Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 228 (2003) 69–80

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Liquid–air partitioning of volatile compounds in coffee: dynamic measurements using proton-transfer-reaction mass spectrometry

Philippe Pollien[a], Alfons Jordan[b], Werner Lindinger[b], Chahan Yeretzian[a,*]

[a] *Nestlé Research Center, P.O. Box 44, CH-1000 Lausanne 26, Switzerland*
[b] *Institut für Ionenphysik, Leopold-Franzens-Universität, Technikerstr. 25, A-6020 Innsbruck, Austria*

Received 21 February 2003; accepted 14 April 2003

Abstract

Recently we introduced a dynamic approach to determine Henry's law constants (HLCs) of volatile organic compounds (VOCs) in water, and applied it to a series organic compounds dissolved in pure water. Here, we *first* discuss a further development of the original approach such that it can be applied to complex liquid food systems (coffee). *Second*, we examine the impact of non-volatile constituents on the HLC. More specifically, we evaluate the impact of non-volatile coffee constituents on the HLC of 2-methylpropanal, 3- and 2-methylbutanal, dimethylsulfide, dimethyldisulfide and ethyl-2-methylbutyrate. Finally, we demonstrate that the concentration on the VOC in solution does not affect the HLC, over the investigated concentration range of 10^{-4} to 10 ppm.

1. Introduction

This paper is concerned with the partitioning of volatile organic compounds (VOCs) between an aqueous solution and air under equilibrium conditions. Liquid–air partition coefficients are of importance to a large range of issues, in particular to medical [2,3], atmospheric [4–6], environmental [7–10], and food related [11–26] topics.

The partitioning of volatiles, under equilibrium conditions, between a liquid and a gas can be expressed in different ways. Here, we are using Henry's law constants (HLCs). It is defined as HLC $= H$ (M/atm) $= c(\mathrm{aq})/p(\mathrm{gas})$, with $c(\mathrm{aq})$ being the molar concentration of the VOC in the liquid, and $p(\mathrm{gas})$ the partial pressure in the gas-phase. HLC is the partition coefficient at standard conditions for an ideal, dilute solution. As concentrations and partial pressures increase, deviations from Henry's law may become noticeable.

HLC is just one way of expressing liquid–gas partitioning. Depending on the field, different definitions are used [10]. One alternative definition used in food-flavour science is $K = ((\mathrm{mg/L})_{\mathrm{gas}}/(\mathrm{mg/L})_{\mathrm{liq}}) = c(\mathrm{gas})/c(\mathrm{aq})$, with c(gas or liq) being the concentrations (w/v) of the VOC in the liquid and in the gas, respectively. While HLC expresses the partitioning as solubility, K defines the partitioning in terms of volatility. Both definitions are related via the following transformation: HLC $= 1/(R \times T \times K)$. R ((L atm)/(mol K)) is the ideal gas constant and T (K) the temperature.

---

[*] Corresponding author. Tel./fax: +41-21-7858615.
E-mail address: chahan.yeretzian@rdls.nestle.com (C. Yeretzian).

1387-3806/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00197-0

In the late 1970s, Leroi et al. [27], Renon and co-workers [28,29] and Mackay et al. [7] published bubbling cell designs to measure HLCs. Based on these, we developed a modified stripping cell coupled to a proton-transfer-reaction mass-spectrometer (PTR-MS) [1], to perform truly dynamic measurements of HLCs. The method was applied to VOCs in pure water. Compared to alternative techniques, it was shown to be accurate, fast and less prone to artefacts.

The objective of this work is two-fold. *First* we demonstrate how the original method, as discussed in Ref. [1], can be modified such that it can be applied to more complex liquid systems. The example we discuss is liquid coffee, where foaming of the liquid during gas stripping has to be prevented. *Second*, we discuss the impact of the liquid coffee matrix on the HLC for a series of coffee volatiles, relative to dilute, pure solutions. Various types of interactions between volatile constituents and non-volatile components may occur in coffee, leading to deviations of the HLCs from the ideal, dilute solution. Finally, we examine the impact of the VOC concentration on volatility.

2. Experimental

2.1. *The stripping cell design*

Fig. 1 gives a schematic overview of the setup used in this study. A flow of clean air or nitrogen is dispersed through a nozzle, into a solution of VOC (Fig. 2). Fig. 3 shows the lower part of the bubbling cell with the gas dispersing nozzle. In the original design, frits were used as gas dispersing elements [1]. This leads to the formation of bubbles of heterogeneous size distribution. Used in coffee, foam was forming already at flow rates below 200 mL/min, in particular for bubbles with small average size distributions (smaller than 0.5 mm). We have, therefore, opted to generate well defined larger bubbles of narrow size distribution.

A series of Plexiglas nozzles were designed. The two shown in Fig. 2 contain 10 cylindrical holes each of 0.2 mm diameter and 1 mm depth. Some of the holes are indicated with arrows in Fig. 2. The bubbles generated by these nozzles have a diameter of approximately 2 mm (more than 70% of the bubble

