



Dissolution of multi-component LNAPL gasolines: The effects of weathering and composition



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ABSTRACT

The composition of light non-aqueous phase liquid (LNAPL) gasoline and other petroleum products changes profoundly over their life once released into aquifers. However limited attention has been given to how such changes affect key parameters such as the activity coefficients which control partitioning of components of petroleum fuel into groundwater and are used to predict long-term risk from fuel releases. Laboratory experiments were conducted on a range of fresh, weathered and synthetic gasoline mixtures designed to mimic the expected changes in composition in an aquifer. Weathered gasoline created under controlled evaporation and water washing, and naturally weathered gasoline, were investigated. Equilibrium concentrations in water and molar fractions in the gasoline mixtures were compared with equilibrium concentrations predicted by Raoult's law assuming ideal behaviour of the solutions. The experiments carried out allowed the relative sensitivity of the activity coefficients of key risk drivers such as benzene, toluene, ethylbenzene and xylene (BTEX) compounds to be quantified with respect to the presence of other types of compounds and where the source LNAPL had undergone different types of weathering. Results differed for the mixtures examined but in some cases higher than predicted dissolved equilibrium concentrations showed non-ideal behaviour for toluene, benzene and xylenes. Comparison of the activity coefficients showed that the naturally weathered gasoline and a 50% evaporated unleaded gasoline present a similar range of values varying between 1.0 and 1.2, suggesting close to ideal partitioning between the LNAPL and water. The fresh and water-washed gasoline had higher values for the activity coefficient, from 1.2 to 1.4, indicating non-ideal partitioning. Results from synthetic mixtures demonstrated that these differences could be due to the different molar fractions of the nC5 and nC6 aliphatic hydrocarbons acting on the molecular interactions, while differences in molar volumes seemed to have less of an influence on ideality.

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1. Introduction

Groundwater contamination by petroleum fuels present as light non-aqueous phase liquids (LNAPLs) is a common environmental problem especially due to the widespread use and storage of fuels in urban and industrial areas. The

relatively low solubilities of the constituent components of petroleum fuels in groundwater mean that chemicals of concern may pose an ongoing and long-term risk to groundwater and receiving environments (Davis et al., 1993, 1999; Peter et al., 2008). Dissolution rates of NAPL contaminants in soils and aquifers depend on a range of factors such as the properties of the organic phase constituents; the NAPL distribution, its saturation and interfacial area; and the hydrodynamic conditions of the porous medium including

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its morphology, its flow through rates and relative permeability variations (Cho et al., 2005; Chrysikopoulos and Kim, 2000; Geller and Hunt, 1993; Imhoff et al., 1993; Miller et al., 1990; Nambi and Powers, 2000; Oostrom et al., 2005; Powers et al., 1998). A key point of interest has been the conditions under which partitioning between the non-aqueous and aqueous phases (i.e. dissolution) may be considered to be an equilibrium process. For single component NAPLs, both non-equilibrium and local equilibrium approaches have been used in numerical modelling of dissolution and mass transfer processes in groundwater systems (Geller and Hunt, 1993; Kim and Chrysikopoulos, 1999; Nambi and Powers, 2003; Oostrom et al., 2003; Parker and Park, 2004; Tiruta-Barna et al., 2006).

