VOLATILIZATION OF KETONES FROM WATER

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Abstract. The overall mass-transfer coefficients for the volatilization from water of acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone were measured simultaneously with the oxygen-absorption coefficient in a laboratory stirred water bath. The liquid-film and gas-film coefficients of the two-film model were determined for the ketones from the overall coefficients, and both film resistances were important for volatilization of the ketones.

The liquid-film coefficients for the ketones varied with the 0.719 power of the molecular-diffusion coefficient, in agreement with the literature. The liquid-film coefficients showed a variable dependence on molecular weight, with the dependence ranging from the $-0.263$ power for acetone to the $-0.378$ power for 2-octanone. This is in contrast with the literature where a constant $-0.500$ power dependence on the molecular weight is assumed.

The gas-film coefficients for the ketones showed no dependence on molecular weight, in contrast with the literature where a $-0.500$ power is assumed.

1. Introduction

Volatilization is one of the physical processes of importance in determining the fate of many organics occurring in streams and rivers. There have been experimental studies of the volatilization process, for example, Dilling et al. (1975) and Dilling (1977), and theoretical studies, for example, Mackay and Wolkoff (1973) and Mackay and Leinonen (1975). These studies have generally been limited to low-solubility organics.

However, several classes of organics, for example, the ketones, have members with large solubilities, and these are expected to have volatilization characteristics different from those of slightly soluble organics (Mackay and Yuen, 1979). Ketones, moreover, are widely used and have been found in various types of waters. Acetone, 2-butanone, and 4-methyl-2-pentanone were among the 34 large-volume industrial solvents considered by Lee et al. (1979). They also concluded that 4-methyl-2-pentanone was one of the 12 solvents having a potentially high risk to man. A number of ketones have been found in a drinking water supply (Coleman et al., 1980). Ketones have also been found in natural water samples (Nowicki et al., 1979) and in the water effluents from procedures used in the processing of oil shale (Pellizzari et al., 1979). The environmental significance of acetone and 2-butanone was discussed by Tai (1978). Biological effects of many ketones have been summarized by Verschueren (1977). To predict adequately the fate of ketones in the waters of our environment requires a knowledge of their volatilization characteristics.

This report describes a laboratory study of the volatilization characteristics of acetone, 2-butanone, 2-pentanone, 3-pentanone, 4-methyl-2-pentanone, 2-heptanone, and 2-octanone. Oxygen-absorption coefficients were measured simultaneously with the measurement of the ketone volatilization coefficients.
2. Theoretical Considerations

The volatilization of organic solutes from water is usually described by the two-film model of Lewis and Whitman (1924). This model assumes that the solute is uniformly mixed in the water and air phases, except near the interface where thin films of water and air exist in which mass transport is by molecular diffusion. Steady-state conditions are assumed so that the mass fluxes through the films are equal. This is a very simplified model of the volatilization process, but it has been widely used. Details of the model have been presented by several researchers, for example, Liss and Slater (1974) and Mackay and Cohen (1976).

The basic equation of the two-film model is

\[
\frac{1}{K_L} = \frac{1}{k_L} + \frac{RT}{Hk_G}
\]

where \( K_L \) is the overall mass-transfer coefficient based on the liquid phase in meters per day; \( k_L \) and \( k_G \) are the liquid-film and gas-film mass-transfer coefficients, respectively, in meters per day; \( R \) is the gas constant in standard atmospheres cubic meter per (gram mole Kelvin); \( H \) is the Henry's Law constant in standard atmospheres cubic meter per (gram mole); and \( T \) is the temperature in Kelvin.

Because the reciprocal of a transfer coefficient is the resistance to mass transport, the first term on the right-hand side of Equation (1) is the resistance in the liquid film, \( r_L \), and the second term is the resistance in the gas film, \( r_G \). The left-hand side is, therefore, the overall resistance to mass transport, \( r_T \). In equation form

\[
r_T = r_L + r_G
\]

where

\[
r_T = \frac{1}{K_L}
\]

\[
r_L = \frac{1}{k_L}
\]

and

\[
r_G = \frac{RT}{Hk_G}.
\]

Application of Equation (1) for two limiting cases provides insight into the volatilization process. For solutes with large Henry's Law constants, as is true for slightly soluble organics, it follows from Equation (1) that \( K_L \) is approximately equal to \( k_L \). Thus, the resistance in the liquid film dominates for these solutes. Conversely, for solutes with small Henry's Law constants, as is true for very soluble organics, it follows from Equation (1) that \( 1/K_L \) is approximately equal to \( RT/Hk_G \). Thus, the resistance in the gas film dominates for these solutes. For compounds with intermediate values of the Henry's Law constant, both resistances are important.

Mackay et al. (1979) have shown for dilute aqueous solutions that the Henry's Law constant in Equation (1) can be calculated from