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Capacity ratios in supercritical fluid chromatography Effect of mobile and stationary phases on hexasubstituted benzenes¹

Cornelia B. Kautz, Uwe H. Dahlmann, Gerhard M. Schneider*

Lehrstuhl für Physikalische Chemie II, Fakultät für Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

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Abstract

Capacity ratios k'_i were determined for benzene, hexafluoro-, hexachloro- and hexamethylbenzene from supercritical fluid chromatography. The measurements were performed in the temperature range 305–330 K and at pressures up to 20 MPa. Nucleosil 100-5 C₁₈, Nucleosil 100-5 NO₂ and Nucleosil 100-5, respectively, were used as stationary phases and supercritical carbon dioxide was used as the mobile phase. Influences of the mobile phase density on the capacity ratios as well as peak sequence and selectivity of hexachloro- and hexamethylbenzene are discussed. For different stationary phases the enthalpy of solute transfer from stationary to mobile phase is calculated as a function of mobile phase density. © 1997 Elsevier Science B.V.

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1. Introduction

Supercritical fluid chromatography (SFC) uses compressed gases in the critical temperature range as mobile phases in combination with packed and capillary columns. This chromatographic method supplements well-known techniques such as gas chromatography (GC) or high-performance liquid chromatography (HPLC). The properties of the mobile phase can be varied by programming temperature, pressure and composition [1–6]. Additionally, a variation of the stationary phase in the columns is possible in order to optimize separation or purification problems [1,5–7]. Reviews of SFC

applications and the determination of physico-chemical data are given elsewhere [6–16].

For purification as well as separation processes the knowledge of the capacity ratios of the substances involved is of fundamental importance. The capacity ratio k'_i of the component i is given by [10,16]:

$$k'_i = \frac{c_i^s}{c_i^m} \cdot \frac{V^s}{V^m} = K_i \cdot \frac{V^s}{V^m} \quad (1)$$

(c_i = concentration of component i , V = volume, here the superscripts s and m denote the stationary and mobile phases, respectively). The partition coefficient K_i depends on temperature and pressure, and, therefore, density of the mobile phase. In chromatography the capacity ratio is determined from the retention times $t_{R,i}$ of a substance i and t_0 of an unretained substance according to

*Corresponding author.

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$$k'_i = \frac{t_{R,i} - t_0}{t_0} \quad (2)$$

The main assumptions for the derivation of Eq. (2) are specified elsewhere [14]. Additionally, the separation between two substances i and j is characterized by the selectivity α_{ij} defined by

$$\alpha_{ij} \equiv k'_i / k'_j = K_i / K_j. \quad (3)$$

Furthermore the dependence of the capacity ratio on the temperature at a constant density can be used to calculate the enthalpy of solute transfer ΔH^0 from the mobile phase to the stationary phase.

The enthalpy of transfer is given by the following relationship [1,6–8,10–13]:

$$\left(\frac{d \ln k'_i}{dT^{-1}} \right)_\rho = - \frac{\Delta H^0}{R} + \frac{\Delta V^0 \cdot T}{R} \cdot \left(\frac{dp}{dT} \right)_\rho \quad (4)$$

Here ΔH^0 is the molar enthalpy of solute transfer, ΔV^0 the molar volume change of solute transfer, ρ the density, p the pressure, and T the temperature of the mobile phase. For measurements far from the critical point the second term on the right side of Eq. (4) is negligible compared with the first term.

In the following recent results of SFC experiments on selected aromatic compounds with supercritical carbon dioxide as mobile phase and three different stationary phases are presented. The capacity ratio, the selectivity, the peak sequence and the enthalpy of transfer are discussed as a function of the mobile and stationary phases, respectively.

