



Determination of partition coefficients of refrigerants by gas liquid chromatographic headspace analysis

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ABSTRACT

Gas–water partition coefficients, K_w , and gas–solvent partition coefficients, K_s , have been determined for chlorodifluoromethane and for 1,1,1,3,3,3-hexafluoropropane by headspace analysis, using a very simple experimental procedure. These partition coefficients then yield water–solvent partition coefficients, P_s . Where comparisons can be made there is excellent agreement with literature values for K_w and P_s . The obtained values of K_s and P_s can be used to obtain physicochemical properties, or descriptors, for the refrigerants. Combination of these descriptors with previous equations we have developed enables partition coefficients to be obtained for a host of systems.

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1. Introduction

A standard procedure for the determination of water–solvent partition coefficients is the ‘shake-flask’ method. A compound is partitioned between water and an immiscible, or a partly immiscible solvent, and after equilibration the concentration of the solute in each phase is determined, often through UV/vis analysis [1,2]. Another well-known method involves determination of the capacity value of a compound on a suitable reversed-phase HPLC system that has been calibrated using a number of reference solutes [3]. Analysis is again often carried out using UV/vis spectrometry. There are a number of compounds, however, for which determination of partition coefficients by these methods is difficult. These include compounds that are not UV/vis active and very volatile compounds for which specific manipulation techniques have to be used. We wished to obtain water–solvent partition coefficients for 1,1,1,3,3,3-hexafluoropropane, R-236fa, bp -1°C , and chlorodifluoromethane, R-22, bp -41°C , and decided to use GLC headspace analysis to obtain gas–water partition coefficients, K_w , and gas–solvent partition coefficients, K_s , from which the corresponding water–solvent partition coefficients, P_s , can be obtained.

The use of headspace analysis to obtain gas–solvent partition coefficients or activity coefficients in a given solvent is well-known [4–6], but we wished to introduce a modification that leads

to gas–solvent partition coefficients with almost no calibration required.

2. Materials and methods

Gas–water, K_w , or gas–solvent, K_s , partition coefficients can be defined in terms of equilibrium concentrations of the solute, through Eq. (1). Then K_w and K_s are dimensionless.

$$K_s = \frac{\text{Conc. of solute in solvent, in mol dm}^{-3}}{\text{Conc. of solute in the gas phase, in mol dm}^{-3}} \quad (1)$$

Water–solvent partition coefficients, P_s , can be obtained through Eq. (2). If K_w and K_s refer to the pure water and solvent phases, then P_s will refer to transfer of a solute from water to the pure solvent phase. However, P_s values determined by the ‘shake flask’ method refer to transfer from water saturated with the organic solvent to the organic solvent saturated with water, so care has to be taken over possible differences between the two types of partition coefficient.

$$P_s = \frac{K_s}{K_w} \quad (2)$$

The usual method for the determination of K_s by head space analysis is to equilibrate the solute between a solvent and the headspace above the solvent and then to determine the concentration of the solute in each phase by GLC analysis. Zenkevich and Makarov [6] have suggested the use of two reference solutes, but we found this to be unnecessary.

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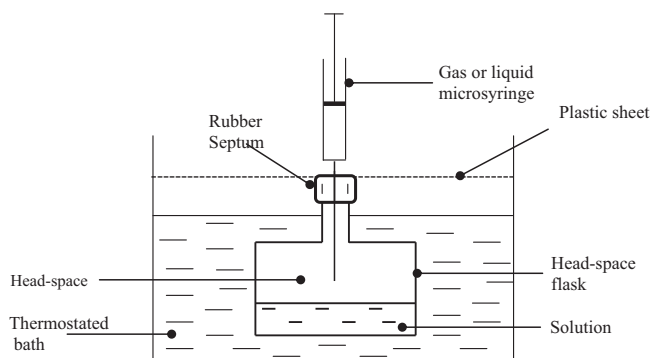


Fig. 1. The head space system used to measure air-solvent partition coefficients.

The refrigerants were kind gifts from Mexichem Fluor, solvents were from Aldrich, and wet octanol was prepared by saturating octanol with distilled water. A solution of a gaseous refrigerant in a given solvent was obtained by bubbling the refrigerant through the solvent contained in the vessel shown in Fig. 1 for approximately 10 min. The vessel was then sealed, stirred for 20 min using a magnetic stirrer, and placed in a thermostated bath at $25\text{ }^{\circ}\text{C} \pm 0.5\text{ }^{\circ}\text{C}$. After about 1 h the first samples were withdrawn from the solvent and from the head space using hypodermic syringes and analysed by GLC. Volumes taken from the vapour phase range from 6 to $200\text{ }\mu\text{L}$, and volumes from the liquid phase range from 0.3 to $50\text{ }\mu\text{L}$. These samples taken from the vapour and liquid phases were injected straight onto a Perkin Elmer F-33 flame ionization gas chromatograph. The column was Carbowax 20M and the oven temperature was $51\text{ }^{\circ}\text{C}$. The vessel shown in Fig. 1 had a volume of 200 cm^3 and the volume of the solvent in the vessel was normally around $20\text{--}30\text{ cm}^3$. The system is illustrated in Fig. 1. Samples were withdrawn through a rubber septum that was pierced by a hypodermic needle (not shown) to maintain atmospheric pressure inside the head space flask. A thin plastic sheet was placed over the entire thermostat. The sheet rested on the rubber septum and samples were withdrawn by puncturing both the plastic sheet and the rubber septum. We found this procedure to be essential. The plastic sheet fulfils a number of functions. It ensures a constant temperature throughout the flask, and in the case of multi-component systems such as water-ethanol solvents it prevents condensation of the more volatile components near the top of the flask.

