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Journal of Chromatography A, 830 (1999) 353–363

JOURNAL OF
CHROMATOGRAPHY A

Determination of Henry's law coefficients by combination of the equilibrium partitioning in closed systems and solid-phase microextraction techniques

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Received 20 August 1998; received in revised form 16 October 1998; accepted 19 October 1998

Abstract

This paper describes the determination of Henry's law coefficients by means of the EPICS (equilibrium partitioning in closed systems) technique in combination with SPME (solid-phase microextraction). The use of solid-phase microextraction-sampling allowed us to extend the possibilities of the equilibrium partitioning in closed systems technique with respect to the range of Henry's law coefficients which can be measured. Whereas the equilibrium partitioning in closed systems technique is limited to determine air–water equilibrium partitioning of volatile compounds with Henry's law coefficients of at least 0.06 (dimensionless), the current method allowed to measure coefficients between 0.0023 and 13.5. In this way Henry's law coefficients of 20 compounds, being in a range covering five orders of magnitude, were measured with relative standard deviations between 1.0 and 19.8% (mean standard deviation: 5.7%; median of standard deviations: 4.8%, $n=99$). Several types of compounds were examined i.e. aliphatic hydrocarbons, monocyclic and polycyclic aromatic hydrocarbons, chlorinated and fluorinated compounds, ethers and esters, biphenyl and N-containing compounds, including compounds for which availability of experimental Henry's law coefficients is limited. Measurement of the equilibrium partitioning in the 2 to 25°C range allowed to establish relations of Henry's law coefficient as a function of temperature. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Equilibrium partitioning in closed systems; Solid-phase microextraction; Extraction methods; Thermodynamic parameters; Henry's law coefficients; Volatile organic compounds

1. Introduction

The partitioning of organic compounds over different environmental compartments is one of the key processes in their environmental behaviour. Whereas partitioning between a solid fraction (sediment or

soil) and a fluidum (air, water) is a more complex process due to the heterogeneity of the solid-phase, air–water partitioning is a better defined process. If the air–water partitioning behaviour of organic compounds has to be modeled in an environmental system, then in many cases Henry's law coefficients determined in laboratory conditions can be implemented if temperature and salinity data are available. In some cases additional parameters need to be

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estimated. If e.g. the dissolved organic matter (DOM) fraction is high and compounds with relatively high $\log K_{ow}$ values are considered (K_{ow} = octanol–water partitioning coefficient), then the role of the DOM fraction in the partitioning process has to be taken into account [1,2].

Staudinger and Roberts [2] intensively reviewed available and experimental data for Henry's law coefficients. Two main types of experimental techniques are described in the literature. First, dynamic methods are described, such as the batch air stripping technique, first developed by Mackay et al. [3]. Next, static equilibration techniques are used, such as the multiple phase equilibration technique, first described by McAuliffe [4], and the EPICS (equilibrium partitioning in closed systems) technique. The EPICS technique was first developed by Lincoff and Gossett [5], and further applied with modifications by Gossett [6], Ashworth et al. [7] and Dewulf et al. [8]. Other static techniques are the vapor phase calibration method [9] and the phase ratio variation method [10].

In view of the determination of Henry's law coefficient as a function of temperature, static techniques are more flexible, since only the temperature of the incubation bath has to be changed, whereas in the batch air stripping technique the temperature of the incoming gas and water column has to be controlled. Moreover, fast experimental determination of Henry's law coefficient by the stripping technique requires that the compounds can be monitored on-line (e.g. UV detection), so that the scope of compounds which can be studied in this way of operation is limited.

All techniques work especially well if the compounds have relatively high Henry's law coefficients ($H > 0.1$; with H = Henry's law coefficient in mole m^{-3} air over mole m^{-3} water). Batch Air Stripping is less time consuming if the compounds are volatile. Also static techniques are favoured by a high volatility of the compounds because they are based on sampling of the headspace volume of a closed equilibrated system. Additionally, the EPICS technique shows large relative standard deviations for compounds with relatively low air–water partitioning coefficients ($H < 0.06$) [2]. These technical limitations for all these different techniques may have contributed to a more extensive data set of

air–water equilibrium partitioning data for volatile compounds and a more limited data set for less volatile compounds in the literature.

In this work the potential of the combination of the EPICS technique with SPME (solid-phase microextraction) is investigated in determining Henry's law coefficients. SPME becomes a sampling technique with a large number of new applications and possibilities in analytical chemistry [11–14]. The strength of the technique is its simplicity by the integration of sampling, extraction and concentration in one step. Moreover, it allows the determination of compounds both in the liquid (e.g. [15–20]) and gas phase (headspace) (e.g. [21–23]). Since the SPME coating is able to concentrate the compounds from a headspace, the SPME can give new possibilities to the concept of the EPICS technique, because it may allow the measurement of less volatile compounds in the headspace of the closed two-phase systems. This paper describes the elaboration of the combination of EPICS with SPME and investigates the potential applications of the combination.

