

Short communication

Experimental determination and calculation of distribution coefficients between air and fiber with polydimethylsiloxane coating for some groups of organic compounds

Valery A. Isidorov*, Vera T. Vinogorova

Institute of Chemistry, Białystok University, 15-399 ul. Hurtowa 1, Białystok, Poland

Received 6 October 2004; received in revised form 1 March 2005; accepted 8 April 2005

Available online 13 May 2005

Abstract

This paper reports the results of experimental determination of distribution coefficients K_{fa} for five terpene hydrocarbons and five aliphatic ketones between air and polydimethylsiloxane (PDMS) coating for solid-phase microextraction. To estimate the values of K_{fa} for compounds of the same classes, which did not undergo experiments, it is proposed to use an empirical two-parameter equation in which various physico-chemical and structural characteristics weakly correlated with each other are used as descriptors. It is also shown that for these purposes it is possible to use distribution coefficients of compounds in any other two-phase heterogeneous system, e.g. octanol–water or hexane–acetonitrile. This approach was applied to estimate K_{fa} values of 92 volatile organic compounds.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid-phase microextraction; Terpenes; Ketones; Alcohols; Aromatic hydrocarbons; Distribution coefficients; Calculation; Log K_{ow}

1. Introduction

Solid-phase microextraction (SPME) is a relatively new technique of sample preparation. It is widely used in the analysis of environmental objects, in industrial, food, and clinical analyses. A great interest in this method and its wide application are shown by the fact that during one year six reviews were devoted to it in one journal [1–6].

Theoretical basis and various applications of SPME are described in monographs [7,8]. One of the SPME variants, headspace (HS) SPME, is based on the sorption of analytes present in the headspace above the sample by a liquid polymeric or porous solid phase immobilized over the surface of a fused-silica fiber. Substances concentrated in the fiber coating are transferred to the analytical apparatus for desorption, separation and analysis. The basis of the quantitative use of

HS-SPME is the distribution law:

$$C_a = \frac{C_f}{K_{fa}} \quad (1)$$

where C_a is the analyte concentration in air; C_f is their concentration in the fiber coating, and K_{fa} is the temperature dependent distribution coefficient of the analyte between coating and air. The main approaches to the experimental determination of distribution coefficients K_{fa} are described in the literature. The implementation of one of them requires preparation of gas mixtures with a precisely known concentration of analytes, as well as preliminary calibration of the chromatographic detector [9–11]. In this case the analytically measured parameter is the mass m_f of the analyte sorbed by the fiber after the equilibrium is attained between the gas phase and fiber coating at a given temperature.

A simpler variant includes preparation of gas mixtures of the analytes and successive sampling into the chromatographic column of a fixed volume of the gas phase and SPME

* Corresponding author. Tel.: +48 85 746 10 48; fax: +48 85 746 10 48.
E-mail address: isidorov@uwb.edu.pl (V.A. Isidorov).

injection. Gas phase sampling can take place with the aid of a gas-tight syringe [12,13] or by an automatic headspace injection system assembled on a GC unit [14]. In the latter variant, precise data on analyte content in standard gas mixtures are not required. However, it should be lower than the concentrations at which the adsorption-type SPME coatings are saturated [15]. Here the analytically measured parameters are peak areas.

Unfortunately, experimental K_{fa} values are only available for few organic compounds and coatings. Therefore, it is very topical to determine further distribution coefficients of volatile organic compounds present in the environment and in other objects of analysis. The number of such analytes is very great and, therefore, one cannot hope for rapid accumulation of experimental K_{fa} values. Hence, apart from experimental determination, it is also necessary to develop calculation methods which make it possible to evaluate these parameters rapidly and with sufficient precision.

In this communication, we report the results of the experimental determination of distribution coefficients of terpene hydrocarbons and aliphatic ketones between air and polydimethylsiloxane fiber coating for SPME. Moreover, in this work, the evaluation of K_{fa} is reported for some aliphatic alcohols and aromatic hydrocarbons. This evaluation is based upon an approach similar to that used previously to evaluate chromatographic retention indices of terpenes [16] and distribution coefficients of aromatic hydrocarbons and esters in the hexane–acetonitrile system [17].

