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Quantification of octanol–water partition coefficients of several aldehydes in a bubble column using selected ion flow tube mass spectrometry

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ABSTRACT

The octanol–water partition coefficient, K_{OW}, of 2-heptenal, 2-octenal, 2-nonenal, 2-nonanone and octanal was obtained from headspace vapour concentrations in a bubble column determined by selected ion flow tube mass spectrometry (SIFT-MS) with and without addition of 1-octanol to the water solution. Experimental values for $\log K_{OW}$ at 299 K range from 2.06 ± 0.12 (2-heptenal) to 2.31 ± 0.14 (1-octanal). Partition enthalpies, $-\Delta^0 H_{w\to o}$, of 19.9 ± 6.2 kJ mol^{-1} (1-octanal) up to 118.1 ± 8.5 kJ mol^{-1} (2-nonanone) were obtained. In conjunction to the determination of K_{OW}, Henry's law coefficients of $(2.76 \pm 0.38) \times 10^{-3}$ mol$_g$ mol$_l$ m$_g^{-3}$ m$_l^3$ for 2-heptenal to $(2.79 \pm 0.16) \times 10^{-2}$ mol$_g$ mol$_l$ m$_g^{-3}$ m$_l^3$ for 1-octanal were experimentally obtained.

1. Introduction

The octanol–water partition coefficient, K_{OW}, describes equilibrium partition of a compound between octanol and water, mutually immiscible, phases [1]. This parameter describes relative lipophilicity and hydrophilicity and, as such, it can be used in the assessment of environmental and in vivo fate and transport of organic compounds [2,3]. Therefore, K_{OW} or the frequently used logarithmic value, $\log K_{OW}$, is one of the most important physico-chemical characteristics related to sorption on the soil or sediments and bioaccumulation.

Values for K_{OW} can be obtained by direct methods, using experimental measurements, or by indirect methods, i.e., via calculation using semi-empirical correlations or group contributive calculations [4,5]. The classical experimental static headspace method or the so-called 'shake-flask' method for the determination of the octanol–water partition coefficient can be used to determine K_{OW} and also to determine the Henry's law coefficient [6–9]. A second experimental possibility is the so-called 'slow-stirring' or the 'stir-flask' method for very hydrophobic compounds, i.e., $\log K_{OW} > 5$ [10–13]. The so-called 'generator-column method' uses liquid chromatography [8,14,15]. Counter-current chromatography or centrifugal partition chromatography [16,17], microemulsion electrokinetic chromatography [18] and flow injection extraction [19] have been also applied in the experimental determination of the octanol–water partition coefficient.

As an alternative to exact experimental methods, approximate semi-empirical group contributive calculation methods of the octanol–water partition coefficient are available, such as the methods proposed by Hansch and Leo [20] or Meylan and Howard [21]. Also, correlations have been proposed to link the octanol–water partition coefficient versus several descriptors such as dipole–dipole interaction parameters, hydrogen-bond formation parameters and solute molar volume, corresponding to the method using the so-called 'Abraham solvation' parameters [22–25]. A linear correlation for polycyclic aromatic compounds has been proposed by Alves de Lima Ribeiro and Ferreira [26], using molar weight and the solute molar volume as descriptor. Other calculation methods estimate the octanol–water partition coefficient by means of one descriptor, e.g., based on the so-called 'electrotopological index' [27]. Also, quantum-chemical descriptors can be used in the prediction of $\log K_{OW}$ [28–31]. Extensive research was done to compare results of experimental and theoretical methods in the determination of $\log K_{OW}$ by e.g. Machatha and Yalkowski [32].

The absolute variation of the octanol–water partition coefficient with temperature is usually in the order of 0.01–0.10 K^{-1} if the solvents are not very miscible with each other [4,8,33]. For the sake of comparison, this range corresponds to an absolute value for the enthalpy change from the water into the octanol phase, $-\Delta^0 H_{w\to oct}$, of 6.9–68.6 kJ mol^{-1} at 298 K. The temperature dependency of the octanol–water partition coefficient is

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Table 1
m/*z* values for the precursor and product ions of the used compounds in their reaction with NO^+. Values in the brackets are the reaction coefficients (in 10^{-9} cm^3 s^{-1}).

Compound	M_w (g mol^{-1})	Precursor ion (*m*/*z*)[a]	Product ion (*m*/*z*)
2-Heptenal	112	30 (3.90), 48 (2.43), 66 (2.19)	111, 142
2-Octenal	126	30 (4.10), 48 (3.42), 66 (3.07)	125, 156
2-Nonenal	140	30 (3.80), 48 (3.16), 66 (2.82)	139, 170
2-Nonanone	142	30 (2.50), 48 (2.08), 66 (1.85)	141, 172
1-Octanal	128	30 (3.00), 48 (2.50), 66 (2.24)	127, 158

[a] Reaction coefficients for *m*/*z* = 48 and 66 are obtained from the bimolecular ion-molecule coefficient with precursor ion NO^+ using Eq. (S6).

extensively addressed in literature in the range of −32.0 to 62.5 kJ mol^{-1} [9,15,34–38].

This manuscript describes a new experimental methodology obtain the octanol–water partition coefficient, K_{OW}, using a bubble column set-up in combination with headspace concentration measurement using selected ion flow tube mass spectrometer (SIFT-MS) [39]. The bubble column is modelled as a continuous stirred tank reactor (CSTR) including continuity equations for the water phase and the octanol phase both in quasi-equilibrium with the gas phase. This gives rise to a newly developed formula for the calculation of the octanol–water partition coefficient from measurable experimental parameters.