2. Materials and methods

2.1. Stock solutions

The following compounds were dissolved in methanol (Merck) to prepare a 25 ml stock solution A: 1,1-dichloroethene (500 μ l), cyclohexane (10 μ l), 1,2,3-trichlorobenzene (3 mg) (Aldrich), trichloroethylene (500 μ l) (Janssen Chimica), toluene (360 μ l) and 1,3,5-trichlorobenzene (15.5 mg) (Fluka). 25 ml methanol stock solution B was prepared with 1,1,2-trichlorotrifluoroethane (500 μ l), chlorobenzene (170 μ l) (Aldrich), 1,2-dichloropropane (500 μ l), 1,2,4-trichlorobenzene (14 μ l), hexachloro-1,4-butadiene (4 μ l) (Fluka) and 1,1,2-trichloroethane (500 μ l). Mixture C was prepared with fluorobenzene (500 μ l), naphthalene (2 mg) (Aldrich), phenyl methyl ether (500 μ l) and biphenyl (1 mg) (Fluka) and mixture D with pyridine (500 μ l) (Merck), nitrobenzene (35 μ l) (UCB), 3-hexanone (400 μ l) (Aldrich) and ethyl acetate (500 μ l) (Lab-scan).

2.2. Preparation of the closed two-phase systems

For the determination of the Henry's law coefficient of compounds of one single mixture, six vials with a total volume of 118 ml each were used. Into three vials 0.5 ml demineralised water was injected. Into the other set of three vials 90 ml demineralised water was pipetted. Subsequently a magnetic stirring bar (volume 0.55 ml) was put into each vial and 5 μ l of a stock solution was injected under the water surface, followed by immediate closure of the vial by a Mininert valve (Alltech). The masses added to the closed two phase systems varied between 0.2 μ g (biphenyl) and 160 μ g (1,1,2-trichlorotrifluoroethane). These amounts were calculated as follows. First the Henry's law coefficient was estimated from vapour pressure and solubility data. Second, considering this estimated air–water equilibrium partitioning coefficient and the headspace and liquid volumes, a mass balance over the two phase system was made for each compound. From this mass balance it was calculated what amount of compound was allowed to be added to the closed two-phase system in order to obtain final water equilibrium concentrations being maximally one tenth of the maximum aqueous solubility.

It has been shown previously that the use of mixtures of compounds and the application of methanol at concentrations below 1% (v/v) do not affect the air–water equilibrium partitioning [6,8]. The vials were incubated overnight in a thermostatic water bath (2.0 ± 0.1 , 6.0 ± 0.1 , 10.0 ± 0.1 , 18.0 ± 0.1 and $25.0 \pm 0.1^\circ\text{C}$). A magnetic stirrer was placed under this incubator in order to accelerate equilibration. Previous studies have shown that overnight incubation is sufficient to reach equilibrium partitioning [5,6].

2.3. Analysis

After incubation, the headspace was sampled with a SPME fiber for 30 min. The headspace of closed two-phase systems with compounds of mixtures A, B and C were sampled with a 100 μ m dimethylpolysiloxane fiber (Supelco). For the compounds of mixture D, a more polar solid-phase was used, i.e. a 65 μ m divinylbenzene–Carbowax fiber (Supelco). Prior to sampling, fibers were conditioned

in a GC-injector (220°C , 5 min). After sampling, the analysis was carried out with a Varian gas chromatograph (model 3700) (injector at 220°C , flame ionization detector at 250°C), equipped with a 30 m CP-SIL 5 CB column (film thickness 5 μ m, 0.53 mm I.D., 100% dimethylpolysiloxane) (Chrompack) and a HP3388A integrator. The temperature of the GC oven was kept at 45°C for 5 min and raised to 240°C at 5°C min^{-1} for the analysis of mixtures A and B. For the analysis of mixtures C and D, the temperature of the GC oven was held at 40°C for 5 min, followed by a temperature rise of 8°C min^{-1} up to 240°C . GC carrier gas was helium at a rate of 6.4 ml min^{-1} and the flame ionization detector was fed by air at 244 ml min^{-1} and hydrogen at 35 ml min^{-1} .

2.4. Calculations

The Henry's law coefficient was calculated based on experimental results of the determination of the headspace concentration of one vial with a low liquid content and one with a high liquid content. At equilibrium, the mass of a compound (M , in mol) brought into a vial is partitioned over the two phases:

$$M = C_w V_w + C_g V_g \quad (1)$$

where C_w and C_g are the aqueous and headspace concentration of the compound (mol m^{-3}) and V_w and V_g are the volume of the water body and the headspace (m^3). If the Henry's law coefficient is defined as $H = C_g / C_w$, then H can be calculated from

$$H = \frac{rV_{w1} - V_{w2}}{V_{g2} - rV_{g1}} \quad (2)$$

where r is the ratio of the headspace concentrations ($r = C_{g1} / C_{g2}$ with C_{g1} and C_{g2} the concentration (mol m^{-3}) in the closed two-phase systems with a low and a high liquid content respectively) and with V_{g1} and V_{g2} the gas volumes and V_{w1} and V_{w2} the liquid volumes of the closed two-phase systems. The subscripts 1 and 2 indicate the systems with a low and high liquid volume respectively. It has to be mentioned that the ratio r in the EPICS method was directly calculated from the ratio of the peak areas in the chromatograms, so that external calibration is not necessary.