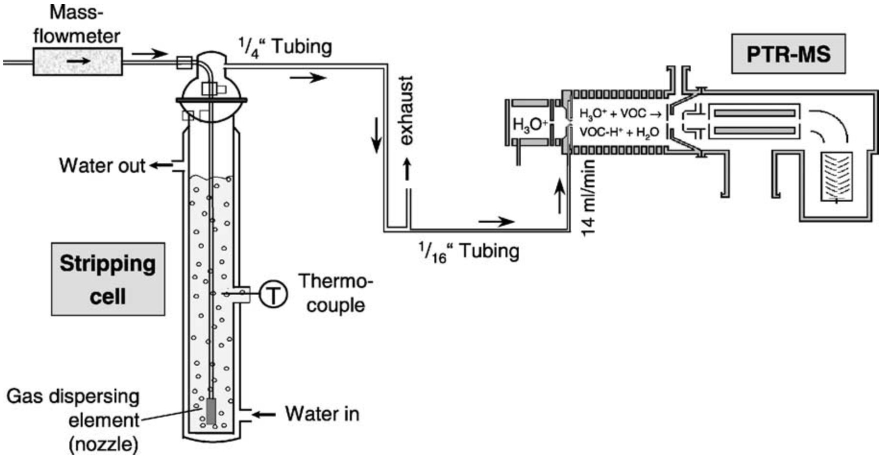

Fig. 1. Experimental setup to measure HLCs [1]. Humidified zero air is introduced through a gas dispersing element into the solution ($V = 100$ mL, liquid height = 40 cm). The gas bubbles through the solution, removing dissolved VOCs, according to Henry's law. The concentration of the VOCs as a function of time is measured online by continuously introducing the stripped gas into the PTR-MS. Experiments were performed with 40–200 mL/min flows of strip gas. Since only 14 mL/min is introduced into the PTR-MS, the additional gas volume used to strip the solution is released into a gas exhaust line. Tubings are made of stainless steel, with a quartz coating (silicosteel®, Restec GmbH, Germany), and heated to prevent adsorption and condensation. Here tubings were heated to 60 °C, which is sufficiently above the temperature of the experiment (room temperature) but not too high to limit thermal stress on thermally labile volatiles. Thermostatised water (jacketed stripping cell) controls the temperature of the experiment.

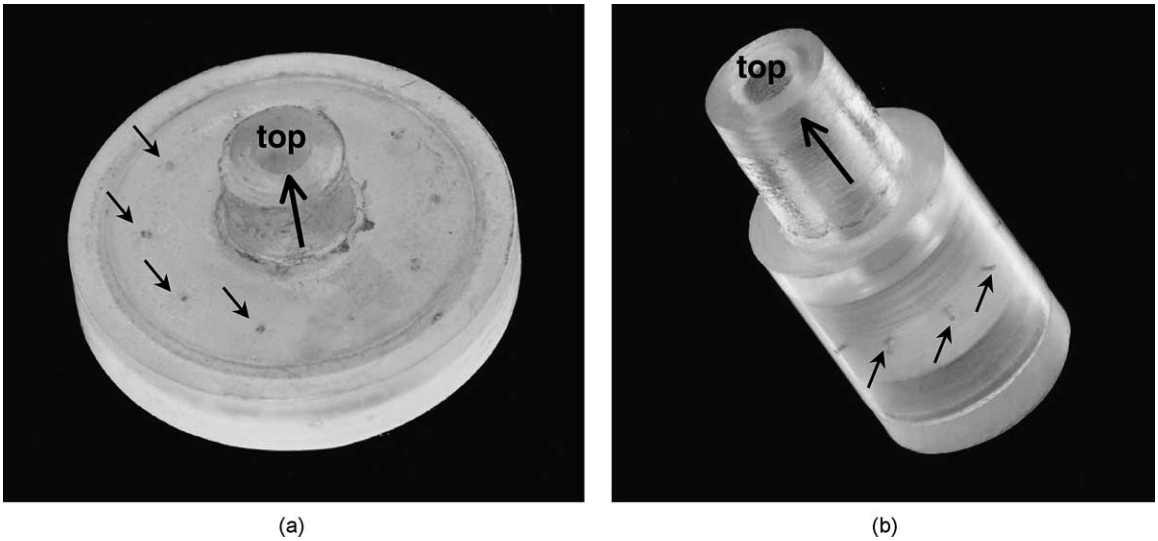

Fig. 2. Two gas dispersing elements to generate gas bubbles of homogeneous size distribution (made of Plexiglas). The pieces are fixed onto a glass tube by tightly inserting the parts marked “top” into the inner diameter of the glass tube. Gas bubbles are released into the solution through a series of 10 cylindrical holes each of 0.2 mm diameter and 1 mm depth, some of which are indicated by small arrows.

diameters were in the range 1.5–2.5 mm), as assessed by image analysis. This was performed by measuring manually the distribution of bubble diameters on pictures similar to the one shown in Fig. 3. While other designs were tested, these two turned out to perform well and were used throughout these studies. Both give identical HLCs and similar bubble size distributions. The nozzle shown in Fig. 2a generates the gas bubbles horizontally on the top side of the disc, and the bubbles are immediately and completely released into the solution. The nozzle shown in Fig. 2b generates the bubbles vertically on the walls of the Plexiglas disk. The bubbles rise initially along the Plexiglas walls, before they detach and are fully surrounded by the solution. The gas dispersing element is attached to a glass tubing by tightly introducing the “top” into the inner diameter of a glass tube, through which gas is delivered to the nozzle.

The cell contains either doubly distilled water and traces of pure VOCs, or liquid coffee with added VOCs. On their way up through the solution, VOCs dissolved in the liquid equilibrate with the gas phase confined within the air bubbles until equilibrium is reached, according to Henry’s law. Ensuring equili-

Fig. 3. Picture of the lower part of the stripping cell. It shows the gas-dispersing element releasing gas bubbles at the bottom of the solution. The bubbles rise through the solution and equilibrate with dissolved VOCs, during their residence time in the solution.

bration is one of the key premises of the experiment. Therefore, we have explored this issue in a series of experiments that we reported in a separate paper [1]. A depth of 20 cm between nozzle and liquid surface was sufficient to ensure that equilibrium is reached for all VOCs investigated. The gas exiting the cell was directly introduced into the PTR-MS, and the concentration of the VOCs was measured online. From the rate of concentration-change in the stripped gas, the HLC can be calculated (see below). For details and reviews on PTR-MS, please see Refs. [30–35].