2. Experimental

A recent description of the fluid chromatograph

used is given elsewhere [7,14]. The chromatograph is suitable for temperatures up to approximately 353 K and pressures up to 20 MPa. Carbon dioxide is condensed into an ISCO (Lincoln, NE, USA) SFC-500 syringe pump under its own vapor pressure at subcritical temperatures. In order to heat the mobile phase up to a supercritical temperature an air thermostat is installed. The column as well as a 6-port Rheodyne (Cotati, CA, USA) Model 7725i valve that is used for the injection of the solutions are placed in the air thermostat. The temperature of the column is measured by means of a platinum resistance thermometer. For the detection of the substances an Uvikon 720 LC UV-Vis spectrophotometer (Kontron Technik, Neufahrn, Germany) and a X-dipole array detector (Polytec GmbH/IKS Optoelectronic, Waldbronn, Germany), respectively, with a 8 μ l pressure resistant flow-through cell is used. Detection takes place at column pressure and temperature. In addition the pressure is measured by a high-precision pressure transducer. The pressure drop across each column is between 0.1 and 0.4 MPa, so the density was calculated from the arithmetic average pressure [17].

At the outlet of the chromatographic system the flow-rate of the expanded mobile phase is measured with a soap bubble flow meter. All data are sampled and handled by a personal computer.

The mobile phase is carbon dioxide (Messer-Griesheim, Düsseldorf, Germany) with a purity of 99.995%. In Table 1 the columns and the stationary phases are characterized. Samples were benzene (purity 99.8% (GC); Merck, Darmstadt, Germany), hexafluoro- (purity >99% (GC); Fluka, Neu-Ulm, Germany), hexachloro- (purity 99%; Aldrich, Steinheim, Germany) and hexamethylbenzene (puri-

Table 1
Column data

Column ^a	Length (mm)	I.D. (mm)	Dead volume (cm ³)	Stationary phase	
				Surface	Supplier
Nucleosil 100-5 C ₁₈	125	3	0.67	Reversed phase (octadecyl) resilanized with HMDS	Macherey-Nagel, Düren, Germany
Nucleosil 100-5 NO ₂	120	4	1.05	(1-Nitro-4-propyl-benzene)	Dr. Ing. Herbert Knauer, Berlin, Germany
Nucleosil 100-5	120	4	1.18	Polar (silanol groups)	Dr. Ing. Herbert Knauer

^a Particle diameter 5 μ m and pore diameter 100 Å.

ty >99%; Fluka). The substances were dissolved in trichloromethane (concentration: 10^{-2} – 10^{-3} mol l $^{-1}$) and in each case 1–2 μ l of the solution were injected.

The measurements were performed under isobaric and isothermal conditions with a constant flow-rate. The flow-rate \dot{V}_A varied between 1.2 and 2.0 cm 3 s $^{-1}$ (NTP). In order to calculate the dead volume of each column, the retention time of an air-peak caused by a refraction index gradient was measured.

3. Results and discussion

The measurements were performed at constant values of temperature and pressure from 305 to 330 K and 10 to 20 MPa, respectively. In these temperature and pressure ranges the density of carbon dioxide was calculated by use of an EOS [18], it varied from 0.62 to 0.87 g ml $^{-1}$. For several columns the variation of k'_i as a function of the density at a constant temperature of 310 K is shown in Fig. 1a,b. For all columns the capacity ratios decrease with increasing density of the mobile phase. As shown earlier, the $\log k'_i$ versus $\log(\rho/\rho^0)$ isotherms are nearly straight lines [1,4,6,7,11,12]. The slopes of these lines are not appreciably affected by the nature of the stationary phase. This agrees with the theoretical relationship of Chimowitz et al. [19] as well as the measurements of Jinno et al. [20].

Additionally, Fig. 1a,b show the dependence of the capacity ratios on different stationary phases. The smallest capacity ratios of the substances under test are observed on Nucleosil 100-5. For hexafluorobenzene and benzene the capacity ratios increase from Nucleosil 100-5 C $_{18}$ up to Nucleosil 100-5 NO $_2$ (see Fig. 1a), whereas the capacity ratios of hexachlorobenzene increase from Nucleosil 100-5 NO $_2$ up to Nucleosil 100-5 C $_{18}$ (see Fig. 1b). Here the capacity ratio of hexamethylbenzene shows no significant difference on the two chemically modified stationary phases. In contrast to the polarity of the stationary phase, which increases from the C $_{18}$ -modified to the NO $_2$ -modified up to the non-modified silica, the highest capacity ratios for hexafluorobenzene and benzene on Nucleosil 100-5 NO $_2$ can be explained from the tendency of forming charge-transfer complexes with the aromatic system. In the

