

UNIFAC MODELING OF MULTICOMPONENT NONAQUEOUS PHASE LIQUIDS
CONTAINING POLYCYCLIC AROMATIC HYDROCARBONS

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Abstract—Multicomponent nonaqueous phase liquid (NAPL) contaminants that are mixtures of polycyclic aromatic hydrocarbons (PAHs) are examined using UNIFAC. The NAPL phase activity coefficients for constituent compounds of four different coal tar materials are estimated. The group contribution approach is adapted to describe representative molecular structures of the uncharacterized fractions of the tar materials, determined from average molecular weights and nonparametric regressions of the functional group parameters against molecular weight. The molecular structure characterization of the tars elucidates the similar chemistry of the materials from different sites, despite their different chemical compositions. Nearly ideal behavior is predicted for most tar constituents, with the majority of activity coefficients in the range of 0.9 to 1.1. These results provide a firm theoretical basis for an assumption of NAPL-phase ideality for many tar constituents. The robustness of this conclusion is indicated through comparable results across different tar materials and through a sensitivity analysis of the effect of the estimated characteristics of the uncharacterized fractions.

Keywords—Nonaqueous phase liquid Polycyclic aromatic hydrocarbons Coal tar UNIFAC Multicomponent

INTRODUCTION

Many nonaqueous phase liquid (NAPL) environmental contaminants are complex mixtures of organic compounds with no single predominant component. An example is coal tar, which primarily consists of polycyclic aromatic hydrocarbons (PAHs) [1]. One of the important parameters for prediction of aqueous solubility [2,3], and for prediction of NAPL-phase solidification due to aging [4] is the activity coefficient γ_i of constituent compounds in the NAPL phase. Assuming ideality in the NAPL phase ($\gamma_i = 1$) is valid if the constituent compounds are comprised of similar functional groups and if the components have similar size and shape. If the molecular interactions between NAPL component i and unlike molecules are not comparable to those in a fluid of pure i , then the excess enthalpy is nonzero. If the molecular arrangements (sizes and shapes) are not comparable to those in a fluid of pure i , then the excess entropy is nonzero. Because of its simplicity, the assumption of ideality is extremely attractive, and it is commonly assumed on the principle of chemical similarity alone. However, in coal tar NAPLs it is not clear whether significant excess entropies result from the size and shape variations represented by the range of constituent compounds, including monoaromatic compounds up to very large PAHs.

This paper presents a theoretical examination of NAPL solution ideality for complex mixtures of PAHs. The analysis involves application of the UNIFAC model to describe molecular structure characteristics of a variety of PAH-NAPLs, to predict enthalpic and entropic contributions to excess Gibbs energy, and to estimate activity coefficients for constituent compounds. The analysis was conducted for four tar contaminants from manufactured gas plant (MGP) sites for which composition and property data have been published. The the-

oretical predictions are then discussed in relation to published experimental findings related to coal tar phase equilibria.

METHODS

Tar materials

The composition and properties of a field sample of coal tar, obtained from the subsurface at the MGP site in Stroudsburg, Pennsylvania, USA, have been previously reported [2]. The number-average molecular weight was found to be 210. The mixture has numerous compounds, 43 of which have been identified and quantified. The Stroudsburg tar has a predominance of PAHs, negligible amount of monoaromatic hydrocarbons, and absence of acid-extractable organics (e.g., phenols), which is consistent with MGP facilities using the carburetted water gas process and anthracite coal. Three additional coal tars are those from sites 1, 4, and 5 in a study of the characteristics of MGP site tars [5]. Their number-average molecular weights are 250, 230, and 250, respectively. The MGP facilities at sites 1, 4, and 5 were primarily operated with carburetted water gas processes, although there were years when coal carbonization processes were also in place at sites 4 and 5.

UNIFAC modeling

In the UNIFAC group-contribution framework, each molecule is considered the sum of its functional groups, and the thermodynamic properties of the solution are computed in terms of the functional group properties. The activity coefficient is modeled as having a combinatorial (C) term and a residual (R) term, $\gamma_i = \gamma_i^C \gamma_i^R$, where γ_i^C is computed using molecular size and shape parameters describing the dominant entropic contributions and γ_i^R depends on interactions between functional groups capturing the enthalpic contributions. The utility of UNIFAC has previously been demonstrated for suc-

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cessful prediction of the solubility of large hydrophobic molecules such as PAHs in various organic liquids [6]. The original UNIFAC equations [7] were used for this work. The parameter database used is an updated set obtained from liquid-liquid equilibrium (LLE) data [8]. We chose to use LLE-derived parameters rather than vapor-liquid equilibrium (VLE)-derived parameters because the compounds of interest are high molecular weight compounds with low vapor pressures.

Uncharacterized fraction

The primary challenge in UNIFAC application to tar materials derives from the fact that the high molecular weight material not quantifiable by chromatographic analyses remains uncharacterized. We have derived a method of analysis that permits modeling of partially characterized NAPLs. The representative molecular structure of the uncharacterized fraction (UF) is inferred from the average molecular weight of the tar and nonparametric regressions of functional group characteristics against molecular weight. The number-average molecular weight (\bar{W}) is the sum of the constituent molecular weights (W_i) weighted by their mole fractions. This can be separated into two summations

$$\bar{W} = \sum_{CF} x_i W_i + \sum_{UF} x_i W_i \quad (1)$$

where the first summation is for compounds that have been quantified, the characterized fraction (CF), and the second summation is for compounds in the uncharacterized fraction (UF). Rewriting the second summation as $x_{UF} \bar{W}_{UF}$ defines $x_{UF} \equiv (1 - \sum_{CF} x_i)$ as the cumulative mole fraction of the UF and \bar{W}_{UF} as the average molecular weight of the UF. Equation 1 can then be rewritten as an expression for computation of \bar{W}_{UF} in terms of composition data for the characterized fraction and the mixture's average molecular weight.