Due to mass transport of dissolved VOC by means of the air bubbles, the VOC concentration in the solution, and thus in the headspace (HS), decreased as a function of time according to

$$\ln\left(\frac{C(t)}{C_0}\right) = -\frac{F}{H \times V \times R \times T}t \tag{1}$$

where C_0 is the initial concentration in the HS, and $C(t)$ the concentration at time t. F (L/s) is the gas flow through the vessel, H (M/atm) is the Henry's law constant, V (L) is the liquid volume, R is the molar gas constant (0.08205 L atm/mol K) and T (K) is the temperature.

The measured quantity is counts-per-seconds (cps), and absolute concentrations C_0 and $C(t)$ are a priori not known. Yet, it is one of the features of PTR-MS that a simple relation can be derived, which relates measured cps to absolute HS concentrations [1,36].

$$C(t) = [\mathrm{VOC}] = \frac{1}{k_{R_{\mathrm{rate}}} \times t_{R_{\mathrm{time}}}} \times \frac{\mathrm{cps}(\mathrm{VOC} \times \mathrm{H}^+)}{\mathrm{cps}(\mathrm{H_3O}^+)} \tag{2}$$

The HS concentration of protonated VOCs, [VOC], is proportional to the ratio between measured count rates of protonated VOCs, cps(VOC $\times$ H^+) and of protonated water, cps(H_3O^+), and is inversely proportional to the reaction rate, $k_{R_{\mathrm{rate}}}$ [37,38], and the reaction time, $t_{R_{\mathrm{time}}}$ ($\approx$105 μs), for proton transfer in the chemical ionisation cell. Using this relationship between concentration and count rates, Eq. (1) can be transformed to:

$$\ln(\mathrm{cps}(t)) = -\frac{F}{H \times V \times R \times T} \times t + \ln(\mathrm{cps}_0) \tag{3}$$

By plotting the logarithmic of counts-per-seconds vs. time, we obtain a linear relation. The only unknown in the slope is the HLC. Solving the equation for the HLC we obtain:

$$H\ (\mathrm{M/atm}) = -\frac{F\ (\mathrm{L/s})}{\mathrm{slope}\ (\mathrm{s}^{-1}) \times V\ (\mathrm{L}) \times R\ (\mathrm{L\ atm/mol\ K}) \times T\ (\mathrm{K})} \tag{4}$$

Since only the ratio between count rates is needed to calculate the HLC (no absolute values), the system does not have to be calibrated and experimental errors originating from adsorption on glass surfaces and tubings are cancelled out [39]. Furthermore, fragmentation or switching reactions via the $H_2O \times H_3O^+$-cluster in the drift-tube do not affect the results [34,40].

2.2. Time-scale of experiment—striping rate

The accuracy of the method relies, among others, on the efficacy with which volatile compounds are stripped by the gas. The HLC is determined as the slope from the ln(cps) vs. time trace. Considering that a signal of 10^5 cps may have an average noise of approximately 0.5%, one ought to reduce the concentration in the liquid by about 10%, in order to have a $\Delta\{\ln(\mathrm{cps})\}$ of better than 10× the signal-to-noise. For highly volatile compounds, this can be achieved with a moderate gas flow within minutes. For less volatile compounds longer stripping times are required.

In order to characterize the time-scale of the experiment as dependent on the volatility, we analysed three typical coffee aroma compounds in water, which have very different volatilities: ethyl-2-methylbutyrate (high volatility), 2-methylbutanal (medium volatility), and 2,3-pentandione (low volatility). Each compound was analysed separately and concentrations were kept low enough to ensure that the stripping rate was not influenced by the initial concentrations of the odorants. Using 100 mL solutions and a flow of 100 mL/min, Fig. 4 shows the ln(cps) vs. time plot for all three compounds on identical scales. Ethyl-2-methylbutyrate

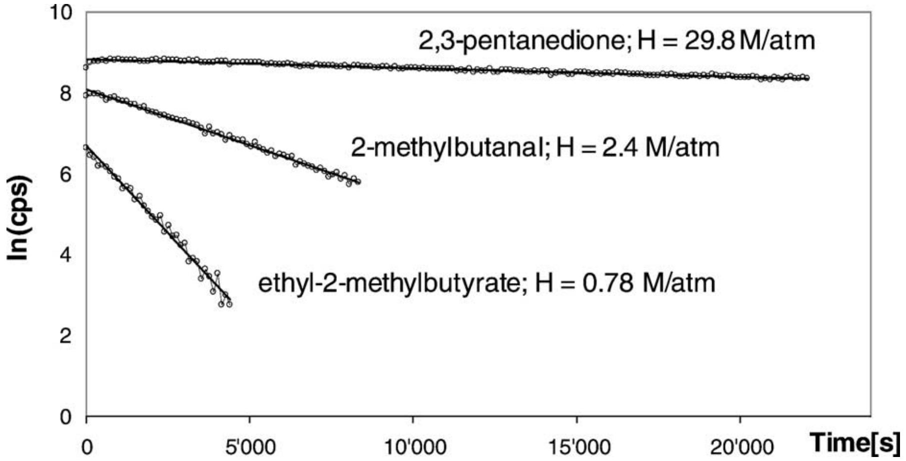

Fig. 4. 100 mL solutions of three compounds of different volatility were stripped at a gas flow of 100 mL/min, and their HLCs were determined. The initial concentrations of the compounds were around 100 ppm in water.

can be stripped to more than 50% within 30 min, which is more than enough for an accurate determination of the HLC. In contrast, hardly any reduction is observed in the case of pentanedione within the same time scale. This large spread in volatility of aroma active compounds in coffee requires adapting the time-scale for the experimental determination of the partition coefficients. Under typical experimental conditions (100 mL/min flow; 100 mL solution), as presented in Fig. 4, we can state that:

- for highly volatile compounds (HLC < 1), the slope can be determined within 1 h;
- for medium volatile compounds ($1 <$ HLC < 10), the liquid must be stripped for a few hours;
- for low volatile compounds (HLC > 10), the time for analysis can exceed 10 h.