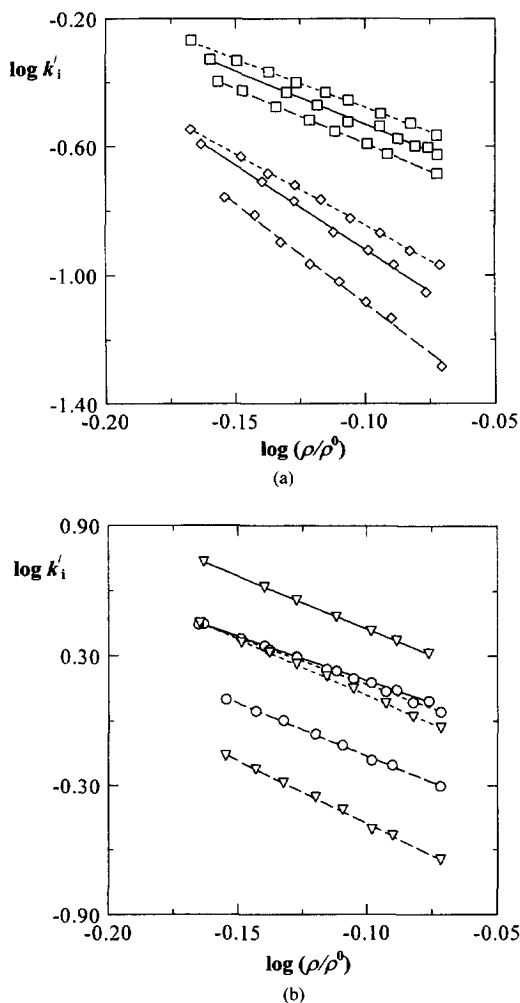


Fig. 1. $\log k'_i$ ($\log(\rho/\rho^0)$) isotherms of (a) hexafluorobenzene (\diamond) and benzene (\square), and of (b) hexamethylbenzene (\circ) and hexachlorobenzene (∇), as a function of the density of the mobile phase (CO_2 ; 310 K, $\rho^0 = 1$ g ml $^{-1}$) using three different columns: (Nucleosil 100-5 C $_{18}$ (—), Nucleosil 100-5 (---), Nucleosil 100-5 NO $_2$ (-----)).

case of hexachloro- and hexamethylbenzene the formation of the charge-transfer complex is hindered by the substituents.

The experiments on Nucleosil 100-5 NO $_2$ exhibit an intersection point of the $\log k'_i$ versus $\log(\rho/\rho^0)$ isotherms of hexachloro- and hexamethylbenzene. In Fig. 2 the change of peak sequence is demonstrated with some chromatograms at 320 K. For all tempera-

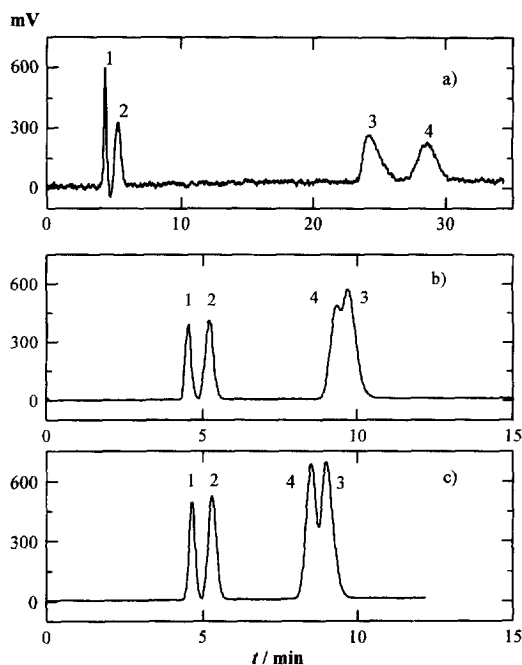


Fig. 2. Chromatograms of the substances (1) hexafluorobenzene, (2) benzene, (3) hexamethylbenzene, and (4) hexachlorobenzene on Nucleosil 100-5 NO₂ at $T=320$ K and $\lambda=260$ nm, (a) $p=10.27$ MPa, $\rho=0.493$ g ml⁻¹, \dot{V}_A (NTP)=1.88 ml s⁻¹, (b) $p=16.28$ MPa, $\rho=0.725$ g ml⁻¹, \dot{V}_A (NTP)=1.83 ml s⁻¹, (c) $p=19.06$ MPa, $\rho=0.792$ g ml⁻¹, \dot{V}_A (NTP)=1.83 ml s⁻¹.

tures the intersection points have been found to be situated at a constant density of about 0.67 g ml⁻¹.