2. Experimental

2.1. Chemicals

Commercial α -pinene, 3-carene, limonene, γ -terpinene and terpinolene were purchased from Carl Roth (Warsaw, Poland). 2-Butanone, 2-pentanone, 2- and 3-hexanone, 2-heptanone, and bis(trimethylsilyl)trifluoroacetamide (BSTFA) with addition of 1% trimethylchlorosilane were purchased from Sigma-Aldrich (Poland). All chemicals were used as purchased.

2.2. Preparation of analyte mixtures

Gas mixtures of analytes were prepared in 4 L glass bottles. These bottles were prewashed with a 10% solution of BSTFA in toluene, then washed with methanol and after that dried at 80 °C. The aim of this operation was to decrease losses of analytes due to their adsorption on bottle walls. The septum sealed first bottle was spiked with 1–2 μ L of liquid terpenes. Gas mixture prepared from five hydrocarbons was magnetically stirred (1.5 h) at a temperature of 25.0 ± 0.1 °C in an air conditioning laboratory. Solution in air of five C₄–C₇ ketones was prepared in the second bottle by spiking 1–2 μ L of the single compound into it.

2.3. Syringe and SPME sampling and GC analysis

Sampling of 20 μ L of the prepared gas solutions was made with a 50 μ L Hamilton gas-tight syringe. For the SPME analysis of the mixtures, SPME Holder 57330-U (Supelco, Bellefonte, PA, USA) with the fiber of fused silica 1.00 cm in length coated with a 100 μ m thick film of polydimethylsiloxane (PDMS) was used. Preliminary fiber conditioning was performed in the conditions recommended by Supelco Inc. The septum of bottle with gas mixture was picked by a needle of an SPME Holder and the fiber was exposed to a gas phase for 45 min. The adsorbed components were desorbed by introducing the SPME fiber for 10 min into the injection port of an HP-4890D gas chromatograph with a flame ionization detector. The injector temperature was 260 °C. Analytes were separated on a capillary HP-1 fused silica column (30 m \times 0.25 mm) in splitless mode. The initial thermostat temperature was 80 °C and then it was increased to 150 °C at a rate of 10°/min. Helium was used as carrier gas at 1 mL/min. The SPME and syringe injections of the gas mixtures were performed in triplicate.

Distribution coefficients between fiber coating and air were calculated directly from the average area responses in syringe and SPME injections according to Eq. (2).

$$K_{fa} = \frac{S_f V_a}{(S_a V_f)} \quad (2)$$

where S_f is the area of the chromatographic peak of the component sorbed on the fiber for SPME, S_a is the area of the peak of the same compound recorded after the analysis of standard gas mixture with a gas-tight syringe, and V_a is the gas sample volume (20 μ L). The volume of the fiber coating (V_f) equal to 0.69 μ L was accepted [9].

3. Results and discussion

3.1. Experimental values of distribution coefficients between PDMS-100 fiber coating and air

The simplest approach developed in Ref. [12,13] was used by us for the experimental determination of distribution coefficients of terpene hydrocarbons and aliphatic ketones. Nilsson et al. [12] have established that in the analysis of gas mixtures containing up to five analytes with the concentration of each up to 1 μ g/L the mutual effect of mixture components is not observed. This observation was confirmed in the present work. The same authors reported that 30 min are sufficient for establishing equilibrium when PDMS 100 fiber is used at 25 °C. However, our experiments demonstrated that peak areas of the most highly boiling monoterpenes (γ -terpinene and terpinolene) increase when extraction time is prolonged to 45 min. In our work, the influence of relative humidity (RH) on the sorption process by fiber coating was not taken into account. As shown by Chai and Pawliszyn [18], the relative humidity reduces the

Table 1

Experimental values of retention indices (LTPRI^{HP-1}) and log K_{fa} between PDMS fiber coating and air for some monoterpenes hydrocarbons and aliphatic ketones at 289 K