One means of reducing the stripping time is to increase the flow rate. But there are limits to that, since foam forms at higher flow rates. Coffee foams at strip rates above 100–200 mL/min. This problem can be addressed in two ways. Either a modified stripping configuration is used as discussed in Ref. [1]. Alternatively, the gas dispersing element is designed such as to generate large bubbles (approximately 2 mm diameter) of homogeneous size distribution, as used in this study.

2.3. Partitions coefficients in liquid coffee

Liquid coffee was prepared at 25 °C, as an extract with 0.5% solid content (0.5 g coffee solid in 100 mL bidistilled water = 0.5% T_c). Coffee solutions were subsequently spiked at various concentrations with one of six coffee flavour compounds: 3-methylbutanal from 0.2 to 1 ppm (1 ppm = 1 mg-VOC/L-H_2O), 2-methylbutanal (0.2–1 ppm), 2-methylpropanal (0.1–1 ppm), dimethylsulfide (0.05–0.2 ppm), dimethyldisulfide (0.2–0.5 ppm), and ethyl-2-methylbutyrate (0.2–0.5 ppm). The concentration ranges were selected to increase the PTR-MS signal intensities of the respective compounds by more than a factor of two, relative to their natural concentrations in coffee beverage. This allowed to unambiguously identifying the compound. The HLCs of the solution were determined in the setup shown in Fig. 1, and the values are reported in Table 1. While the liquid volume was 100 mL in all experiments, the strip rate was varied over the range from 40 to 200 mL/min.

2.4. Dependence on VOC concentration

The effect of the VOC concentration on the liquid–air partitioning was examined using xylene, 2-butanone, 2,3-butanedione and propanol. They were chosen such as to cover a wide range of volatilities

Table 1

Measured HLCs in water and in coffee at 25 °C (if not otherwise noted) with their standard deviations given in percent of their respective values

Compound	HLC_{water} (M/atm), literature	K_{water} ((mg/L)/(mg/L)), literature	Reference	HLC_{water} (M/atm)	K_{water} ((mg/L)/(mg/L))	Standard deviation (%)	$HLC_{0.5\%\ coffee}$ (M/atm)	$K_{0.5\%\ coffee}$ ((mg/L)/(mg/L))	Standard deviation (%)	$\sum(K_{i,j} \times C_j)$
3-Methylbutanal	2.02(28 °C)	2.00×10^{-2}	[49]	2.6	1.6×10^{-2}	3.4	2.6	1.5×10^{-2}	1.4	0.8×10^{-2}
2-Methylbutanal	2.51 (30 °C)	1.60×10^{-2}	[1]	2.3	1.8×10^{-2}	10.0	2.3	1.7×10^{-2}	0.3	3.1×10^{-2}
2-Methylpropanal	5.11	0.80×10^{-2}	[50]	3.4	1.2×10^{-2}	10.9	3.9	1.1×10^{-2}	1.3	13.9×10^{-2}
Dimethylsulfide	0.615 (20 °C)	6.76×10^{-2}	[51]	0.5	8.5×10^{-2}	–	0.5	8.8×10^{-2}	4.9	0.0×10^{-2}
Dimethyldisulfide	0.840 (20 °C)	4.95×10^{-2}	[51]	0.6	6.7×10^{-2}	0.0	0.6	6.4×10^{-2}	1.4	4.9×10^{-2}
Ethyl-2-methylbutyrate	2.68 (30 °C)	1.50×10^{-2}	[52]	0.9	4.6×10^{-2}	15.6	1.1	3.6×10^{-2}	2.5	28.4×10^{-2}

Standard deviations were determined based on triplicate or quadruple determinations. No standard deviation is given for dimethylsulfide, since only one measurement was performed on this compound. We also included values from the literature. Personal communication by P. Pollien and D. Roberts.

Table 2
The effect of VOC concentration in water and coffee on air–water partitioning was examined over four orders of magnitude

Compounds	R^2 (water)	R^2 (coffee)
Xylene	1.0000	0.995
2-Butanone	1.0000	0.9993
2,3-Butanedione	1.0000	0.996
2-Propanol	1.0000	0.976

In columns 2 and 3, the regression coefficients from the linear fits—HS vs. liquid concentration—for each of the four VOCs are shown. Considering that all regression coefficients are essentially 1, we conclude that HLCs are not affected by the VOC concentration, over the investigated concentration range.

(see Table 2). Two series of experiments were performed, one in pure water and one in 2% coffee solution.

In the first series, solutions of VOCs over the concentration range 10^{-4} to 10 ppm ($=10^{-4}$ to 10 μg-VOC/g-H_2O) were prepared for each of the four VOCs in bidistilled water. Each solution was equilibrated for 60 min at room temperature (22 °C) in a closed/sealed vial, and equilibrium HS concentrations were measured by PTR-MS. In a second series, liquid coffee solutions at 2% T_c were spiked with the same amount of VOC as in the pure water experiments and the HS concentrations were calculated via Eq. (2). In Figs. 5 and 6, we plotted the liquid vs. the HS concentrations (double logarithmic plots) for pure water and liquid coffee systems, respectively. In addition to the all-C^{12} compound peaks, the intensities of the C^{13} isotopically substituted compounds were also analysed. For xylene, 2-butanone and 2,3-butanedione, the HS concentrations were calculated based on the mass spectral intensity of the pure C^{12} protonated parent mass intensity as well as of the singly and doubly C^{13}-substituted compounds. For xylene this corresponded to the ion masses *m/z* 107, 108 and 109. For 2-butanone we recorded *m/z* 73, 74 and 75, and for 2,3 butanedione the ion signals at *m/z* 87, 88 and 89 were recorded. In the case of propanol, the protonated parent fragments nearly quantitatively into mass 43 (97%; loss of H_2O), with only 2% appearing at the parent mass [36]. Hence, propanol was monitored at 43 amu (all-C^{12}) and 44 amu (one-C^{13}).