3. Results and discussion

3.1. Experimental results

The technique based on SPME and EPICS as described in the Materials and methods section, was tested for the determination of Henry's law coefficient of compounds with different functionalities (aliphatic hydrocarbons, monocyclic and polycyclic aromatic hydrocarbons, chlorinated and fluorinated compounds, ketones, ethers and esters, biphenyl and N-containing compounds). The EPICS approach generates nine estimations of the Henry's law coefficient for each compound at one temperature by combining the results of six headspace analyses: analyses of three vials with a low liquid content and three vials with a high liquid content, all incubated simultaneously at the same temperature. It has to be mentioned that, although this is the typical EPICS calculation approach [5,6,8], these nine obtained data sets are not completely independent. The calculation results are shown in Table 1 for all compounds at five different temperatures.

3.2. Precision and range of applicability

The set of 100 data shows Henry's law coefficients between 0.00042 (nitrobenzene at 2.0°C) and 13.5 (CFC-113 at 25°C). For nitrobenzene at 2.0°C, a high relative standard deviation is noticed: 41.3% ($n=9$). For Henry's law coefficients in the range between 0.0023 (nitrobenzene at 6.0°C) and 13.5 (CFC-113 at 25.0°C), covering five orders of magnitude, relative standard deviations are lower than 10% R.S.D. in 84% of the cases. In 16 percent of the measurements, R.S.D.s vary between 10% and 20%. In conclusion, for 99 cases, the 25 to 75 percentile range of the data set of standard deviations is 2.4 to 8.1% (50-percentile=4.8%).

The precision of the EPICS technique can be estimated based on the variances on the parameters used in the calculation of H by means of Eq. (2) [6,8]. The variance contributions of the headspace analysis (3.5% R.S.D.), the weighing of the added mass (0.23%), the vial volume (0.23%), the low liquid volume (0.41%) and the high liquid volume (1.51%) were used in the estimation of the relative standard deviation. This estimation is presented in

Fig. 1 and compared with the experimental results. It can be seen that the experimental values generally follow the expected trend, although a large variation is noticed. This variation can mainly be attributed to differences in precision of the headspace analysis since an averaged R.S.D. is used in the calculation. Next, the estimation of the relative standard deviations in the EPICS–SPME method is compared with estimations of relative standard deviations in previous applications of the EPICS technique [6,8]. It can be seen that the current technique is especially an improvement in precision for the determination of low Henry's law coefficients ($H < 0.1$). Basically this is due to the higher ratio of the two liquid volumes (V_{w2}/V_{w1}) in the closed two-phase systems. This higher ratio has been only made possible due to the combination with SPME sampling. Indeed, the use of SPME sampling allows to sample low headspace concentrations because of the high fiber/headspace concentration ratio, which is especially important for compounds with low H values, generating low headspace concentration levels. Next, the concentration in the SPME-fiber allows to introduce low masses in the closed two-phase system, which is needed if low liquid volumes ($V_{w1}=0.5$ ml) are used with respect to aqueous solubility limitations. On the other hand, it can be seen from Fig. 1 that the current technique is not an improvement compared to the previously elaborated techniques for very volatile compounds with $H > 10$ because of higher overall relative standard deviation. However, the number of compounds with H values in this range is rather limited compared to those in the lower ranges.

When the current technique is compared to the batch air stripping technique, it can be mentioned that it is a fast technique especially for compounds with low H values since these compounds give rise to a low stripping velocity in the stripping technique. Moreover, fast operation of the batch air stripping requires compounds which are on-line detectable (e.g. aromatic compounds with UV detection [3]) or a more complex method with sampling on cartridges [24]. The limitations of the previously developed techniques may have contributed to the limited availability of experimental Henry's law coefficients of compounds considered in this work, such as 1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, hexachloro-1,3-butadiene, fluorobenzene, phenyl methyl ether

Table 1

Experimental results of the determination of Henry's law coefficients with the EPICS–SPME technique with T =temperature, H =Henry's law coefficient (mol l^{-1} over mol l^{-1}), R.S.D.=relative standard deviation in per cent ($n=9$)