Compound	LTPRI ^{HP-1}	log K_{fa}	
		Present work	Literature data
Monoterpene hydrocarbons			
Isoprene	501 ± 1	–	1.76 [19]
α-Pinene	930 ± 1	3.66 ± 0.02	3.65 [9]
Myrcene	983 ± 2	–	3.93 [12]
3-Carene	1000 ± 1	3.94 ± 0.03	–
Limonene	1021 ± 1	4.04 ± 0.02	4.04 [9]; 4.11 [12]
γ-Terpinene	1049 ± 1	4.14 ± 0.01	–
Terpinolene	1079 ± 2	4.25 ± 0.01	–
Aliphatic ketones			
Acetone	500 ± 2	–	2.13 [19]; 2.06 [12]
2-Butanone	575 ± 1	2.40 ± 0.02	–
2-Pentanone	708 ± 1	2.99 ± 0.02	2.99 [12]
3-Hexanone	786 ± 1	3.25 ± 0.02	–
2-Hexanone	790 ± 2	3.27 ± 0.01	–
2-Heptanone	892 ± 2	3.60 ± 0.02	–
3-Octanone	953 ± 3	–	3.91 [12]

amounts extracted by PDMS fiber at room temperature by less than 10% at up to 75% RH. Moreover, the effect of humidity is nearly constant for the RH range of 25–75%.

Table 1 presents values determined by us and literature values of log K_{fa} for terpenes and aliphatic ketones at 25 °C as well as measured values of linear temperature programmed retention indices (LTPRI) on a column with a nonpolar polydimethylsiloxane stationary phase. It can be seen that a very good agreement is observed between the measured and literature values of log K_{fa} for α-pinene, limonene, and 2-pentanone. Terpene hydrocarbons and ketones are placed in Table 1 in order of increasing boiling temperatures and retention indices. This data confirm the relationship reported previously [9,12] according to which higher boiling (and less volatile) compounds are characterized by higher K_{fa} values than more volatile compounds.

3.2. Evaluation of K_{fa} values on the basis of physico-chemical characteristics of analytes

Since any well-developed theory of solutions is absent, our information about distribution coefficients in heterogeneous systems is mostly of an empirical character [20,21]. To predict distribution coefficients in the hexane–acetonitrile system [17,22], we have previously successfully used the empirical two-parameter equation of the type:

$$\log K_p^{\text{Hex-Acn}} = a \log X + bY + c \quad (3)$$

For calculating $K_p^{\text{Hex-Acn}}$ values, various weakly mutually correlating physico-chemical and structural characteristics were used as descriptors X and Y : retention indices, boiling temperatures, total solubility, the number of rings in the

molecule, and the number of carbon atoms in the side chain of cyclic compounds [17]. In this work we used this equation to evaluate K_{fa} values.

Calculations were carried out according to Eq. (3) by the method of the least squares. Numerical data necessary for calculations were taken from a home-made database. It contains the values of distribution coefficients in hexane–acetonitrile system ($K_p^{\text{Hex-Acn}}$), log K_{ow} values and randomized values of LTPRI for 3500 compounds of different classes on capillary columns packed with polydimethylsiloxane (HP-1 type), polydimethylsiloxane with the addition of 5% of phenyl groups (HP-5 type) and polyethylene glycol (Innowax type).

Table 2 lists the results of calculations for terpene compounds. The first part of the Table contains initial data for calculation of coefficients a , b , and c from Eq. (3). Boiling temperatures of seven compounds were used as descriptor X and retention indices on an HP-1 column were used as descriptor Y . It can be seen that the equation with calculated values of coefficients a , b , and c is characterized by a high determination coefficient R^2 . The F -test value is larger than the critical value for significance level $\alpha = 0.01$, which means that Eq. (3) is significant at the 99% significance level.

The second part of Table 2 contains the results of the evaluation of log K_{fa} for 13 monoterpenes which are encountered most often in essential oils and in volatile emissions of plants [23,24]. It is interesting to note that the inclusion of a hemiterpene, isoprene, in addition to monoterpenes, into the calculation of coefficients in Eq. (3), does not make the results of the calculation less precise.