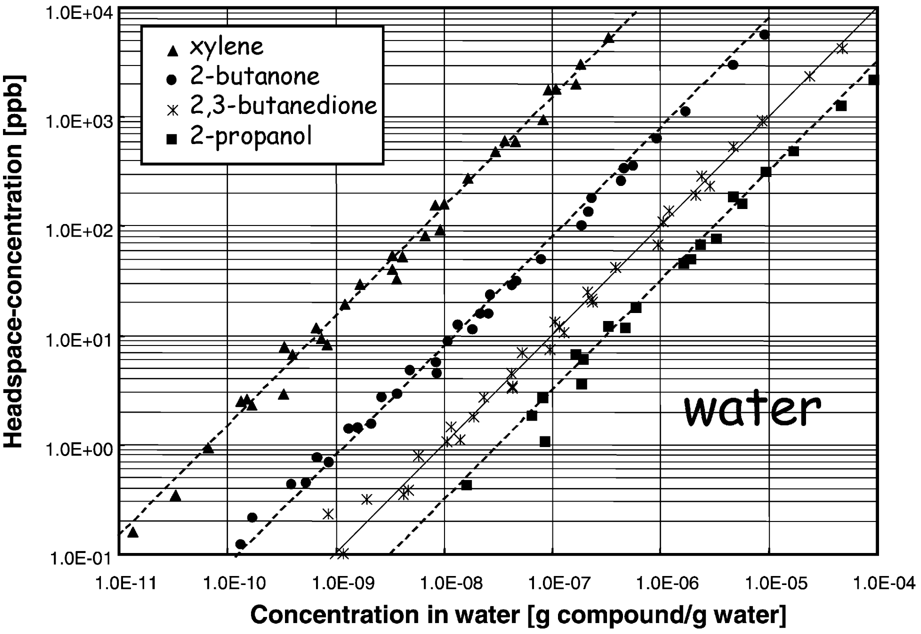

Fig. 5. Measured headspace concentrations above pure dilute solutions of xylene, 2-butanone, 2,3-butanedione and propanol (10^{-9} g-VOC/g-H_2O = 1 ppb).

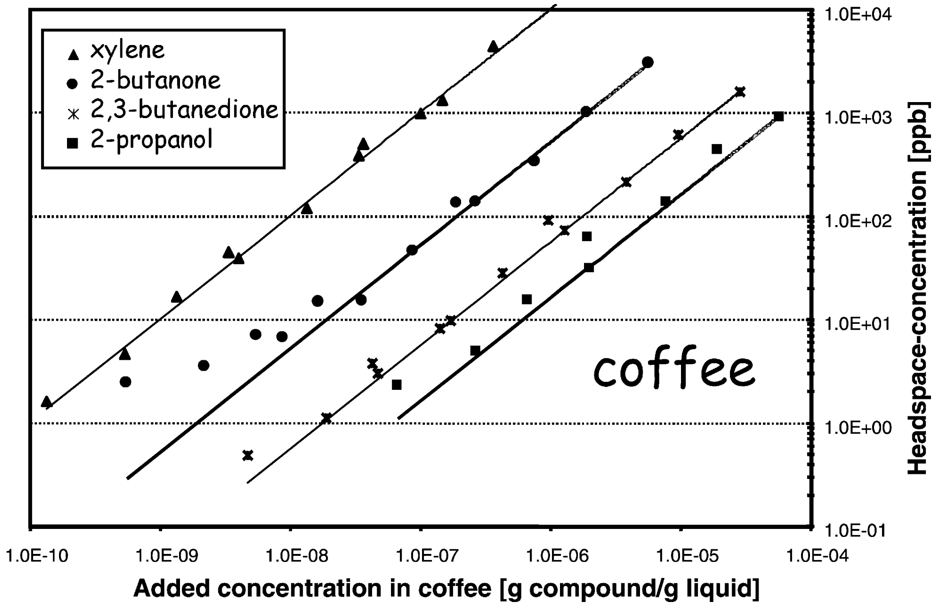

Fig. 6. Headspace concentrations of xylene, 2-butanone, 2,3-butanedione and propanol above 2% coffee solutions. The coffee solutions were spiked over a large concentration range. The lines included in the graph correspond to the linear regressions obtained in pure water (Fig. 5). They are included to show potential deviations of the coffee from the pure water values. We see that, except for the low concentration range, the liquid coffee values fit well with the pure water values.

3. Result and discussion

3.1. HLCs in liquid coffee: impact of coffee non-volatiles

The concept of HLC is rigorously valid only in the limit of infinitely diluted solutions where interactions among VOCs can be neglected (typically below 0.001 mol fraction) [10]. Yet, in many real world situations, solute concentrations may exceed 0.01 mol fraction, and the question arises how far into the range of finite concentrations Henry's law remains valid. It is known that organic matter (dissolved or suspended) may reduce the HS concentration of dissolved volatiles [10,41,42], while salts drive them out [10,43–46]. Here we examine whether non-volatile constituents of liquid coffee affect the partitioning of volatile coffee aroma compounds.