Compound	T (°C)	H	R.S.D. (%)	Compound	T (°C)	H	R.S.D. (%)
1,1-Dichloroethene	2.0	0.379	1.8	1,2,4-Trichlorobenzene	2.0	0.055	2.5
	6.0	0.438	5.0		6.9	0.099	10.5
	10.0	0.547	6.6		10.0	0.111	10.5
	18.0	0.824	2.7		18.0	0.128	1.1
	25.0	1.086	6.1		25.0	0.159	3.1
Cyclohexane	2.0	2.380	4.1	Hexachloro-1,3-butadiene	2.0	0.157	1.8
	6.0	2.989	15.7		6.0	0.256	16.3
	10.0	3.521	13.9		10.0	0.297	16.2
	18.0	5.997	6.6		18.0	0.440	8.5
	25.0	7.331	15.3		25.0	0.624	10.9
Trichloroethylene	2.0	0.120	1.6	Fluorobenzene	2.0	0.089	1.9
	6.0	0.144	4.8		6.0	0.112	1.2
	10.0	0.186	5.2		10.0	0.142	2.3
	18.0	0.302	1.9		18.0	0.210	4.7
	25.0	0.415	4.0		25.0	0.269	1.7
Toluene	2.0	0.082	1.3	Phenylmethylether	2.0	0.0042	4.0
	6.0	0.096	5.1		6.0	0.0057	1.3
	10.0	0.122	5.6		10.0	0.0073	3.5
	18.0	0.197	1.7		18.0	0.011	4.7
	25.0	0.268	4.0		25.0	0.015	1.2
1,3,5-Trichlorobenzene	2.0	0.081	5.7	Naphthalene	2.0	0.013	8.6
	6.0	0.089	3.1		6.0	0.012	12.2
	10.0	0.114	6.5		10.0	0.018	5.0
	18.0	0.188	3.8		18.0	0.024	6.9
	25.0	0.214	8.6		25.0	0.031	5.4
1,2,3-Trichlorobenzene	2.0	0.037	6.6	Biphenyl	2.0	0.021	15.1
	6.0	0.045	4.8		6.0	0.015	8.8
	10.0	0.057	5.3		10.0	0.027	10.1
	18.0	0.086	3.8		18.0	0.045	4.8
	25.0	0.108	9.4		25.0	0.053	9.1
CFC-113	2.0	4.503	5.7	Pyridine	2.0	0.016	3.0
	6.0	5.823	5.6		6.0	0.018	3.0
	10.0	6.476	19.8		10.0	0.015	6.4
	18.0	10.95	10.5		18.0	0.011	4.6
	25.0	13.49	19.0		25.0	0.0086	8.3
1,2-Dichloropropane	2.0	0.036	2.9	Nitrobenzene	2.0	0.00042	41.3
	6.0	0.047	1.0		6.0	0.0023	16.7
	10.0	0.057	4.2		10.0	0.0038	8.5
	18.0	0.084	2.4		18.0	0.0069	8.2
	25.0	0.112	1.9		25.0	0.013	2.5
1,1,2-Trichloroethane	2.0	0.011	3.2	3-Hexanone	2.0	0.039	6.6
	6.0	0.014	1.4		6.0	0.055	2.0
	10.0	0.018	5.8		10.0	0.054	4.8
	18.0	0.027	1.7		18.0	0.050	3.8
	25.0	0.037	1.2		25.0	0.052	2.9
Chlorobenzene	2.0	0.049	2.2	Ethyl acetate	2.0	0.032	4.9
	6.0	0.067	1.1		6.0	0.043	1.2
	10.0	0.078	5.9		10.0	0.041	3.3
	18.0	0.117	2.0		18.0	0.037	3.8
	25.0	0.155	1.5		25.0	0.040	8.1

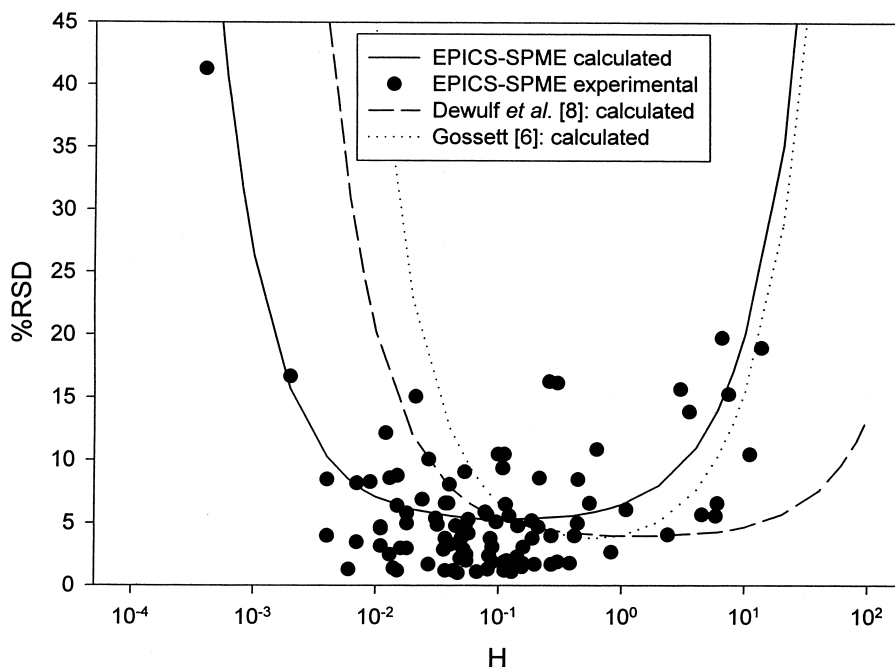


Fig. 1. Experimental relative standard deviations as a function of H (dimensionless) and expected R.S.D.s from calculations for the application of the EPICS method with the conditions of this work (EPICS–SPME), Gossett [6] (volume of bottles: 158.8 ml, liquid volumes: 25 and 100 ml) and Dewulf et al. [8] (volume of bottles: 118 ml, liquid volumes: 5 and 115 ml).

and 3-hexanone. For these compounds no experimental data are mentioned in the extensive overviews of Mackay and Shiu [25], Staudinger and Roberts [2] and Sander [26].