The plots of $\log k'_i$ versus $1/T$ at a constant density are linear and the slope of each plot is related to the enthalpy of solute transfer according to Eq.

(4). In the range of our experiments the first term on the right-hand side of Eq. (4) was larger than the second one by a factor of 50–100.

Table 2 presents the enthalpy of solute transfer from the stationary phase to the mobile phase as a function of the stationary phase and the density of the mobile phase. The enthalpies decrease with increasing density. Probably, the high enthalpies at low densities are a result of the low solubilities of the substances under test in the mobile phase and an increase in attractive interactions between the stationary phase and the solute.

The dependence of transition enthalpy on the mobile phase density increases with increasing polarity of the stationary phase. This is probably a result of decreasing attractive interactions between the stationary phase and the aromatic solute, and, additionally, of the dependence of the solubility on the mobile phase density.

The density dependence of the transition enthalpy is higher for hexachloro- than for hexamethylbenzene, probably because of the higher dependence of the solubility on density for hexachlorobenzene. For hexamethylbenzene the constant enthalpy of transfer for different densities on the C₁₈-modified stationary phase is assumed to be mainly a result of the more or less constant attractive interactions between the stationary phase and the solute. K. Sakaki et al. [21] showed that the plot of $\log k'_i$ versus \log (solubility) at constant temperature gave one straight line that was independent of the mobile phase used. It would therefore be interesting to measure the solubilities of the solutes in different mobile phases [7,12,22].

Table 2
 $\Delta_s^m H^0$ in kJ mol⁻¹ as a function of mobile phase density and stationary phase

Column	$\rho/\text{kg m}^{-3}$	Hexafluorobenzene	Hexachlorobenzene	Hexamethylbenzene
Nucleosil 100-5	600	27.4±3.9	19.9±2.0	17.9±1.4
	700	14.3±1.4	12.3±1.1	13.9±0.7
	800	3.0±1.5	5.7±0.6	10.5±0.4
Nucleosil 100-5 NO ₂	600	15.4±0.7	17.3±0.6	14.1±0.2
	700	8.4±0.1	14.2±0.4	13.2±0.2
	800	2.2±0.4	11.4±0.5	12.3±0.4
Nucleosil 100-5 C ₁₈	600	18.3±1.8	20.6±0.3	17.7±0.2
	700	15.6±1.7	19.8±0.1	17.7±0.2
	800	13.2±3.2	19.1±0.1	17.7±0.2

4. Conclusions

For all columns the capacity ratios decrease with increasing density of the mobile phase. The capacity ratios for hexafluorobenzene and benzene increase from C₁₈- up to NO₂-modified stationary phase, whereas the capacity ratio of hexamethylbenzene shows no significant difference on these two chemically modified phases. In contrast the capacity ratio of hexachlorobenzene increases from NO₂- up to C₁₈-modified stationary phase. The high capacity ratios for hexafluorobenzene and benzene on the NO₂-column were explained from the tendency of forming charge-transfer complexes with the aromatic system. The log k'_i versus log (ρ/ρ^0) isotherms of hexachloro- and hexamethylbenzene show an intersection point, which for all temperatures has been found to be situated at about the same density.

From the slope of the log k'_i versus $1/T$ plots the enthalpies of transfer were determined. The enthalpies decrease with increasing density. Additionally, the dependence of the enthalpy on the density increases with increasing polarity of the stationary phase. These two phenomena were explained from the solubilities of the substances in the mobile phase and the interactions between the stationary phase and the solute [7]. The investigations are being continued [22].

Acknowledgments

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