As already mentioned, different characteristics can be used as descriptors in Eq. (3). Table 3 shows the results of K_{fa} calculations for aliphatic ketones for which LTPRI on a more polar column of the HP-5 type were used as descriptor X and molecular weight (MW) of homologues served as descriptor Y . In the second part of Table 3 values of log K_{fa} given for 20 C₃–C₈ ketones were calculated from the empirical dependence which we obtained.

Table 4 contains the results of calculations of distribution coefficients for aliphatic alcohols. The required experimental values of log K_{fa} for five compounds of this series were taken from the literature [12]. Two series of calculations were carried out. The first of them included only four primary and secondary saturated alcohols. The second series contained linalool in addition. This substance has a very different structure because it is a tertiary diene alcohol. Therefore, it might be expected to obtain quite different calculation results in the first and the second series. However, the differences in K_{fa} values calculated in both series did not exceed 7%. Hence, we believed it to be possible to include in the second part of Table 4 not only saturated alcohols but also some alkenols from those characterized by boiling temperatures and retention indices.

Components distribution in different heterogeneous systems is determined by the same relationships [25]. Therefore, distribution coefficients determined for one two-phase

Table 2

Evaluation of $\log K_{fa}$ values of monoterpenes for PDMS 100 fiber at 298 K by using regression equation $\log K_{fa} = a\log X + bY + c$

Hydrocarbon	$X = \text{b.p. (K)}$	$Y = \text{LTPRI}^{\text{HP-1}}$	$\log K_{fa}^{\text{Exp}}$	$\log K_{fa}^{\text{Calc}}$	$ \Delta \log K_{fa} $
Isoprene	295.15	501	1.76	1.76	0.00
α -Pinene	429.15	930	3.66	3.66	0.00
Myrcene	440.15	983	3.93	3.87	0.06
3-Carene	445.15	1000	3.94	3.96	0.02
Limonene	451.15	1021	4.04	4.07	0.03
γ -Terpinene	456.15	1049	4.15	4.17	0.02
Terpinolene	459.15	1079	4.25	4.24	0.01

 $a = 1.7595$; $b = 0.00007$; $c = -4.1382$; $n = 7$; $R^2 = 0.9994$; $F_{2,5} = 3331$; $F_{2,5,\alpha=0.01} = 13.3$

Results of calculation

Tricyclene	426.15	921	–	3.62	–
α -Thujene	427.15	923	–	3.63	–
Camphene	431.65	947	–	3.70	–
α -Fenchene	431.65	948	–	3.72	–
4-Carene	433.65	960	–	3.75	–
Sabinene	437.15	966	–	3.81	–
β -Pinene	438.15	971	–	3.83	–
2-Carene	440.15	984	–	3.87	–
α -Phellandrene	444.65	996	–	3.95	–
α -Terpinene	447.15	1007	–	4.00	–
β -Phellandrene	448.65	1022	–	4.03	–
Sylvestrene	449.15	1016	–	4.03	–
β (Z)-Ocimene	451.15	1029	–	4.07	–

Table 3

Evaluation of $\log K_{fa}$ values for aliphatic ketones at 298 K

Compound	$X = \text{LTPRI}^{\text{HP-5}}$	$Y = \text{MW}$	$\log K_{fa}^{\text{Exp}}$	$\log K_{fa}^{\text{Calc}}$	$ \Delta \log K_{fa} $
Acetone	500	58.08	2.06	2.08	0.02
2-Butanone	575	72.11	2.40	2.38	0.02
2-Pentanone	708	86.13	2.99	2.98	0.01
3-Hexanone	786	100.16	3.25	3.24	0.01
2-Hexanone	790	100.16	3.27	3.27	0.00
2-Heptanone	892	114.19	3.60	3.64	0.04
3-Octanone	978	128.21	3.91	3.90	0.01

 $a = 1.3726$; $b = -0.0018$; $c = -3.2813$; $n = 7$; $R^2 = 0.999$; $F_{2,5} = 1998$; $F_{2,5,\alpha=0.01} = 13.3$