3.3. Comparison to literature data and potential bias of the EPICS–SPME technique

The data of Henry's law coefficients determined at 25°C by the EPICS–SPME method are compared with literature data in Table 2. The mentioned literature data were obtained by batch air stripping and static techniques and by calculations based on vapour pressure and aqueous solubility data. The current determinations compare well with available data determined with static techniques for 1,1-dichloroethene, cyclohexane, trichloroethylene, toluene, CFC-113, 1,2-dichloropropane, 1,1,2-trichloroethane and chlorobenzene, with ratio's $H_{\text{EPICS-SPME}}$ over (averaged) $H_{\text{Static techniques}}$ between 0.98 and 1.13. Only for 1,2,4-trichlorobenzene a discrepancy is noticed ($H=0.159$ versus $H=0.087$).

For the other compounds in Table 2, no experimental data determined by static techniques were found in the literature. Similarity of the data determined by the EPICS–SPME method and the batch air stripping technique is observed for trichloroethylene, toluene, 1,2-dichloropropane, 1,1,2-trichloroethane, chlorobenzene (ratio's $H_{\text{EPICS-SPME}}$ over (averaged) $H_{\text{Static techniques}}$ between 0.96 and 1.10) and in a smaller extend for 1,1-dichloroethane ($H=1.086$ versus 1.512) and naphthalene ($H=0.031$ versus 0.020). Large discrepancies are noticed for biphenyl (0.053 versus 0.017), pyridine ($H=0.0086$ versus 0.00045 and 0.00037) and nitrobenzene ($H=0.013$ versus 0.00095). Differences of H data for pyridine might be related to differences in pH in the experimental set-ups, since the $\text{p}K_{\text{a}}$ of pyridine is 5.23 [29]. However, for all of these three compounds values of H determined with the batch air stripping technique are systematically lower than the experimental data of this work. Lower data from the batch air stripping method might be created if some assumptions made in this technique, e.g. non-equilib-

Table 2

Comparison of experimental data of the Henry's law coefficient at 25°C determined by the EPICS–SPME method with literature data

Compound	$H_{\text{EPICS-SPME}}$	$H_{\text{Static techniques}}$	$H_{\text{Batch air stripping}}$	$H_{\text{Calculated}}$
1,1-Dichloroethene	1.086	1.017 ^a ; 1.044 ^b	1.512 ^c	0.627 ^d
Cyclohexane	7.331	7.310 ^a		6.524 ^d ; 7.830 ^e ; 7.507 ^e ; 6.498 ^e
Trichloroethylene	0.415	0.423 ^a ; 0.383 ^b ; 0.415 ^f ; 0.420 ^g ; 0.351 ^h ; 0.411 ⁱ	0.402 ^c ; 0.353 ⁱ	0.502 ^d ; 0.459 ^d ; 0.438 ^j
Toluene	0.268	0.272 ^a ; 0.263 ^g ; 0.272 ^g ; 0.224 ^h	0.264 ^c ; 0.272 ^k	0.263 ^d ; 0.277 ^j
1,3,5-Trichlorobenzene	0.214			0.448 ^j ; 0.094 ^e ; 0.036 ^e
1,2,3-Trichlorobenzene	0.108			0.124 ^e ; 0.065 ^e
CFC-113	13.49	11.95 ^a		21.51 ^l
1,2-Dichloropropane	0.112	0.107 ^a	0.117 ^c	
1,1,2-Trichloroethane	0.037	0.040 ^a ; 0.033 ^m ; 0.031 ⁿ	0.034 ^c	0.034 ^d ; 0.049 ^e
Chlorobenzene	0.155	0.158 ^a	0.134 ^c ; 0.154 ^k	0.164 ^d ; 0.152 ^e
1,2,4-Trichlorobenzene	0.159	0.087 ^a		0.058 ^d ; 0.113 ^j ; 0.177 ^e ; 0.128 ^e
Hexachloro-1,3-butadiene	0.624			0.412 ^d ; 1.126 ^j
Fluorobenzene	0.269			0.255 ^e ; 0.252 ^j ; 0.258 ^l
Phenylmethylether	0.015			
Napthalene	0.031		0.020 ^k	0.020 ^d ; 0.017 ^j
Biphenyl	0.053		0.017 ^k	0.012 ^e ; 0.017 ^e
Pyridine	0.0086		0.00045 ^o ; 0.00037 ^p	
Nitrobenzene	0.013		0.00095 ^p	
3-Hexanone	0.052			0.0051 ^l
Ethyl acetate	0.040			

$H_{\text{EPICS-SPME}}$ are data of this work; $H_{\text{Static techniques}}$ are literature data determined with the EPICS, the variable headspace or vapor phase calibration technique; $H_{\text{Batch air stripping}}$ are data determined with the batch air stripping method and $H_{\text{Calculated}}$ are literature data based on calculations with vapour pressure and solubility data.

