Henry's Law Constant for C-8 in Water

Henry's Law for a component in water is a useful approximation of the partial pressure of that component above a specified composition in aqueous solution. In its most general form, the equation that defines Henry's Law is

$$f_1 = H_1 * x_1$$

where

f_1 = Pure component fugacity of component 1
H_1 = Henry's Law Constant for component 1
x_1 = Liquid phase mole fraction of component 1

Henry's Law is fundamentally valid only as $x_1 \rightarrow 0$ and for ideal solutions, but is commonly used as an approximation tool at low concentrations.

Given the equation above, the Henry's Law constant can be calculated from the knowledge of the pure component fugacity and liquid composition. For the case of C-8, we can readily estimate the Henry's Law constant from the knowledge of the pure component vapor pressure and the aqueous phase mole fraction at saturation. The fact that C-8 forms micelles (which are essentially equivalent to a second liquid phase) makes the application of Henry's Law more valid than in other cases since the pure component vapor pressure is the actual vapor pressure exerted by the C-8 in solution (assuming pH < pKa; see subsequent discussion).

The Henry's Law constant for C-8 is estimated as follows:

$$H_{C-8} = \frac{v.p. = f(T)}{Solu = f(T)}$$

$$\boxed{H_{C-8} = \exp\left\{-22.86 + 9444.3/TC^5\right\}}$$

where

TC = temperature in Centigrade, and
H_{C-8} = Henry's Law constant in atm-m^3/gmole.

The Henry's Law constant is documented in the open literature with many different units, generally the units are "atm-m^3/gmole". The exact units chosen for the Henry's Law constant are not important, so long as the units are conserved when applying the constant within the Henry's Law equation.

Henry's Law Constant for C-8 in Water as a Function of pH

The standard application of Henry's Law involves the volatilization of a sparingly soluble component from an aqueous phase. For components such as Methane (CH_4), Oxygen (O_2), or Benzene (C_6H_6), which are non-electrolytes, the application of Henry's Law is straight-forward in that the Henry's Law constant is essentially only a function of temperature. For other components, specifically those components that undergo reaction with or in water to form other dissociated or hydrolyzed compounds, the Henry's Law constant is, in fact, also a function of pH in the solution. Examples of this phenomenon include

$$\text{Acetic Acid} = H^+ + \text{Acetate}^-$$
$$H_2S = H^+ + HS^-$$
$$CO_2 + H_2O = H^+ + HCO_3^-$$

Ions are not volatile from aqueous solutions within normal temperature ranges (at temperatures less than the critical point of water). Therefore, if the component in question exists as an ion in solution, the Henry's Law constant will still be valid, but the mole fraction of component will be the mole fraction of the un-dissociated molecular species in solution, not the total concentration. The mole fraction of un-dissociated compound can be calculated from the dissociation constant, and for the general reaction

$$\text{Salt} = \text{Cation}^+ + \text{Anion}^-$$

is expressed as

$$K_I = \frac{[Cation^+] * [Anion^-]}{[Salt]}$$

K_I is a thermodynamic property which is a function of the components and temperature.

For C-8, $K_I = 4570$, so up to the point of saturation (where a second phase of un-dissociated C-8 exists) only a very small fraction of the C-8 in aqueous solution will be available for volatilization.