Results of calculation

3-Methyl-2-butanone	661	86.13	–	2.71	–
3-Pentanone	700	86.13	–	2.94	–
4-Methyl-2-butanone	750	86.13	–	3.23	–
2-Methyl-3-pentanone	749	100.16	–	3.04	–
4-Methyl-2-pentanone	750	100.16	–	3.04	–
3-Methyl-2-pentanone	755	100.16	–	3.07	–
4-Methyl-3-hexanone	830	114.19	–	3.30	–
5-Methyl-3-hexanone	836	114.19	–	3.33	–
3-Ethyl-2-pentanone	838	114.9	–	3.34	–
2-Methyl-3-hexanone	839	114.19	–	3.35	–
3-Methyl-2-hexanone	844	114.19	–	3.37	–
4-Methyl-2-hexanone	846	114.19	–	3.39	–
5-Methyl-2-hexanone	859	114.19	–	3.46	–
4-Heptanone	871	114.19	–	3.52	–
3-Heptanone	887	114.19	–	3.61	–
2-Methyl-4-heptanone	923	128.21	–	3.60	–
3-Methyl-4-heptanone	929	128.21	–	3.63	–
2-Methyl-3-heptanone	930	128.21	–	3.64	–
5-Methyl-3-heptanone	943	128.21	–	3.71	–
4-Octanone	970	128.21	–	3.85	–

Table 4
Evaluation of $\log K_{fa}$ values for aliphatic alcohols at 298 K

Compound	X = b.p. (K)	Y = LTPRI ^{HP-5}	$\log K_{fa}^{Exp}$ [12]	Set 1		Set 2	
				$\log K_{fa}^{Calc}$	$\Delta \log K_{fa} $	$\log K_{fa}^{Calc}$	$ \Delta \log K_{fa} $
2-Butanol	372.65	583	2.76	2.76	0.00	2.76	0.00
2-Methyl-1-propanol	380.95	635	2.91	2.91	0.00	2.90	0.01
3-Methyl-1-butanol	404.25	730	3.14	3.14	0.00	3.14	0.00
3-Octanol	444.15	982	4.06	4.06	0.00	4.09	0.03
Linalool	471.15	1098	4.58	–	–	4.55	0.03

Set 1: $a = -0.89535$; $b = 0.00059$; $c = 2.3995$; $n = 4$; $R^2 = 0.9999$; $F_{2,2} = 5000$; $F_{2,2,\alpha=0.01} = 99$
Set 2: $a = -0.82701$; $b = 0.00059$; $c = 2.2249$; $n = 5$; $R^2 = 0.9997$; $F_{2,3} = 3332$; $F_{2,3,\alpha=0.01} = 31$

Results of calculation

1-Butanol	390.85	665	–	2.96	–	2.96	–
3-Methyl-2-butanol	386.05	680	–	3.05	–	3.05	–
2-Pentanol	392.45	700	–	3.09	–	3.09	–
4-Methyl-2-pentanol	404.75	758	–	3.26	–	3.26	–
1-Pentanol	411.05	767	–	3.25	–	3.26	–
2-Methyl-3-pentanol	399.65	772	–	3.36	–	3.36	–
3-Hexanol	408.15	795	–	3.40	–	3.40	–
2-Hexanol	413.15	802	–	3.39	–	3.40	–
2-Methyl-1-pentanol	422.15	834	–	3.48	–	3.49	–
4-Methyl-1-pentanol	425.05	837	–	3.47	–	3.48	–
2-Ethyl-1-butanol	420.15	841	–	3.52	–	3.54	–
3-Methyl-1-pentanol	426.15	845	–	3.50	–	3.52	–
5-Methyl-3-hexanol	421.15	852	–	3.57	–	3.58	–
1-Hexanol	430.75	870	–	3.58	–	3.60	–
4-Heptanol	429.15	890	–	3.70	–	3.71	–
2-Methyl-1-hexanol	437.15	896	–	3.67	–	3.69	–
2-Heptanol	432.15	902	–	3.73	–	3.75	–
3-Methyl-1-hexanol	442.15	922	–	3.76	–	3.80	–
5-Methyl-1-hexanol	443.15	931	–	3.80	–	3.82	–
6-Methyl-2-heptanol	447.15	965	–	3.94	–	3.97	–
1-Heptanol	449.55	970	–	3.95	–	3.98	–
4-Octanol	449.95	990	–	4.06	–	4.09	–
2-Octanol	453.15	1002	–	4.10	–	4.13	–
2-Ethyl-1-hexanol	457.75	1030	–	4.22	–	4.25	–
2-Nonanol	468.45	1100	–	4.55	–	4.59	–
1-Octanol	468.25	1102	–	4.56	–	4.55	–
3-Buten-1-ol	386.15	637	–	–	–	2.88	–
2-Methyl-2-propen-1-ol	387.65	646	–	–	–	2.91	–
2-Buten-1-ol	391.15	666	–	–	–	2.96	–
2-Methyl-4-penten-2-ol	392.65	710	–	–	–	3.13	–
3-Methyl-3-buten-1-ol	403.35	731	–	–	–	3.15	–
1-Hexen-3-ol	407.15	789	–	–	–	3.38	–
3-Methyl-2-buten-1-ol	413.15	776	–	–	–	3.29	–
4-Penten-1-ol	414.15	754	–	–	–	3.18	–
(Z) 3-Hexen-1-ol	429.15	854	–	–	–	3.54	–
(E) 3-Hexen-1-ol	429.65	855	–	–	–	3.54	–
(E) 4-Hexen-1-ol	432.15	879	–	–	–	3.64	–