^aAshworth et al. [7]; ^bGossett [6]; ^cLeighton and Calo [24]; ^dStaudinger and Roberts [2]; ^eMackay and Shiu [25]; ^fGossett et al. [27];

^gRobbins et al. [28]; ^hDewulf et al. [8]; ⁱLincoff and Gossett [5]; ^jSchwarzenbach et al. [1]; ^kMackay et al. [3]; ^lHoward and Meylan [29];

^mHansen et al. [30]; ⁿHansen et al. [31]; ^oHawthorne et al. [32]; ^pBetterton [33].

rium partitioning between the water vessel and the leaving purge gas, are not fulfilled.

Bias in the EPICS–SPME technique could be generated by employing too high concentrations, changing the overall liquid polarity. However, this would result in lower Henry's law coefficients because of the decreasing polarity of the aqueous phase with increasing concentration of organic compounds. On the other hand systematic deviation could be generated by the SPME sampling technique in two ways. First, sufficient sampling time is needed to allow equilibrium partitioning between the liquid, gas and exposed SPME fiber phase. Two mass transfer processes occur during sampling: transfer from liquid to gas and from gas to fiber [34]. If the gas-to-fiber transfer is rate limiting, then equilibrium

can be achieved in a few minutes [34]. If however the mass transfer from liquid to gas determines the equilibration time, then the extraction velocity is lower. This is especially of importance if the headspace capacity is low, i.e. if the fiber–air partitioning coefficient is high and the Henry's law coefficient and the volume of the headspace are small [34]. Therefore it has been checked if the sampling time of 30 min was sufficient to reach sorption equilibrium in the most critical case, viz. for vials with the smallest headspace volume containing mixture D, in which the least volatile compounds were present. Absorbed amounts in the fiber after 30 min of exposure proved to be 97.9, 83.5, 103.0 and 102.0% of the amount extracted after 46 min of exposure for pyridine, nitrobenzene, 3-hexanone and ethyl acetate

respectively. So it can be concluded that the applied sampling conditions allow sufficient sorption equilibrium.

Secondly, when using SPME, the amount extracted by the fiber has to be considered in making mass balances [34]. Indeed, if the fiber acts as a third phase in which, next to the headspace and the water phase, a significant fraction of the compounds accumulates, then the mass balance has to be established over three phases instead of over two phases as in Eq. (2). If the fiber–air or fiber–water equilibrium partitioning coefficient is known (respectively K_g and K_w , both in mol m^{-3} over mol m^{-3}), then H can be calculated, based on a mass balance over the three partial volumes:

$$H = \frac{rV_{w1} - V_{w2} - (1-r)K_wV_f}{V_{g2} - rV_{g1}} \quad (3)$$

or

$$H = \frac{rV_{w1} - V_{w2}}{V_{g2} - rV_{g1} + (1-r)K_gV_f} \quad (4)$$

with V_f the volume of the fiber polymer ($=6.6 \cdot 10^{-10} \text{ m}^3$ for a 100 μm fiber). For toluene, 1,2-dichloropropane and 1,1,2-trichloroethane, reported K_g data are 818 [35], 251 and 1995 [36], respectively. For trichloroethylene, K_w is reported as 1259 [36]. Based on these data of K_g and K_w (all at 25°C) and the new mass balance, H values for toluene, 1,2-dichloropropane, 1,1,2-trichloroethane (Eq. (4)) and trichloroethylene (Eq. (3)) were calculated for all temperatures mentioned in Table 1. When values for H calculated according to Eqs. (3) and (4) (data not shown) are compared with the data in Table 1, it is found that the differences between data for H obtained with the two compartment model and three compartment model are lower than 1.5% in all cases. In a mathematical approach the generated deviation $\Delta (= (H_{\text{generated by Eq. (2)}} - H_{\text{generated by Eq. (4)}}) / H_{\text{generated by Eq. (2)}}$) can be determined as:

$$\Delta = \frac{K_gV_f}{V_t + K_gV_f} \cdot (1 - H_{\text{generated by Eq. 4}}) \quad (5)$$

with V_t the total volume of a vial. This means that the slope of the linear relation between Δ and $H_{\text{generated by Eq. (4)}}$ is independent on r and so independent on H . The calculated deviations for differ-

ent H values and K_g values are plotted in Fig. 2. From the simulation it can be seen that the deviation increases when K_g increases: the larger the fraction sorbed into the extraction polymer, the more important the deviation can be. Next, it is noticed that the more H is different from 1, the higher the deviation can be, resulting in positive deviations if $H < 1$ and negative deviations if $H > 1$. However, in the range between 0 and 2 for H , it is noticed that the deviation is expected to be below 6% if $K_g \leq 10000$. This means that the deviations generated by using Eq. (2) are limited, being in the order of the %R.S.D. of the technique. The limited deviation is also illustrated in Fig. 2 for the four compounds for which K_g -values are available. In order to show that a negative deviation is generated for a compound with $H > 1$, the K_g value of cyclohexane has been estimated from the Kováts index I_k from the correlation ($r = 0.997$, $n = 11$) [14]:

$$\ln K_g = 0.00975I_k - 0.2477 \quad (6)$$

For an experimentally determined $I_k = 655$ and $H = 6.06$ at 20°C (from the temperature dependent relation of H ; see further on), a K_g -value of 463 is found for cyclohexane. In this way, the generated deviation is shown in Fig. 2 for cyclohexane, illustrating that a negative deviation is observed if $H > 1$. Because of the limited deviation generated by Eq. (2), it can be concluded that differences between literature data and the data from the EPICS–SPME technique cannot be attributed to the two-phase approach in the calculation of the mass balances.