The solid content of liquid coffee mainly consists of dissolved or suspended organic matter (non-volatile ≙NV), while the volatile fraction accounts for less than 1% of the total solid [47,48]. One consequence of NVs in coffee is that they may enhance the apparent solubility of some VOCs. Volatile compounds exist either in free (hydrated) or adsorbed form, but only the free form can directly participate in the air–water exchange. One can, therefore, distinguish between the pure water $\mathrm{HLC}^{\mathrm{pure}}$ and the apparent $\mathrm{HLC}^{\mathrm{app}}$, as it is observed in real liquid systems. Chiou and co-workers [41,42] and Staudinger and Roberts [10] have proposed a simple relation, which links the apparent HLC to the pure HLC for a particular VOC_I:

$$\mathrm{HLC}_i^{\mathrm{app}} = \frac{C_{i,\mathrm{gas}}}{C_{i,\mathrm{liq,total}}} = \frac{\mathrm{HLC}_i^{\mathrm{pure}}}{1+\sum_j (K_{i,j} \times C_j)} \qquad (5)$$

where the $\mathrm{HLC}_i^{\mathrm{app}}$ and $\mathrm{HLC}_i^{\mathrm{pure}}$ are given in atm/M (inverse to above definition). $C_{i,\mathrm{liq,total}}$ is the total concentration of one specific VOC_i in the aqueous phase (both adsorbed and free species) in mol/L, $C_{i,\mathrm{gas}}$ is the VOC_i partial pressure in the gas phase in atm, $K_{i,j}$ is the partition coefficient of VOC_i with one particular NV_j, expressed in L/mol, and C_j is the concentration of the respective NV_j in water in mol/L. $\sum(K_{i,j} \times C_j)$ runs over all NV_j present in the solution.

In liquid coffee, we expect various VOC-NV partitionings to co-exist, each one with a particular $K_{i,j}$, in addition to irreversible chemical reactions. Hence, Eq. (5) is only a rough approximation for liquid coffee. Nevertheless, the degree of VOC-NV interaction in coffee solutions can be estimated. We take the value of $\sum(K_{i,j} \times C_j)$ as a rough measure of the impact of the non-volatile coffee constituents on the volatilities of VOC_i. We call this term the *Interaction Factor*, since it expresses an aggregated measure for the $NV\text{-}VOC_i$ interactions.

We have measured the HLCs for six volatile coffee flavour compounds in pure water and in liquid coffee at 0.5% T_c. Table 1 shows the measured values in units of HLC (M/atm) and K ((mg/L-air)/(mg/L-water)), together with the standard deviations expressed in percent of the average K. Considering the standard deviations, the partition coefficients in pure water and coffee beverage are significantly different for ethyl-2-methylbutyrate and barely different for 2-methylpropanal. For the other four compounds, the pure water and liquid coffee values are indistinguishable within the precision of the experiment. We calculated $\sum(K_{i,j} \times C_j)$ from the measured apparent and pure HLCs. They are included in the last column of Table 1. For 2-methylbutanal, 3-methylbutanal, dimethylsulfide and dimethyldisulfide, whose partition coefficients are insignificantly affected by coffee non-volatiles (within experimental precision), we obtain interaction factors smaller than 5×10^{-2}. In contrast, ethyl-2-methylbutyrate which shows significant interaction yields an *Interaction Factor* close to 30×10^{-2}.

3.2. Dependence on VOC concentration

In the preceding sections we have discussed the impact of coffee non-volatiles on the liquid–air partitioning of VOCs. Here we will assess whether the liquid–air equilibrium is affected by the concentration of the VOC in the liquid (water and coffee). Potential effects of VOC concentration on liquid–air partitioning have been studied by Munz and Roberts, based on thermodynamic theory [53]. They predicted an increased solubility with increasing VOC concentration, yet the effect was relatively insignificant, and they predicted little, if any, measurable effect. Experimental studies have confirmed that, for any practical purpose, the HLC is independent of VOC concentration [53–56].

Four VOCs of different volatilities and polarity were selected (Table 2). These are xylene, 2-butanone, 2,3-butanedione and propanol, in order of decreasing volatility. According to published values, xylene is the most volatile and least polar one, with a HLC in the range of 0.12–0.29 M/atm [9,45,57–61]. In order of decreasing volatility, the HLCs of 2-butanone, 2,3-butanedione and propanol are 4.1–21 M/atm [39,43,44,46,51,60,62–67], 57–74 M/atm [65,67], and 89–170 M/atm [65,66], respectively.

The objective here was to examine the dependence of the gas-phase concentration (or equivalently the cps) from the liquid concentrations, and determine whether it deviates from linearity at higher concentrations. Hence, it was not intended to measure explicitly the HLC. First we measured the HS concentrations over a large range of liquid concentrations in pure water. We then spiked coffee solutions with the same four VOCs over the analogous concentration range and determined their HS concentrations.

Plotting the measured HS concentrations vs. the known concentrations in pure water for all four compounds, a highly linear relationship over the entire concentrations range is found, as can be seen from Fig. 5. Similarly a linear relationship was found between liquid- and gas-phase concentrations in spiked liquid coffee, except at very low concentrations (Fig. 6). This is confirmed by the linear regressions coefficients, R^2. For all four compounds in water, deviations of R^2 from 1 are smaller than 10^{-8} (Table 2). In pure water this amounts to saying that for VOC-concentrations smaller than $100\,\mu\text{g-VOC/g-H}_2\text{O} = 100\,\text{ppm}$, no deviations from the ideal situation are observed.

In coffee, we also obtained regression coefficients close to one. Yet, at low concentrations, some deviations for 2-butanone, 2,3-butanedione and propanol appeared, whereas xylene did not show any deviation from linearity. We explain these deviations at low concentrations by the fact that we neglected VOCs already present in coffee. The liquid concentrations plotted in Fig. 6 correspond only to the amount added by spiking coffee. Yet, coffee is known to contain 2-butanone, 2,3-butanedione and propanol, and isobaric compounds might additionally contribute to measured ion intensities, e.g., the intensity at m/z 73 in coffee is mainly due to 2-butanone, but also to other compounds (parent or fragment) that contribute to the PTR-MS intensity at mass 73, such as butanal and isobutanal [36]. Similar arguments hold for 2,3-butanedione and propanol and explain the deviations from linearity at low concentrations (Fig. 6). Overall, our results are in agreement with former studies, which did not reveal any significant differences in HLCs as a function of VOC concentration [53].