The GLC areas of the resulting peaks from the vapour phase (A_g) and from the liquid phase (A_s) were measured and used in Eq. (3) to determine the air-solvent partition coefficient, K_s . The volumes of the gas phase and solvent that were withdrawn are denoted as V_g and V_s . No calibration is needed at all, other than to ascertain that for any given solute the GLC peak area was linear with solute concentration over the entire range of A_g and A_s .

$$K_s = \frac{C_s}{C_g} = \frac{A_s \cdot V_g}{A_g \cdot V_s} \quad (3)$$

The gas-solvent and water-solvent partition coefficients determined for a given solute can then be used to obtain descriptors for the solute, as we have described before [7,8]. The method involves the use of Eqs. (4) and (5).

$$SP = c + eE + sS + aA + bB + \nu V \quad (4)$$

$$SP = c + eE + sS + aA + bB + lL \quad (5)$$

The dependent variable, SP , is some property of a series of solutes in a given system. SP may be partition coefficients as, $\log P_s$, for a series of solutes in a given water-solvent system or may be $\log K_s$ for a series of solutes in a given gas-solvent system. The former are mostly used in Eq. (4) and the latter in Eq. (5). Other systems can

Table 1

Peak area per microlitre of phase for chlorodifluoromethane in the air-toluene system, at $25\text{ }^{\circ}\text{C}$.

Measurement	Air (C_g)	Toluene (C_s)	K_s
Measurement 1	11,712	225,189	19.23
Measurement 2	11,468	225,950	19.70
Measurement 3	11,604	235,387	20.28
Measurement 4	10,879	226,297	19.82
Average	11,416	228,206	19.76
SD	372	4810	0.43

also be used. For example SP in Eq. (5) can be a set of retention data for a series of solutes on a given GLC stationary phase.

The independent variables, or descriptors, in Eqs. (4) and (5) are properties of solutes as follows [7–10]: E is an excess molar refraction in $\text{cm}^3\text{ mol}^{-1}/10$, S is a combined dipolarity/polarizability descriptor, A is the overall solute hydrogen bond acidity, B is the overall solute hydrogen bond basicity, V is McGowan's [11] characteristic molecular volume in $\text{cm}^3\text{ mol}^{-1}/100$ and L is the gas to hexadecane partition coefficient at $25\text{ }^{\circ}\text{C}$, as $\log K$.

The set of coefficients, c, e, s, a, b, ν and l characterize the system and are determined by multiple linear regression analysis. These coefficients are not just fitting coefficients, but represent the complementary properties of the system: e gives the contribution in Eqs. (4) and (5) of the solute-system general dispersion interaction, s is the solvent dipolarity (plus some polarizability), a is the system hydrogen bond basicity (the complimentary property to solute hydrogen bond acidity) and b is the system hydrogen bond acidity (the complimentary property to solute hydrogen bond basicity). The coefficients ν and l reflect general dispersion interactions that aid solubility of a solute and the solvent-solvent interactions in the system that oppose solubility.

In Eqs. (4) and (5) there are six solute descriptors that have to be determined, E, S, A, B, V and L . If values of SP are known in six systems for which the coefficients have been determined, six simultaneous equations can be set up to yield the six solute descriptors. Of course, the more systems that can be used, the better, and if there are more known systems than unknown descriptors, the latter can be found by a 'best fit' method.

Once the descriptors in Eqs. (4) and (5) are known for a given solute, it is then possible to predict further values of $\log P_s$ and $\log K_s$ for a very large number of solvents [9], as well as numerous biological properties.

3. Results

In each system of solute and solvent, four samples of the gas phase and the solvent phase were withdrawn. Typical results are shown in Table 1 for the partition of chlorodifluoromethane between the gas phase and toluene, leading to $K_s = 19.76$ with a standard deviation, SD, of 0.43; $\log = 1.296$. The complete set of results for chlorodifluoromethane is in Table 2, together with a number of values previously determined. Walsh [12] determined $\log K_s$ in hexadecane as 0.690 through measurement of the specific retention volume on hexadecane at $25\text{ }^{\circ}\text{C}$, and this has been confirmed by Wahlström and Vamling [13] who obtained values of 0.692 and 0.663 by two different methods. $\log K_s$ on olive oil at $37\text{ }^{\circ}\text{C}$ is available [14]. A value for $\log P_s$ of 1.08 for transfer from water to wet octanol is known [15] so that $\log K_s = 0.989$ through Eq. (2). Bruno et al. [16] have determined Kovats retention indices, I , for numerous halocarbons, including chlorodifluoro-methane and 1,1,1,3,3,3-hexafluoropropane, on a hexafluoropropylene epoxide-modified carbon black at various temperatures. We used values of $I/1000$ so as not to weight the data unduly; they are in Table 2.

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