36) Discussion of the determination of Air-Water partition coefficient of PFBS from vapor pressure and water solubility

**Determination of the Air-Water Partition Coefficient of Perfluorobutane Sulfonate, potassium salt (PFBS) from its Vapor Pressure and Water Solubility**

**Introduction:**

The air-water partition coefficient ($K_{AW}$) is a unitless way of expressing the Henry's law constant (H) of a chemical substance. The Henry's law constant is the ratio of the concentration of a chemical in air to the concentration of the chemical in water phase at equilibrium. Values of H for a chemical vary with temperature, and H is usually measured at 25°C. H can have a variety of units because different units are often used to measure the concentration in the air and the concentration in the water. The air-water partition coefficient, or unitless Henry's law concentration is obtained when the same units, e.g., mol/$m^3$, are used for both the concentration in air and in water. Thus, the units cancel in the air concentration to water concentration ratio.

The most common way of expressing the Henry's Law constant is as the pressure of the chemical in air, e.g. in units of Pascals, Pa, divided by the concentration of the chemical is water, e.g., in moles/$m^3$. The ratio thus has units, such as, Pa·$m^3$/mol, which are the preferred SI units for Henry's law constant. Since the Henry's Law constant is independent of the water concentration, it can be measured at the water solubility or at a fraction of the water solubility. When H is measured at the water solubility (S) of the chemical, the equilibrium concentration in the air is the vapor pressure (VP) of the chemical. Thus, one can determine the Henry's law constant for a compound from its vapor pressure and solubility.

**Calculations:**

Measurements have been made of the vapor pressure and water solubility of PFBS at 20°C. The Henry's law constant of a compound is equal to its vapor pressure divided by its water solubility. Thus:

$$H = VP/S \qquad (1)$$

The Pascal (Pa) is a unit of pressure P, and the gas law states:

$$P = nRT/V = (n/V)\,RT \qquad (2)$$

P is pressure, n is the number of moles, R is the gas constant, T is the absolute temperature, and V is volume. If P is in Pascals and the water concentration (n/V) is in units of moles/$m^3$, then R, the gas constant has a value and units of 8.314 Pa·m3/mol·K, and T, the temperature is measured in degrees Kelvin.

From equation 2, the equilibrium pressure in air over the concentration in water (H) can be expressed as:

$$H = ((n/V)_{air}\,RT)/(n/V)_{water} \qquad (3)$$

We also know from the definition of $K_{AW}$ that:

$K_{AW} = (n/V)_{air} / (n/V)_{water}$ (4)

Combining equations 3 and 4, one can convert from H measured as $Pa \cdot m^3/mol$ to $K_{AW}$ as follows:

$K_{AW} = H/RT$ (5)

The vapor pressure of PFBS has been determined to be $< 1.22 \times 10^{-5}$ Pa at 20°C.(1) The Water solubility of PFBS has been determined to be 46.2 g/L at 20 °C.(2) With a MW of 338.2, this water solubility is equivalent to 0.137 mol/L or 137 $mol/m^3$.

Substitution of these solubility and vapor pressure values into equation (1) yields the Henry's law constant of PFBS at 20°C:

$H < 1.22 \times 10^{-5}/137$ $Pa \cdot m^3/mol$ (6)

$H < 8.91 \times 10^{-8}$ $Pa \cdot m^3/mol$ (7)

Substitution of this H value, the gas constant in units of Pa·m3/mol·K, and the temperature (20°C = 293°K) into equation (5) enables calculation of the air-water partition coefficient at 20°C:

$K_{AW} = H/RT < (8.91 \times 10^{-8}$ Pa·m3/mol)/(8.314 Pa·m3/mol·K)(293 K) (8)

**$K_{AW} < 3.65562 \times 10^{-11}$ (unitless)** (9)

$\log K_{AW} < -10.4$ (10)

Put another way, this means that at equilibrium with air greater than 99.999999996% *is* in the water phase.

References:

1. Lezotte FJ, Van Hoven RL, Nixon WP, Determination of the Vapor Pressure of Perfluorobutanesulfonate, Potassium Salt (PFBS) Using the Spinning Rotor Guage Method, Wildlife International, Ltd. Project Number 454C-127, April 29, 2002

2. Van Hoven RL, MacGregor JA, Nixon WP, Determination of the Water Solubility of Perfluorobutane Sulfonate, Potassium Salt (PFBS) by the shake Flask Method.

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