



## Effect of compositional heterogeneity on dissolution of non-ideal LNAPL mixtures



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### ARTICLE INFO

#### Article history:

Received 3 December 2015

Received in revised form 9 September 2016

Accepted 17 September 2016

Available online 20 September 2016

#### Keywords:

Activity coefficient

Effective solubility

Multicomponent dissolution

Non-ideal

Non-aqueous phase liquid

UNIFAC

### ABSTRACT

The extent of dissolution of petroleum hydrocarbon fuels into groundwater depends greatly on fuel composition. Petroleum fuels can consist of thousands of compounds creating different interactions within the non-aqueous phase liquid (NAPL), thereby affecting the relative dissolution of the components and hence a groundwater plume's composition over long periods. Laboratory experiments were conducted to study the variability in the effective solubilities and activity coefficients for common constituents of gasoline fuels (benzene, toluene, *p*-xylene and 1,2,4-trimethylbenzene) (BTX) in matrices with an extreme range of molar volumes and chemical affinities. Four synthetic mixtures were investigated comprising BTX with the bulk of the NAPL mixtures made up of either, ethylbenzene (an aromatic like BTX with similar molar volume); 1,3,5-trimethylbenzene (an aromatic with a greater molar volume); *n*-hexane (an aliphatic with a low molar volume); and *n*-decane (an aliphatic with a high molar volume). Equilibrium solubility values for the constituents were under-predicted by Raoult's law by up to 30% (higher experimental concentrations) for the mixture with *n*-hexane as a filler and over-predicted by up to 12% (lower experimental concentrations) for the aromatic mixtures with ethylbenzene and 1,3,5-trimethylbenzene as fillers. Application of PP-LFER (poly-parameter linear free energy relationship) model for non-ideal mixtures also resulted in poor correlation between experimentally measured and predicted concentrations, indicating that differences in chemical affinities can be the major cause of deviation from ideal behavior. Synthetic mixtures were compared with the dissolution behavior of fresh and naturally weathered unleaded gasoline. The presence of lighter aliphatic components in the gasoline had a profound effect on estimating effective solubility due to chemical affinity differences (estimated at 0.0055 per percentage increase in the molar proportion of aliphatic) as well as reduced molar volumes (estimated at  $-0.0091$  in the activity coefficient per unit increase in molar volume, mL/mol). Previously measured changes in activity coefficients due to natural weathering of 0.25 compares well to 0.27 calculated here based on changes in the chemical affinity and molar volumes. The study suggests that the initial estimation of the composition of a fuel is crucial in evaluating dissolution processes due to ideal and non-ideal dissolution, and in predicting long term dissolution trends and the longevity of NAPL petroleum plume risks.

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### 1. Introduction

Non-aqueous phase liquid (NAPL) in groundwater environments can remain a source of exposure and risk for decades to centuries and entrain significant management costs (Davis et al., 1999; Frind et al., 1999;

Clement et al., 2004). Where a NAPL source is a complex mixture such as a petroleum fuel, the efficacy of remediation strategies and understanding over the long-term of groundwater plumes can be confounded by the necessity to account for multi-component partitioning, where the NAPL composition changes over time. A Raoult's law-based approach has been successfully applied to predict effective solubility under ideal equilibrium dissolution conditions (Feenstra, 1997; McCray and Dugan, 2002; Tien et al., 2015). According to Raoult's law, the equilibrium concentration of a component in the aqueous phase can be obtained by multiplying the pure aqueous solubility of the component with its mole

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fraction in the non-aqueous phase. However, such an approach can be difficult to apply in the case of gasoline and other petroleum fuels, because the sheer number of compounds (perhaps 1000 s) which make quantification of the molar fractions, on which the Raoult's law-based approach is based, problematic (Garg and Rixey, 1999; Russo et al., 2009; Liu et al., 2012; Vasudevan et al., 2016). Further, partitioning behavior may range from ideal to non-ideal depending on particular compositions as observed when NAPL 'weathers' in the subsurface. As a result, the activity coefficients describing the partitioning will vary (Lekmine et al., 2014). Deviations from ideal behavior (activity coefficients deviating from unity) arise from various sources, including chemical heterogeneity of the components of the mixture and the molar volumes, which are not incorporated into the common application of Raoult's law (Lekmine et al., 2014). Non-ideal dissolution is found to be predominant for compounds having low NAPL phase mole fractions, especially when the compounds co-exist with many dissimilar compounds having significant differences from the average characteristics of the mixture (McCray and Dugan, 2002; Padgett et al., 2014).

