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Equilibrium Partitioning of Polycyclic Aromatic Hydrocarbons from Coal Tar into Water

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■ Partitioning of several polycyclic aromatic hydrocarbons (PAHs) from eight coal tar samples into water was measured. The measured partition coefficients were used to evaluate a model derived using Raoult's law convention for activity coefficients and hypothetical supercooled liquid solubilities. Our analysis suggests that the extent of deviations from "ideal" behavior for coal tar–water partitioning is sufficiently small, similar to earlier reports for gasoline–water and diesel–water partitioning of PAHs. The concentrations of PAHs in groundwater in equilibrium with these complex wastes, estimated from the model presented, may be considered as a reasonable approximation for most field-scale applications. The likely reasons for deviations from the ideal behavior are discussed, as are sources of analytical and computational errors.

Introduction

In the late 1800s and early 1900s, gas was manufactured from coal and oil for residential, commercial, and industrial uses. Manufactured gas plants (MGPs) were present in most major cities throughout the United States. The gas manufacturing plants generated a variety of process wastes such as tars, spent oxides, ash, sludge, ammonia liquors, and lampblack. The wastes generated from various methods of gas production were similar; however, the specific type and quantity of waste contamination at a given MGP site would be dependent on the feedstock used, the manufacturing process employed, and the time period over which the plant was in operation. In many cases, the wastes were left on-site in pits or containers, placed in nearby ponds or lagoons, or taken to off-site areas for land disposal. Such practices resulted in contamination of soils and groundwater at most former MGP sites.

Coal tars make up a large portion of the hydrocarbon wastes generated at MGP sites. Eng and Menzies (1) reported that more than 11 billion gallons of coal tar was generated in the United States during the period 1816–1947, but the disposition of several billion gallons is unknown and remains unaccounted. Coal tars are complex mixtures of a large number of hydrocarbons spanning a broad spectrum of molecular weights, with the concentrations of individual constituents varying significantly from one MGP site to another. The coal tar constituents of specific interest in this study are the polycyclic aromatic hydrocarbons (PAHs). These compounds have been detected at former MGP sites and are of particular concern due to their potential carcinogenic nature (2). Several of these compounds have already been included on the U.S. EPA list of priority pollutants.

Near the source of contamination (presence of separate organic phase) at a coal tar disposal site, one of the primary processes controlling the release of organic chemicals is solubility. In the past, it has often been assumed that organic contaminant concentrations in the aqueous phase leaving a coal tar source would be equal to their corresponding pure compound aqueous solubilities. This may be a reasonable estimate if the source of interest was composed of a single contaminant; however, most complex wastes (e.g., coal tar, diesel, and gasoline) consist of mixtures of contaminants. These mixtures may be considered complex on the basis of the number of chemicals that constitute the mixture. On the other hand, complexity of a mixture can be defined by considering how the properties of the mixture deviate from some "ideal" behavior, regardless of the number of components. The former view corresponds to a mixture being *complex in composition*, whereas the latter implies *complexity in behavior*. The important point is that a mixture can be complex in composition without being complex in behavior and vice versa.

The properties of an organic mixture complex only in composition are determined by the properties of its pure components and their concentrations in the mixture. This implies that the chemicals of interest behave ideally in the matrix containing them. Under these conditions, the concentration of a chemical in the aqueous phase is proportional to the mole fraction of the chemical in the organic phase corresponding to Raoult's law. With the stated assumptions, the concentrations of a chemical in the aqueous phase in contact with a complex mixture can be predicted using the following simplified expression based on Raoult's law (3, 4):

$$C_w = x_o S_l \qquad (1)$$

where C_w is the chemical's concentration in the aqueous phase (mol/L) in equilibrium with the organic phase, S_l is the aqueous solubility of the pure liquid chemical (mol/L), and x_o is the mole fraction of the chemical in the organic phase. For compounds that are solid in their standard state, the hypothetical supercooled liquid solubility (S_l) should be used (3). The applicability of Raoult's law has been shown for several mixtures of organic chemicals, including gasoline (4) and diesel fuel (3), for predicting aqueous-phase concentrations.