3.4. Regression of $\ln H$ with temperature

From a theoretical background, a temperature dependence of H is expected as [1]:

$$\ln H = a \cdot \frac{1}{T} + b \quad (7)$$

with a and b regression coefficients and T the temperature in K . Essentially the slope is related to the change of enthalpy:

$$a = -\frac{\Delta H_H}{R} = -\frac{\Delta H_{\text{vap}} - \Delta H_s}{R} \quad (8)$$

with ΔH_H the change in molar enthalpy for the air–water equilibrium process, ΔH_{vap} the enthalpy of

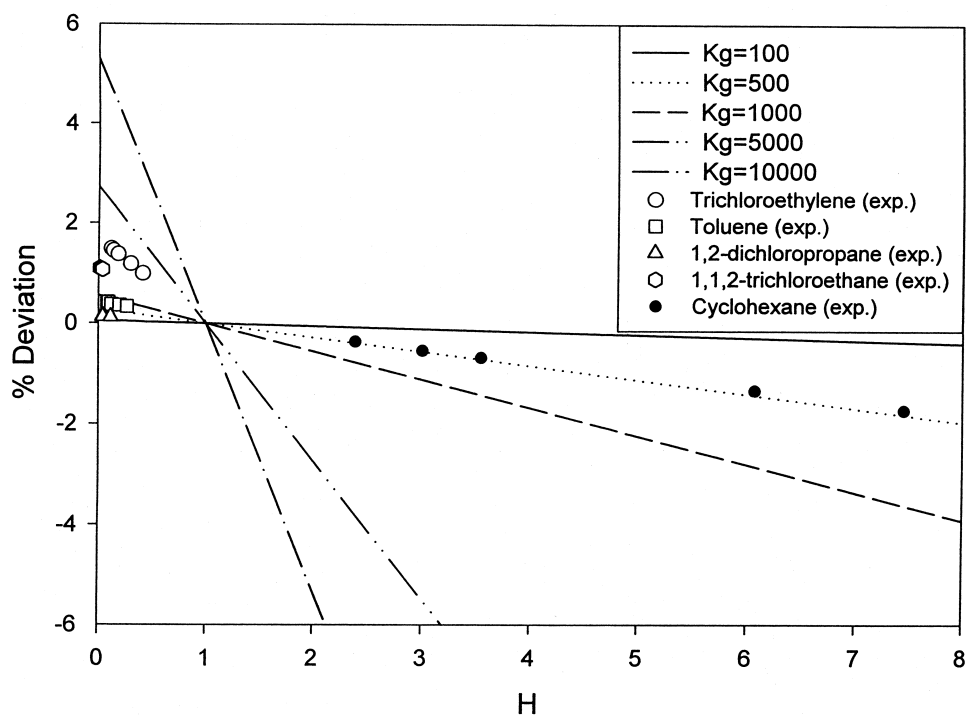


Fig. 2. Simulated deviation ($=H_{\text{generated by Eq. (2)}} - H_{\text{generated by Eq. (4)}}/H_{\text{generated by Eq. (2)}}$) in percent when using Eq. (2) instead of Eq. (4) as a function of $H_{\text{generated by Eq. (4)}}$ for different K_g values. Additionally, the experimental deviations for trichloroethylene ($K_g = K_w/H = 3056$ with $K_w = 1259$ [35]), toluene ($K_g = 818$ [34]), 1,2-dichloropropane ($K_g = 251$ [35]), 1,1,2-trichloroethane ($K_g = 1995$ [34]) and cyclohexane ($K_g = 463$, estimated from the Kováts index [14]) are shown.

vaporization and ΔH_s the enthalpy of solution (all in J mol^{-1}). For all compounds in Table 1, results of the linear regression are shown in Table 3. It can be seen that the experimental correlation confirms the relationship expected from thermodynamic theory ($0.821 < r^2 < 0.997$) except for biphenyl, 3-hexanone and ethyl acetate. For these three compounds, the calculated regression does not match theoretical expectation. Two plausible explanations can be given. First, the assumption that the enthalpies are constant over the considered temperature range might be not valid. Second, the difference in enthalpy of the vaporisation process and the solubilisation process are so close to each other that the net result of their combination ΔH_H becomes insignificantly different from zero. This is confirmed by examining the 95% confidence intervals for the regression parameters. It was found that the 95% confidence interval for the slope (a) encloses zero for 3-hexanone and ethyl acetate ($a = -529 \pm 619$ and

$a = -315 \pm 530$, respectively) so that it can be concluded that $\ln H$ does not show a significant linear relationship with T^{-1} for these compounds. For all other compounds however, the slope was significantly different from zero.