The accurate estimation of equilibrium partitioning processes is pivotal to quantifying the fate and transport of spilled gasoline compounds in the subsurface especially the transition from 'fresh' newly released fuels to a highly weathered and degraded state. Difficulties in sampling from fuel-spill sites and in estimating partitioning coefficients through laboratory experiments, have promoted the practice of using systemic or empirical relations for the prediction of partitioning constants. However, predictions of effective solubility based on Raoult's law have resulted in apparent deviations of 10% to 30% for structurally similar mixtures, and by about 25% to 50% for mixtures of aliphatic and aromatic compounds from their ideal concentrations (Feenstra, 1997). More recently, Lekmine et al. (2014) showed deviations up to 41% for a mixture representative of fresh gasoline. Due to the variability in physical and chemical properties of the components in a real fuel, the assumptions inherent in applying Raoult's law result in over-estimation or under-estimation of the true effective solubility for low solubility fractions in a mixture (Feenstra, 1997). Most modeling studies have been restricted to ideal mixtures, by assuming the activity coefficient to be unity, and therefore are not able to predict the variability in equilibrium dissolution as composition changes (Hansen and Kueper, 2007). The activity coefficients of non-electrolyte liquid mixtures estimated by the UNIFAC (Universal quasi Functional group Activity Coefficient) model have been accepted as reliable since the model reflected the size and surface area of individual functional groups and their energetic interactions between groups (Fredenslund et al., 1975; Chrysikopoulos and Lee, 1998). Being a semi-empirical approach, it has been found to be advantageous in estimating the aqueous phase solubility of NAPL (Broholm and Feenstra, 1995; Chrysikopoulos and Lee, 1998) as well as activity coefficients in multi-component systems (Wang et al., 1998; Peters et al., 1999). In their study, Lekmine et al. (2014) found deviations up to around 10% in UNIFAC predictions of activity coefficients for hydrocarbon mixtures. The PP-LFER (poly-parameter linear free energy relationship) model has also been used to predict and understand partitioning processes based on the molecular level interactions (Goss and Schwarzenbach, 2001; Chiou et al., 2005; Chen et al., 2008; Endo and Goss, 2014).

The study reported in this paper, follows on from Lekmine et al. (2014). They concluded that variations in activity coefficients (non-ideal behavior) could be due to differences in molar volumes and chemical affinities (proportion of aromatic and aliphatic hydrocarbons, especially changes in the proportion of C5 and C6 alkane components) in the mixtures they studied. Their study was primarily aimed at possible differences in the partitioning behavior of fresh and weathered fuels and they observed differences that could be attributed to differences in the chemical affinities (aliphatic and aromatic content) and molar volumes. However, they did not explicitly nor definitively ascertain the cause of non-ideal behavior in terms of differences in molar volumes of the chemicals present, or other chemical attributes such as the possible molecular interactions between aliphatic and aromatic compounds.

In this paper, we report the results of experiments to compare the ideal/non-ideal partitioning behavior of the aromatic compounds (benzene and alkylated benzenes) as key risk-drivers and components of gasoline fuel, in the presence of somewhat extreme choices of single filler compounds to provide definitive trends and outcomes in the dissolution behavior. Four types of synthetic mixtures were prepared, with benzene, toluene, *p*-xylene and 1,2,4-trimethylbenzene (referred to as BTX hereafter) being the base constituents representative of gasoline fuel. The bulk of the NAPL mixture was made up individually of ethylbenzene (being an aromatic compound with a similar molar volume to the BTX), 1,3,5-trimethylbenzene (with increased alkyl interactions and a greater molar volume than the BTX), *n*-hexane (having a lower molar volume) or *n*-decane (having a higher molar volume) as fillers. As indicated, these were chosen to impart different and potentially enhanced (or extreme) interactions within the NAPL and thereby allow differentiation of the effects of the types of compounds during the dissolution process. The aim was to provide insight into the primary reasons for non-ideal behavior during dissolution of gasoline type spills, so that more comprehensive and accurate models of petroleum NAPL dissolution (e.g., Prommer et al., 1999) could be developed and applied to spill releases.

## 2. Experimental methods

### 2.1. Preparation of synthetic mixtures

The four synthetic mixtures tested are shown in Table 1. Benzene, toluene, *p*-xylene and 1,2,4-trimethylbenzene (BTX) were the common base constituents with similar percentage weights in each mixture. The bulk of the NAPL mixture was made up individually of *n*-decane (*n*C10) for the first mixture (M1), *n*-hexane (*n*C6) for the second mixture (M2), ethylbenzene for the third mixture (M3), and 1,3,5-trimethylbenzene (1,3,5-TMB) for the fourth mixture (M4). The general composition was kept similar to the synthetic ideal and non-ideal mixtures of Lekmine et al. (2014) while the filler compounds were altered according to their potential characteristics for non-ideal dissolution.

The alkanes *n*C6 and *n*C10 were selected as bulk filler options for the M1 and M2 NAPL mixtures respectively to investigate the potential non-ideal behavior of BTX dissolution in the presence of aliphatic compounds having different molar volumes (131.3 mL/mol for *n*C6 and 194.5 mL/mol for *n*C10). The mixture M1 also is representative of the changes that can occur due to weathering (loss of lighter alkanes). Additionally, it may represent less refined gasoline products (older leaded gasoline) which had a higher aliphatic content and molecular weight composition.

Ethylbenzene (Eb) was selected as a bulk filler option for the NAPL mixture M3 for its similarity in chemical (aromatic) and molar volume (122.3 mL/mol) characteristics to the BTX. Ethylbenzene was assumed to have similar properties to the other closely related alkylated benzene compounds (particularly xylene which has the same number of alkyl groups) and benzene.

1,3,5-TMB was selected as a bulk filler option for the NAPL mixture M4, because the additional number of alkyl groups on the benzene ring increases the molar volume (138.9 mL/mol) and represents increased alkyl interactions within the aromatics. This type of mixture would reflect changes to highly refined gasoline products (unleaded gasoline) due to weathering and losses of more volatile and water soluble components.

### 2.2. Batch equilibration experiments

Batch equilibration experiments were established to achieve equilibrium partitioning of the compounds between the NAPL mixture and the water phase by continuous slow stirring in sealed vials. A series of batch experiments were conducted in duplicate in 2 mL vials (with three replicates) which had a 1 mm outside diameter stainless steel

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