system may be used to evaluate similar physico-chemical characteristics for another two-phase system. Table 5 gives an example of using descriptor Y in Eq. (3) for calculation of the distribution coefficient of aromatic hydrocarbons in the following quite different systems: hexane–acetonitrile [17], and octanol–water. The experimental values of K_{fa} necessary for calculating coefficients in Eq. (3) were taken from Ref. [10]. The $\log K_{ow}$ recommended for the individual compounds were taken from Ref. [26].

Table 5 consists of three parts. The first part presents the results of calculating the coefficients a , b , and c . The second part of this Table (control set) contains the results of cal-

culating $\log K_{fa}$ for compounds for which the experimental values of this parameter are available but were not used in calculating the coefficients in Eq. (3). It can be seen that the values of $\log K_{fa}$ calculated by two methods are close to each other. Moreover, the greatest deviations from experimental values are level at 2%. Distribution coefficients K_{fa} well correlated to the compound's $K_p^{Hex-Acn}$ and K_{ow} coefficients as indicated by the following linear regressions:

$$\log K_{fa} = 2.795 \log K_p^{Hex-Acn} + 3.064 \quad (n = 20; R^2 = 0.956)$$

$$\log K_{fa} = 0.821 \log K_{ow} + 0.780 \quad (n = 20; R^2 = 0.963)$$

Table 5

Use of distribution coefficients in hexane–acetonitrile, and octanol–water systems in the evaluation of $\log K_{fa}$ for aromatic hydrocarbons by using regression Eq. (3)