4. Conclusion

Henry's law is strictly valid only for ideal, dilute solutions. Yet, liquid coffee contains suspended and dissolved non-volatile organic matter and finite VOC concentrations. The question, therefore, arises of how far into the range of finite concentration the HLC still holds.

Here we have developed an approach for the dynamic stripping of volatiles from a coffee solution. A special gas-dispersing element was introduced that generates a narrow distribution of bubble sizes with an average diameter of 1 mm. This prevents coalescence of gas bubbles and avoids foam formation at the surface of the coffee solution.

Comparing the air–liquid partitioning of six coffee aroma compounds in water and in liquid coffee, we found no significant differences for 3-methylbutanal, 2-methylbutanal, dimethylsulfide and dimethyldisulfide, for the investigated concentrations. In contrast, ethyl-2-methylbutyrate showed significant interactions with coffee non-volatiles, within the precision of the experiment (standard deviations of K). The effect of coffee non-volatiles on 2-methylpropanal was barely significant. We defined an *Interactions Factor*, that roughly aggregates all physical and chemical interactions, and helps classify the various coffee VOCs, based on measured deviations of volatility in coffee, relative to water. Interactions for concentrations outside the range investigated here cannot be excluded.

Examining the impact of VOC concentration in water and liquid coffee on the air–liquid partitioning, we have found no significant concentration effects for xylene, 2-butanone, 2,3-butanedione and propanol, over the liquid concentration range 0.1 ppb to 100 ppm. All four compounds showed linear relationships between the liquid and the HS concentrations, over four orders of magnitude of liquid concentration.

The significance of this work is two-fold. First we introduce an extension of the original approach for the determination of HLCs that can be applied to complex liquid systems, such as coffee. We then apply the method to a series coffee VOCs, and demonstrate that the coffee matrix has little effect on the HLCs (except for ethyl-2-methylbutyrate). Hence, HLC of coffee aroma compounds, determined in dilute, pure water solution, are a good first order approximation of liquid coffee values.

Acknowledgements

We acknowledge Christian Lindinger for technical assistance, O. Breton for machining the gas dispersing nozzles, and thank E. Prior for proofreading the manuscript.

References

[1] T. Karl, C. Yeretzian, A. Jordan, W. Lindinger, Int. J. Mass Spectrom. 223/224 (2003) 383.
[2] W. Lindinger, J. Taucher, A. Jordan, A. Hansel, W. Vogel, Clin. Exp. Res. 21 (1997) 939.
[3] T. Karl, P. Prazeller, D. Mayr, A. Jordan, J. Rieder, R. Fall, W. Lindinger, J. Appl. Physiol. 91 (2001) 762.
[4] C. Warneke, T. Karl, H. Judmaier, A. Hansel, A. Jordan, W. Lindinger, P.J. Crutzen, Global Biogeochem. Cycles 13 (1999) 9.
[5] R. Sander, Surveys Geophys. 20 (1999) 1.
[6] R. Fall, T. Karl, A. Hansel, A. Jordan, W. Lindinger, J. Geophys. Res. 104 (1999) 15.963.

