduced density of the extraction fluid in the quasi-liquid state. Table 2 lists the solubility parameters of the PAHs and carbon dioxide at 80°C and 340 bar.

When increasing pressure at a constant temperature, the solubility parameters of the PAHs remain virtually constant while that of the fluid increases and approaches those of the solutes. Therefore, at a constant temperature, the solubilities of the PAHs increase with pressure. Increasing temperature at a constant density results in a decrease in the solubility parameters of the solutes while that of the fluid remains virtually constant. As a result the solubility will increase. In contrast to the continuous increase of solubility at a constant density, a more complicated situation arises when increasing temperature at a constant pressure. In this case, the solubility parameters of both the solutes and the supercritical fluid will decrease. The actual effects of temperature now depend on the temperature and pressure conditions as well as on the properties of the solutes and the fluid. The solubility parameter theory can, unfortunately, only provide a qualitative explanation for the observed effects of temperature and pressure on solubilities in supercritical fluids. For more quantitative explanations or predictions, more de-

tailed physicochemical parameters that are generally not available, would be required.

3.3. Effects of temperature on solute affinity for the stationary phase in SFC

As described in the Section 1, the explanations of the influence of experimental parameters on SFC retention is very often found to be oversimplified. In this section the effects of temperature and pressure on SFC retention are investigated in more detail. Table 3 lists retention factors of the PAHs at different temperature and pressure conditions. From Table 3 it is clear that the effects of temperature on retention can be quite different at different pressures. At pressures below 200 bar, the retention factors of all the PAHs tested increase rapidly and continuously when raising temperature from 40°C to 100°C. However, at pressures above 300 bar the retention factors first decrease and then increase with temperature. It is interesting to correlate the trends of solubility changes in supercritical carbon dioxide with the variations in observed SFC retention. As has been demonstrated in the previous sections, at pressures above 200 bar, the solubilities of the PAHs increase considerably with temperature (see Table 1). From this result one would expect that at these pressures the retention factors of the PAHs will decrease with temperature. Contrary to this expectation, the retention factors are found to increase considerably rather than decrease as would be expected on the basis of the solubility data. From this it can be concluded that for the prediction of temperature and pressure effects on SFC retention, it is not enough to only consider the solubility of a solute in the supercritical mobile phase. Apparently, the effects of temperature and pressure on the solute's affinity for the stationary phase should also be considered. This, however, has not received enough attention so far. In the following paragraphs some equations were derived to investigate the effects of temperature and pressure on solute affinity for the stationary phase in SFC.

In SFC, retention is governed by the distribution of the component between the stationary phase and the supercritical mobile phase, or in other words, controlled by solubility of the component in the

Table 2
Solubility parameters (MPa^{1/2}) of acenaphthene, anthracene, chrysene and carbon dioxide

Acenaphthene ^a	Anthracene ^a	Chrysene ^a	Carbon dioxide ^b
22.4	22.7	23.6	16.3

^a Estimated according to Fedors [13].

^b At 40°C and 350 bar, calculated according to Giddings et al. [14].

Table 3
Effects of temperature and pressure on retention factors

T (°C)	P (bar)					
	100	150	200	250	300	350
<i>Acenaphthene</i>						
40	9.38	3.30	2.28	1.86	1.61	1.46
50	67.3	4.26	2.52	1.89	1.57	1.39
70	230	11.3	3.54	2.16	1.63	1.33
100	194	27.6	6.83	2.96	1.92	1.39
<i>Anthracene</i>						
40	19.4	5.78	3.82	3.02	2.56	2.27
50	NT ^a	7.84	4.27	3.07	2.48	2.15
70	NT	24.1	6.17	3.57	2.58	2.04
100	NT	68.9	13.8	5.18	3.10	2.16
<i>Chrysene</i>						
40	NT	NT	12.7	9.48	7.71	6.61
50	NT	NT	14.2	9.48	7.27	6.02
70	NT	NT	22.0	11.0	7.29	5.49
100	NT	NT	54.6	17.0	8.72	5.64

^a Not tested.

supercritical fluid and its affinity for the stationary phase. The retention factor (k) can be expressed as

$$k = \frac{K}{\beta} \quad (3)$$

where K is the distribution coefficient between the stationary phase and the mobile phase and β is the phase ratio. It is evident that K is determined by the solubility of the component in the mobile phase and its affinity for the stationary phase, which can be written as

$$K = A \frac{S_{sp}}{S_{mp}} \quad (4)$$

where A is a constant, S_{sp} and S_{mp} (mol/ml) are the affinity of the component for the stationary phase and its solubility in the mobile phase, respectively. Combining Eqs. (3) and (4) yields

$$k = \frac{AS_{sp}}{\beta S_{mp}} \quad (5)$$

In Eq. (5), A and β are constants, while k and S_{mp} can be measured experimentally. Thus, the effect of temperature on S_{sp} can be estimated by

$$\frac{S_{sp,T1}}{S_{sp,T2}} = \frac{k_{T1}S_{mp,T1}}{k_{T2}S_{mp,T2}} \quad (6)$$

By using Eq. (6), the relative solute affinity values for the stationary phase at different temperatures can be calculated. Table 4 lists the affinity values of the PAHs for the stationary phase at various temperatures relative to those at 40°C. As can be seen from Table 4, the affinities of the PAHs for the stationary phase increase considerably with temperature at all pressures tested. It is interesting to note that no effect of pressure on the relative affinity values for the stationary phase was observed. This indicates that

Table 4
Relative affinities of anthracene and chrysene for an ODS stationary phase at different temperatures^a

P (bar)	T (°C)		
	50	70	100
<i>Anthracene</i>			
150	1.31	2.25	4.62
250	1.30	2.25	4.63
350	1.31	2.25	4.62
<i>Chrysene</i>			
200	1.30	2.32	5.12
300	1.30	2.33	5.15
350	1.31	2.32	5.11

^a Values relative to the affinities at 40°C.

the interaction between the solute and the ODS stationary phase is not affected by the pressure of the mobile phase.

From the discussion above, it is clear that the effect of pressure (at constant temperature) on SFC retention is relatively straightforward. A higher pressure will lead to lower retention factors. The effects of temperature (at constant pressure) are, on the contrary, very complicated. Temperature not only affects the vapor pressure of the solute and the density of the supercritical fluid, but also influences the solubility parameters of both the solute and the supercritical fluid. Moreover, temperature changes can affect the affinity of the compound for the stationary phase. The actual effect of temperature on retention is a result of the various mechanisms identified above and will depend on the experimental conditions, the properties of the solutes and those of the supercritical fluid and the stationary phase.

4. Conclusions

The interpretations of temperature effects on solubility in carbon dioxide and retention in SFC presented in literature are sometimes incomplete and oversimplified. The influence of temperature on solubility in supercritical fluids is determined by the properties of the solute and the supercritical fluid as well as by the experimental temperature and pressure conditions. Temperature variations will induce changes in the vapor pressure of the solute, the density of the supercritical fluid and the physico-

chemical properties of both the solute and the supercritical fluid. In literature, the contribution of vapor pressure to the overall solubility is frequently overestimated, especially for semi-volatile or non-volatile compounds. In addition to the effects on solubility, temperature changes can also affect the affinity of solutes for the stationary phase in SFC.

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