Hydrocarbon	$\log K_{fa}^{Lit}$ [10]	X = b.p., K	Set 1			Set 2		
			$Y_1 = K_p^{Hex-Acn}$	$\log K_{fa}^{Calc-1}$	$ \Delta \log K_{fa} $	$Y_2 = \log K_{ow}$	$\log K_{fa}^{Calc-2}$	$ \Delta \log K_{fa} $
Benzene	2.48	353.15	0.74	2.48	0.00	2.13	2.48	0.00
Toluene	2.93	383.78	1.07	2.91	0.02	2.73	2.92	0.01
Ethylbenzene	3.32	409.30	1.39	3.31	0.01	3.15	3.32	0.00
<i>m</i> -Xylene	3.32	412.25	1.44	3.35	0.03	3.20	3.36	0.04
Isopropylbenzene	3.59	425.54	1.70	3.58	0.01	3.39	3.58	0.01
1,3,5-Trimethylbenzene	3.81	437.85	1.88	3.79	0.02	3.50	3.80	0.01
1-Methyl-4-isopropylbenzene	4.01	450.40	2.23	4.02	0.01	3.81	4.01	0.00
1,2,4,5-Tetramethylbenzene	4.39	471.15	2.49	4.40	0.01	4.10	4.38	0.01
Set 1: $a = 1.8629$; $b = 0.0083$; $c = -4.3576$; $n = 8$; $R^2 = 0.9985$; $F_{2,6} = 1664$ $F_{2,6, \alpha=0.01} = 10.9$								
Set 2: $a = 2.1329$; $b = -0.0098$; $c = -5.0197$; $n = 8$; $R^2 = 0.9989$; $F_{2,6} = 2270$ $F_{2,6, \alpha=0.01} = 10.9$								
Control set								
<i>p</i> -Xylene	3.40	411.50	1.42	3.34	0.06	3.15	3.35	0.05
<i>o</i> -Xylene	3.46	417.56	1.49	3.44	0.02	3.12	3.46	0.00
<i>n</i> -Propylbenzene	3.70	432.15	1.81	3.69	0.01	3.72	3.68	0.04
1-Methyl-3-ethylbenzene	3.68	434.14	1.82	3.72	0.04	3.88	3.70	0.02
1-Methyl-4-ethylbenzene	3.79	435.14	1.83	3.75	0.04	3.63	3.75	0.04
1-Methyl-2-ethylbenzene	3.82	438.30	1.86	3.79	0.03	3.53	3.81	0.01
Isobutylbenzene	3.92	445.15	2.15	3.93	0.01	4.01	3.98	0.06
1-Methyl-2-isopropylbenzene	4.08	451.50	2.22	4.04	0.04	3.81	4.01	0.07
1,4-Dimethyl-2-ethylbenzene	4.20	460.06	2.33	4.19	0.01	4.31	4.15	0.05
1,2-Dimethyl-4-ethylbenzene	4.24	462.15	2.36	4.23	0.01	4.38	4.18	0.06
1,3-Dimethyl-2-ethylbenzene	4.26	463.25	2.38	4.25	0.01	4.17	4.22	0.04
1,2-Dimethyl-3-ethylbenzene	4.30	467.06	2.43	4.32	0.02	4.22	4.29	0.01
Results of calculation								
<i>tert</i> -Butylbenzene	–	442.27	1.70	3.84	–	4.11	3.83	–
1,2,4-Trimethylbenzene	–	442.50	1.92	3.86	–	3.78	3.86	–
1,2,3-Trimethylbenzene	–	449.23	1.96	3.98	–	3.66	4.00	–
1,3-Diethylbenzene	–	454.25	2.23	4.08	–	4.44	4.02	–
1-Methyl-3- <i>n</i> -propylbenzene	–	454.90	2.26	4.10	–	4.53	4.03	–
1-Methyl-4- <i>n</i> -propylbenzene	–	456.45	2.28	4.12	–	4.56	4.05	–
<i>n</i> -Butylbenzene	–	456.42	2.35	4.13	–	4.26	4.08	–
1,2-Diethylbenzene	–	456.60	2.27	4.13	–	3.72	4.13	–
1,4-Diethylbenzene	–	456.90	2.28	4.13	–	4.45	4.07	–
1-Methyl-2- <i>n</i> -propylbenzene	–	457.25	2.30	4.15	–	4.38	4.10	–
1,2,3,4-Tetramethylbenzene	–	463.05	2.38	4.25	–	4.00	4.23	–
2,4-Dimethyl-1-ethylbenzene	–	461.56	2.33	4.22	–	–	–	–
1-Methyl-3- <i>tert</i> -butylbenzene	–	462.41	2.59	4.25	–	–	–	–
<i>tert</i> -Pentylbenzene	–	463.15	2.63	4.27	–	–	–	–
1-Isopropyl-3-ethylbenzene	–	465.15	2.62	4.30	–	–	–	–
<i>sec</i> -Pentylbenzene	–	465.15	2.65	4.30	–	–	–	–
1-Methyl-3-isobutylbenzene	–	467.15	2.66	4.34	–	–	–	–
1-Methyl-3- <i>sec</i> -butylbenzene	–	467.15	2.68	4.34	–	–	–	–
1,3-Dimethyl-5-isopropylbenzene	–	467.65	2.70	4.35	–	–	–	–
1-Methyl-4- <i>tert</i> -butylbenzene	–	468.95	2.80	4.38	–	–	–	–
1-Methyl-4- <i>sec</i> -butylbenzene	–	469.15	2.71	4.37	–	–	–	–
Isopentylbenzene	–	471.65	2.60	4.42	–	–	–	–

In the third part of Table 5, evaluations of $\log K_{fa}$ are reported for a series of 22 aromatic hydrocarbons for which they have not been determined experimentally.