In multi-component systems, the dissolution process additionally depends on the relative abundance and interactions between components in the non-aqueous and aqueous phases. These interactions are generally taken into account through Raoult's law in models of transport and mass transfer in porous media (Corapcioglu and Baehr, 1987). In this approach, interactions between components are parameterised by an activity coefficient. While the apparent solubilities of pure compounds can be estimated from batch experiments, molar fractions and activity coefficients remain difficult to quantify accurately for complex and non-ideal mixtures. In fuels, this is due to the preponderance of small molar fractions of numerous compounds that defy measurement and the temporal variations of the molar fractions during weathering processes (Khachikian and Harmon, 2000; Lang et al., 2009; Mukherji et al., 1997). Previous experimental studies of dissolution involving complex mixtures (Eberhardt and Grathwohl, 2002; Schluep et al., 2002) focused on PAHs (polynuclear aromatic hydrocarbons) or BTEX (benzene, toluene, ethylbenzene, xylene). They assumed the mixture to be ideal if the difference between measured concentrations of the main compounds and the theoretical equilibrium concentrations was less than a factor 2. Deviations from unity were considered to be uncertainties in the input molar fractions and solubilities used in Raoult's law (Liu et al., 2013). However, an assumption of ideal behaviour when applying Raoult's law in the presence of a mixture of aliphatic and aromatic hydrocarbons can contribute to appreciable errors in estimates of the total amount of the dissolved compounds in water and the mass transfer coefficients (Cline et al., 1991; Lee et al., 1992). Recent work (Liu et al., 2012) carried out on complex synthetic mixtures has confirmed that the assumption of ideal behaviour of mixtures may not hold and that numerical modelling needs to incorporate variable activity coefficients according to the composition of the mixture. Hence, accurate characterization of the response of molar fractions and activity coefficients for natural mixtures is needed in numerical models of multi-component dissolution and biodegradation (Colombani et al., 2009; Franzmann et al., 1999; Prommer et al., 1999) in the context of predicting the on-going contamination of groundwater by petroleum fuels such as gasoline. This is especially so where weathering processes change the NAPL composition, molar fractions and, potentially, activity coefficients over long periods.

This work focuses on the dissolution of BTEX and isomers of trimethylbenzene (TMB) into groundwater from gasoline

and other NAPL mixtures. Small-scale batch experiments were performed to measure the resulting equilibrium concentrations and molar fractions of BTEX in water and NAPL. For some experiments, the NAPL was altered due to various natural and purposeful (artificial) weathering. Additional experiments were conducted using artificial mixtures of hydrocarbons to further elucidate those factors controlling activity coefficients and deviation from ideal partitioning. Results obtained from artificial mixtures were compared to values produced with the UNIFAC model (Randhol and Engelen, 2000). For the first time, we provide the data that describe the variations from ideal behaviour and correlate that to the type of weathering (water washing or volatilisation) undergone by a gasoline. This is critical to the long term behaviour of a fuel release which commonly resides across the capillary zone and undergoes variable weathering leading to changes in its composition and risk profile.

2. Theory

Commonly petroleum NAPLs are complex mixtures of a variety of chemicals. If the interactions between the compounds in the aqueous phase are negligible, the equilibrium concentration of each individual constituent in a liquid complex mixture in contact with a water phase can be expressed by Raoult's law (Banerjee, 1984):

$$C_i^w = \gamma_i^n \chi_i^n S_i^w \quad (1)$$

where C_i^w [mg/L] is the equilibrium concentration and S_i^w [mg/L] is the solubility in water of the pure compound i , and χ_i^n and γ_i^n are respectively the molar fraction and the activity coefficient in the NAPL phase of the considered compound i . Equilibrium concentrations depend on the chemical properties of the constituents and the initial molar fractions of the mixture which act on the dissolution behaviour. Lower molar fractions χ_i^n in the NAPL phase contribute to relatively lower C_i^w in the aqueous phase (Liu et al., 2009). The preferential dissolution of the most soluble compounds tends to increase the molar fractions in the NAPL of the lower solubility compounds. Hence, temporal changes of the equilibrium concentration are challenging to predict, not only because of the evolution of the NAPL phase and its varying chemical composition but also due to complexity of the hydrodynamic properties of the medium. Gasoline can be particularly affected by significant changes in the mean molar mass due to the loss of the lighter compounds (Schluep et al., 2002). The activity coefficient γ_i^n expresses the excess Gibbs free energy produced by electrostatic interactions in non-ideal situations between the molecules in the NAPL phase. In complex systems, $\gamma_i^n > 1$, the compatibility between molecules i and the other constituents is considered to be less than between the molecules of the compound i . The reverse is the situation for $\gamma_i^n < 1$. When the NAPL phase is assumed as ideal ($\gamma_i^n = 1$), it implies that the molecular interactions with constituents in the NAPL phase are the same as in the presence of the pure compound. Previous studies highlighted this assumption that holds for PAHs (Eberhardt and Grathwohl, 2002; Liu et al., 2012; Mukherji et al., 1997), which is not necessarily the case for other complex mixtures. For instance, the aqueous

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