[7] D. Mackay, W.S. Shui, R.P. Sutherland, Environ. Sci. Technol. 13 (1979) 333.
[8] D. Mackay, W.Y. Shiu, J. Phys. Chem. Data 10 (1981) 1175.
[9] K.C. Hansen, Z. Zhou, C.L. Yaws, T.M. Aminabhavi, J. Chem. Educ. 72 (1995) 93.
[10] J. Staudinger, P.V. Roberts, Crit. Rev. Environ. Sci. Technol. 26 (1996) 205.
[11] C.J. Bennet, Cereal Foods World 37 (1992) 429.
[12] M.S. Brauss, R. Linforth, I. Cayeux, B. Harvey, A.J. Taylor, J. Agric. Food Chem. 47 (1999) 2055.
[13] K.B. de Roos, in: D.D. Roberts, A.J. Taylor (Eds.), Proceedings of the 218th ACS National Meeting on Flavour Release: Linking Experiments, Theory and Reality, New Orleans, American Chemical Society Symposium Series 763, Washington, DC, 2000, p. 126.
[14] K.B. de Roos, E. Graf, J. Agric. Food Chem. 43 (1995) 2204.
[15] E.M. Vroom, J. Mojet, J. Heidema, W. den Hoed, P.G.M. Haring, in: A.J. Taylor, D.S. Mottram (Eds.), Flavour Science: Recent Developments, The Royal Society of Chemistry, Cambridge, UK, Special Publication No. 197, 1996, p. 446.
[16] P. Overbosh, W.G.M. Afterof, P.G.M. Haring, Food Rev. Int. 7 (1991) 137.
[17] C.M. Delahunty, J.R. Piggott, J.M. Conner, A. Paterson, Ital. J. Food Sci. 2 (1996) 89.
[18] R. Linforth, K.E. Ingham, A.J. Taylor, in: A.J. Taylor, D.S. Mottram (Eds.), Flavour Science: Recent Developments, The Royal Society of Chemistry, Cambridge, UK, Special Publication No. 197, 1996, p. 361.
[19] M. Harrison, in: D.D. Roberts, A.J. Taylor (Eds.), Proceedings of the 218th ACS National Meeting on Flavour Release: Linking Experiments, Theory and Reality, New Orleans, American Chemical Society Symposium Series 763, Washington, DC, 2000, p. 179.
[20] M. Harrison, S. Campbell, B.P. Hills, J. Agric. Food Chem. 46 (1998) 2736.
[21] K. Doyen, M. Carey, R. Linforth, M. Marin, A.J. Taylor, J. Agric. Food Chem. 49 (2001) 804.
[22] R. Linforth, F. Martin, M. Carey, J. Davidson, A.J. Taylor, J. Agric. Food Chem. 50 (2002) 1111.
[23] H.O.E. Karlsson, G. Trägardh, Trends Food Sci. Technol. 7 (1996) 78.
[24] A. Pozderovic, T. Moslavac, Acta Alimentaria 28 (1999) 71.
[25] M. Furrer, C. Gretsch, Coffee aroma recovery process, EP 1078576, 2001, Eur. Pat. Appl.
[26] B. Rothfos, Aroma recovery and reapplication, in: Coffee Consumption, GORDIAN-Max Rieck, 1986.
[27] J.-C. Leroi, J.-C. Masson, H. Renon, J.-F. Fabries, H. Sannier, Ind. Eng. Chem. Process Des. Dev. 16 (1977) 139.
[28] D. Richon, H. Renon, J. Chem. Eng. Data 25 (1980) 59.
[29] D. Richon, F. Sorrentino, A. Volley, Ind. Eng. Chem. Process Des. Dev. 24 (1985) 1160.
[30] W. Lindinger, J. Hirber, H. Paretzke, Int. J. Mass Spectrom. Ion Process. 129 (1993) 79.
[31] A. Hansel, A. Jordan, R. Holzinger, P. Prazeller, W. Vogel, W. Lindinger, Int. J. Mass Spectrom. Ion Phys. 149/150 (1995) 609.
[32] W. Lindinger, A. Hansel, Plasma Sources Sci. Technol. 6 (1997) 111.
[33] W. Lindinger, A. Hansel, A. Jordan, Chem. Soc. Rev. 27 (1998) 347.
[34] W. Lindinger, A. Hansel, A. Jordan, Int. J. Mass Spectrom. 173 (1998) 191.
[35] C. Yeretzian, A. Jordan, H. Brevard, W. Lindinger, in: D.D. Roberts, A.J. Taylor (Eds.), Proceedings of the 218th ACS National Meeting on Flavour Release: Linking Experiments, Theory and Reality, New Orleans, American Chemical Society Symposium Series 763, Washington, DC, 2000, p. 763.
[36] C. Yeretzian, A. Jordan, W. Lindinger, Int. J. Mass Spectrom. 223/224 (2003) 115.
[37] G. Gioumousis, D.P. Stevenson, J. Chem. Phys. 29 (1958) 294.
[38] T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183.
[39] R.G. Buttery, L.C. Ling, D.G. Guadagni, J. Agric. Food Chem. 17 (1969) 385.
[40] C. Praxmarer, A. Hansel, A. Jordan, H. Kraus, W. Lindinger, Int. J. Mass Spectrom. Ion Process. 129 (1993) 121.
[41] T.C. Chiou, L.R. Malcolm, I.T. Brinton, E.D. Kile, Environ. Sci. Technol. 20 (1986) 502.
[42] T.C. Chiou, E.D. Kile, I.T. Brinton, L.R. Malcolm, J.A. Leenheer, P. MacCarthy, Environ. Sci. Technol. 21 (1987) 1231.
[43] S.L. Friant, I.H. Suffet, Anal. Chem. 51 (1979) 2167.
[44] X. Zhou, K. Mopper, Environ. Sci. Technol. 24 (1990) 1864.
[45] J. Dewulf, D. Drijvers, H. van Langenhove, Atm. Environ. 29 (1995) 323.
[46] V. Morillon, F. Debeaufort, J. Jose, J.F. Tharrault, M. Capelle, G. Blond, A. Voilley, Fluid Phase Equilibria 155 1999 297.
[47] R. Viani, The composition of coffee, in: S. Garattini (Ed.), Caffeine, Coffee, and Health, Raven Press, Ltd., New York, 1993 (Chapter 2).
[48] W. Grosch, Nahrung 42 (1998) 344.
[49] P.E. Nelson, J.E. Hoff, J. Food Sci. 33 (1968) 479.
[50] J.E. Amoore, R.G. Buttery, Chem. Senses Flavor 3 (1978) 57.
[51] A.G. Vitenberg, B.V. Ioffe, Z. St. Dimitrova, I.L. Butaeva, J. Chromatogr. 112 (1975) 319.
[52] D.D. Roberts, P. Pollien, J. Agric. Food Chem. 45 (1997) 4388.
[53] C. Munz, P.V. Roberts, J. Am. Water Works Assoc. 79 (1987) 62.
[54] E.E. Tucker, S.D. Christian, J. Phys. Chem. 83 (1979) 426.
[55] B.C. Nicholson, B.P. Maguire, D.B. Bursill, Environ. Sci. Technol. 18 (1984) 518.
[56] A. Przyjazny, W. Janicki, W. Chrzanowski, R. Staszewski, J. Chromatogr. 280 (1983) 249.
[57] J. Hine, P.K. Mookerjee, J. Org. Chem. 40 (1975) 292.
[58] G.A. Robbins, S. Wang, J.D. Stuart, Anal. Chem. 65 (1993) 3113.
[59] S.P. Wasik, W. Tsang, J. Phys. Chem. 74 (1970) 2970.

[60] R.A. Ashworth, G.B. Howe, M.E. Mullins, T.N. Rogers, J. Hazardous Mater. 18 (1988) 25.

[61] R.L. Bohon, W.F. Claussen, J. Am. Chem. Soc. 73 (1951) 1571.

[62] L. Rohrschneider, Anal. Chem. 45 (1973) 1241.

[63] G.M. Janini, L.A. Qaddora, J. Liq. Chromatogr. 9 (1986) 39.

[64] A. Chaintreau, A. Grade, R. Munoz-Box, Anal. Chem. 67 (1995) 3300.

[65] J.R. Snider, G.A. Dawson, J. Geophys. Res. 90 (1985) 3797.

[66] J. Hine, R.D. Weimar Jr., J. Am. Chem. Soc. 87 (1965) 3387.

[67] E.A. Betterton, Atm. Environ. 25A (1991) 1473.