Comparison of calculated and experimental data shows that the use of the distribution coefficients in any other heterogeneous system gives good results in evaluating K_{fa} . It seems to us particularly promising to use the value of $\log K_{ow}$ for these purposes because this parameter has been determined for tens of thousands of organic compounds.

Acknowledgement

The authors wish to express their gratitude to Dr. Jonathan Miller for editing of the English text of the manuscript.

References

- [1] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153.

- [2] J. Beltran, F.J. López, F. Fernández, *J. Chromatogr. A* 885 (2000) 389.
- [3] J. Namieśnik, B. Zygmunt, A. Jastrzębska, *J. Chromatogr. A* 885 (2000) 405.
- [4] M.F. Alpendurada, *J. Chromatogr. A* 889 (2000) 3.
- [5] S. Ulrich, *J. Chromatogr. A* 902 (2000) 167.
- [6] G.A. Mills, V. Walker, *J. Chromatogr. A* 902 (2000) 267.
- [7] J. Pawliszyn, *Solid Phase Microextraction-Theory and Practice*, Wiley-VCH, Chichester, 1997.
- [8] J. Pawliszyn (Ed.), *Application of Solid Phase Microextraction*, Royal Society of Chemistry, Cambridge, 1999.
- [9] P.A. Martos, J. Pawliszyn, *Anal. Chem.* 69 (1997) 206.
- [10] P.A. Martos, A. Saraullo, J. Pawliszyn, *Anal. Chem.* 69 (1997) 402.
- [11] A. Saraullo, P.A. Martos, J. Pawliszyn, *Anal. Chem.* 69 (1997) 1992.
- [12] T. Nilsson, T.O. Larsen, L. Montanarella, J.Ø. Madsen, *J. Microbiol. Meth.* 25 (1996) 245.
- [13] N.S. Kim, D.S. Lee, *J. Chromatogr. A* 982 (2002) 31.
- [14] C. Bicchi, S. Drigo, P. Rubiolo, *J. Chromatogr. A* 892 (2000) 469.
- [15] S.N. Semenov, J.A. Koziel, J. Pawliszyn, *J. Chromatogr. A* 873 (2000) 39.
- [16] V. Isidorov, I.G. Zenkevich, T. Sacharewicz, *Chem. Anal. (Warsaw)* 42 (1997) 672.
- [17] V.A. Isidorov, U. Krajewska, E.N. Dubis, M.A. Jdanova, *J. Chromatogr. A* 923 (2001) 127.
- [18] M. Chain, J. Pawliszyn, *Environ. Sci. Technol.* 29 (1995) 693.
- [19] Ch. Grote, J. Pawliszyn, *Anal. Chem.* 69 (1997) 587.
- [20] J.M. Prausnitz, *Science* 205 (1979) 759.
- [21] J. Sangster, *Octanol–Water Partition Coefficients: Fundamentals and Physical Chemistry*, Wiley, Chichester, 1997.
- [22] V.A. Isidorov, I.G. Zenkevich, E.N. Dubis, A. Slowikowski, E. Wojciuk, *J. Chromatogr. A* 814 (1998) 253.
- [23] V.A. Isidorov, *Volatile Emission of Plants: Composition, Emission Rate, and Ecological Significance*, Alga Publ., St. Petersburg, 1994.
- [24] V.A. Isidorov, V.T. Vinogorova, K. Rafalowski, *Atmos. Environ.* 37 (2003) 4645.
- [25] J. Shorter, *Correlation Analysis in Organic Chemistry: An Introduction to Linear Free-Energy Relationships*, Clarendon, Oxford, 1973.
- [26] J. Sangster, *J. Phys. Chem. Ref. Data* 18 (1989) 1111.