Compounds used in this work are 2-heptenal, 2-octenal, 2-nonenal, 2-nonanone and 1-octanal. An advantage of using this combination is the fast determination of the octanol–water partition coefficient in a real water matrix, since it is known that the influence of temperature [9,15,34–37], pH [40–43] and ion composition, e.g. deionized water, tap water [42,44,45] or (artificially) created sea water [46], play a significant role in the value for equilibrium coefficients such as K_{OW}.

2. Experimental

2.1. Bubble column

Experiments were carried out in a laboratory bubble column reactor with a diameter of 0.11 m and a total volume of 0.8 L, using Prague (Czech Republic) tap water (pH 7.55, 33 mg L^{-1} of Ca^{2+}, hardness of 6.2 °dH corresponding to 1.1 mmol L^{-1} of Ca^{2+} and Mg^{2+}, conductivity of 37 mS m^{-1} [47]). The corresponding height of the water is 0.084 m. Fig. S1 in the Supplementary Content gives a schematic overview of the experimental setup, see Section S.1. Compressed air (Messer, F50, 200 bar, $N_2/O_2/Ar = 78/21/1$) (1) enters the bubble column (2) from below was passed through a porous glass-plate diffuser (Robu filter disc 1512, Germany) at 8.35 ± 0.16 L min^{-1}. The exiting gas was lead to the inlet of the SIFT-MS for analysis of the gas phase composition at point (■), see Fig. S1. The temperature of the tap water in the bubble column was varied between 283 and 313 K.

2.2. Materials

A stock solution of 15 mL ethanol, 35 mL water and 500 μL of 2-heptenal (Sigma Aldrich, 97%), 2-octenal (Sigma Aldrich, 94%), 2-nonenal (Sigma Aldrich, 97%), 1-octanal (Sigma Aldrich, 99%) and 2-nonanone (Sigma Aldrich, >99%) was prepared. In each experiment, 0.928 ± 0.002 mL of the stock solution was introduced by a needle (100 Sterican, 0.80 mm × 120 mm, Braun) in the bubble column at injection point (3), see Fig. S1. After injection of the stock solution, 40.3 ± 0.6 mL of 1-octanol (Sigma Aldrich, >99%) was added at 500 s from the top of the bubble column. Every experiment was also repeated without addition of 1-octanol in order to obtain the decay of depletion, only addressed by the passage of the compressed air through the bubble column according to the Henry's law coefficient, see Section 3.

The so-called 'phase ratio', denoted by '*q*', of the water and octanol volume was maintained constant at 0.050 ± 0.003, see Eq. (1):

$$q = \frac{V_{oct}}{V_w} \tag{1}$$

2.3. SIFT-MS

The standard SIFT-MS technique has been described elsewhere [48–54], so a brief summary is given. The quantification of the outlet gas phase concentration of aldehyde vapours by SIFT-MS was carried out using the SIFT-MS Profile 3 instrument (Instrument Science Limited, UK) with the flow tube diameter of 1 cm and reaction length of 4 cm and NO^+ was used as precursor ion for chemical ionization. The sample entered the helium carrier gas (5), see Fig. S1 in Section S.1, via a heated (343 K) capillary tube at a measured rate of 0.45 Torr L/s. The flow tube (7) temperature was 299 K and the flow tube pressure was 1.0 Torr. The multiple ion monitoring (MIM) mode was used to quantify specific volatile compounds [55,56]. In this mode, the analytical mass spectrometer is rapidly switched between selected *m*/*z* values of both the precursor ions and the characteristic product ions, see Table 1. It has to be mentioned that ethanol has reaction products with NO^+ at *m*/*z* = 45, 63, 81 and 99 and, hence, no overlaps with *m*/*z* values of interest, see Table 1, are observed. The reaction products of the compounds, having general mass M, in the reaction with NO^+ have *m*/*z* value of $(M-1)^+$, which is formed by hydride ion transfer, or $(M+30)^+$, which is the result of the ion-molecule association reaction [51]. The known rate coefficients for the analytical reactions were then used to quantify the absolute concentrations of the compounds using the standard SIFT-MS data analysis software and the general method of quantification [55]. Section S.2 gives a brief overview of the theoretical prescriptions for estimating rate coefficients of exothermic ion-molecule reactions. Ionic diffusion and mass discrimination was corrected by the SIFT-MS software [57].

The experimental data, acquired using SIFT-MS, were processed with respect to automatic outlier detection by means using of a two-sided median method for cleaning noisy time series data using the method of Basu and Meckesheimer [58]. Mathematical details on this procedure can be found in Section S.3 in the Supplementary Content.

3. Model

Considering a bubble column, operating with a given inert N_2 flow rate and containing a certain volume of water, after addition of 1-octanol a compound can be present (1) in the water phase of volume V_w, (2) in the octanol phase of volume V_{oct} and (3) in the gas phase. Corresponding concentrations are notated as $C_{w,i}$, $C_{oct,i}$ and $C_{g,i}$.

Similar to the work on PRM partitioning with a vesicular dispersion [39], the bubble column is modelled as a continuous stirred tank reactor (CSTR) and the corresponding continuity equations (CE) for the compounds in the water and the octanol phase are