For 17 compounds from Table 3, it is noticed that the slope is significantly lower than zero, resulting in increasing Henry's law coefficients with increasing temperature. This means that the heat of vaporisation is larger than the heat of solubilisation. Only for pyridine the opposite relation is found: increasing temperatures result in decreasing Henry's law coefficients. This might be due to a high heat of solution of pyridine in water caused by hydrogen bonding between pyridine and water molecules.

In the extensive overview of Staudinger and Roberts [2], only for nine of the 20 compounds regression parameters are found (Table 3). For 1,1-dichloroethane, trichloroethylene, toluene, 1,2-dichloropropane, 1,1,2-trichloroethane and chloro-

Table 3

Linear regression of $\ln H = aT^{-1} + b$ ($n=5$, $275 < T < 298$ K): data of this work and data from Staudinger and Roberts [2], if available

Compound	This work			Staudinger and Roberts		
	<i>a</i>	<i>b</i>	<i>r</i> ²	<i>a</i>	<i>b</i>	<i>r</i> ²
1,1-Dichloroethene	−3871	13.083	0.997	−3652	12.439	
Cyclohexane	−4164	16.014	0.987	−2945	11.873	0.982
Trichloroethylene	−4553	14.415	0.997	−4282	13.471	
Toluene	−4362	13.329	0.996	−3698	11.116	
1,3,5-Trichlorobenzene	−3819	11.341	0.967			
1,2,3-Trichlorobenzene	−3927	10.989	0.994			
CFC-113	−4002	16.068	0.985	−2950	12.379	0.932
1,2-Dichloropropane	−3980	11.181	0.997	−3984	11.243	
1,1,2-Trichloroethane	−4420	11.547	0.997	−4580	12.034	
Chlorobenzene	−4041	11.722	0.994	−3470	9.739	
1,2,4-Trichlorobenzene	−3178	8.892	0.821	−3735	10.093	0.819
Hexachloro-1,3-butadiene	−4578	14.922	0.970			
Fluorobenzene	−3968	12.039	0.995			
Phenyl methyl ether	−4466	10.820	0.995			
Napthalene	−3288	7.552	0.932			
Biphenyl	−4201	11.204 ^a	0.840			
Pyridine	+2599	−13.451	0.922			
Nitrobenzene	−10921	32.598	0.872			
3-Hexanone	−529 ^a	−1.143 ^a	0.196			
Ethyl acetate	−315 ^a	−2.154 ^a	0.105			

^aThe critical value is exceeded in a t-test at $\alpha=0.05$

benzene, the reported regression parameters are based on three to nine independent sets of experimental determinations of the relationship between *H* and temperature [2]. For these compounds both the slope and the intercept data obtained by EPICS–SPME match well the literature data (ratio of slope in literature–slope by EPICS–SPME between 0.97 and 1.18; ratio of intercept in literature–intercept by EPICS–SPME between 0.96 and 1.20). For cyclohexane, CFC-113 and 1,2,4-trichlorobenzene, only one independent set of data was considered to estimate the linear regression parameters [2]. It can be seen that for these compounds there is a greater difference between the slopes and intercepts obtained by the EPICS–SPME and those mentioned in the literature [2]. The ratio of the slopes (EPICS–SPME data/literature data) are 1.41, 1.36 and 0.85 for cyclohexane, CFC-113 and 1,2,4-trichlorobenzene; whereas for the intercepts ratio's of respectively 1.35, 1.30 and 0.88 are noticed.

4. Summary and conclusions

The EPICS approach to determine Henry's law

coefficients has been combined successfully with the SPME headspace sampling technique. The use of SPME allowed to increase the high liquid/low liquid volume ratio of the parallel closed two-phase systems and to measure less volatile compounds in the headspace. This resulted in the measurement of Henry's law coefficients covering a range of five orders of magnitude, with relative standard deviations between 2.4 and 8.1% (=25 to 75 percentile range) for several types of compounds. Only for nitrobenzene at 2.0°C a high standard deviation was noticed ($H=0.00042 \pm 0.00017$).

Further on, it has been shown that the calculation of the Henry's law coefficient in the EPICS–SPME technique with Eq. (2), i.e. with neglecting of the fraction sorbed into the extraction polymer, gives rise to limited deviations on Henry's law coefficient. The generated deviations were in the same order of the R.S.D. of the technique. This means that the EPICS–SPME technique can be implemented without exact knowledge of the fiber–air or fiber–water equilibrium partitioning data of the compounds to be considered.

Next, it has been proven that the technique generates data for Henry's law coefficients, similar

to those generated by other techniques, for volatile compounds, e.g. 1,1-dichloroethene, trichloroethylene, toluene and 1,1,2-trichloroethane. For less volatile compounds (e.g. pyridine, nitrobenzene) however, there is a weak convenience between the Henry's law coefficients obtained by the EPICS–SPME technique and those generated by other methods. However, it must be mentioned that literature data for these type of compounds are scarce. This conclusion indicates that further research on the air–water equilibrium partitioning of these less volatile compounds is recommended, especially with respect to the possibilities and limitations of both the EPICS–SPME method and other experimental techniques.

Acknowledgements

The authors acknowledge financial support of the Belgian Federal Office for Scientific, Technical and Cultural Affairs (contract number MM/DD/12).

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