A new UNIFAC parameter was defined to represent the fraction of compound i that comprises functional group m :

$$X_m^{(i)} \equiv \frac{v_m^{(i)}}{\sum_{m=1}^N v_m^{(i)}} \quad (2)$$

where $v_m^{(i)}$ is the number of groups of type m in the molecule of type i and N is the number of groups in the mixture. Values of $X_m^{(i)}$ were computed for the 57 known compounds in the tars. For each m , a nonparametric regression was performed on the $X_m^{(i)}$ versus W_i data. To estimate the overall molecular structure of the UF the regressions were interpolated or extrapolated to estimate the group fractions at the values of \bar{W}_{UF} for each of the four tars.

Sensitivity analysis

The molecular characteristics of the UF are the most uncertain parameters in this analysis because of the lack of a deterministic relationship between the values of $X_m^{(i)}$ and W_i and because of the potential for error in extrapolation of the regression. A sensitivity analysis was conducted to assess the effects of the values used for the functional group parameters of the UF on the predicted activity coefficients. This analysis was conducted for the Stroudsburg tar only.

RESULTS AND DISCUSSION

Functional group representations

A total of 14 functional groups, listed in Table 1, were found to represent the 57 compounds in the 4 tars. The mixture

Table 1. UNIFAC functional group representation of four manufactured gas plant tars and the overall group fractions in each tar

Group	X_m			
	Stroudsburg	Site 1	Site 4	Site 5
CH ₃	0.0056	2.2×10^{-4}	3.7×10^{-5}	3.2×10^{-4}
CH ₂	0	4.1×10^{-4}	4.5×10^{-5}	0
CH ₂ =CH	0	7.4×10^{-6}	1.3×10^{-4}	3.1×10^{-4}
ACH	0.621	0.584	0.622	0.563
AC	0.324	0.405	0.357	0.424
ACCH ₃	0.036	0.0066	0.018	0.0077
ACCH ₂	0.010	0.0039	8.1×10^{-4}	0.0013
ACCH	0.0028	1.0×10^{-4}	0.0021	0.0030
ACNH ₂	0	8.9×10^{-8}	0	4.3×10^{-7}
C ₃ H ₃ N	0	2.6×10^{-7}	9.0×10^{-8}	5.1×10^{-6}
C ₂ H ₃ N	0	3.3×10^{-6}	1.8×10^{-6}	1.0×10^{-6}
C ₄ S	0.00036	0	1.4×10^{-4}	2.2×10^{-4}
C-O	0	3.0×10^{-4}	8.4×10^{-5}	8.7×10^{-5}
CNH	0	8.6×10^{-5}	1.7×10^{-5}	1.3×10^{-5}

of compounds constituting the Stroudsburg tar is represented by only seven functional groups. The UNIFAC parameter X_m , denoting the fraction of the entire mixture that is made up of functional group m , is shown for each of the four tars in Table 1. This representation of the MGP tars highlights their similarities despite differences in composition. For all four tars, the most prominent groups are ACH, the aromatic carbon with a hydrogen, and AC, the aromatic carbon without a hydrogen. An example of a compound with only these two groups is naphthalene, with eight ACH and two AC. The next most prominent group is ACCH₃, the aromatic carbon with an attached methyl group. The remaining 11 groups are needed for only a few compounds each and thus represent small fractions of the mixtures.

UFs of the MGP tars

The mole fractions of the UF and the inferred \bar{W}_{UF} are shown in Table 2. For all four tars, the average molecular weights of the uncharacterized portions are well above the average molecular weights of the overall tar materials, indicating the very high molecular weight compounds that are present in these fractions.

For ACH, AC, and ACCH₃, the 57 values of $X_m^{(i)}$ are plotted against molecular weight in Figure 1. As expected for PAHs, the AC group increases with molecular weight, relative to the other groups, indicating a more condensed aromatic ring with increasing molecular weight. Estimation of $X_{ACH}^{(UF)}$ and $X_{AC}^{(UF)}$ were determined by extrapolation of the nonparametric regressions (solid curves). The remaining fraction was assumed to be due entirely to ACCH₃. The $X_m^{(UF)}$ values are shown in Table 2. Although it is not required for the UNIFAC analysis, we can conjecture what molecule might be representative of the UF. A PAH molecule with $W_i = 258$ (the \bar{W}_{UF} of Stroudsburg tar)

Table 2. Molecular structure characteristics of the uncharacterized fractions (UF) of the four tars

Tar	x_{UF}	\bar{W}_{UF}	X_m^{UF}		
			ACH	AC	ACCH ₃
Stroudsburg	0.436	258	0.606	0.377	0.017
Site 1	0.568	324	0.542	0.458	0
Site 4	0.716	262	0.602	0.384	0.014
Site 5	0.390	412	0.479	0.521	0

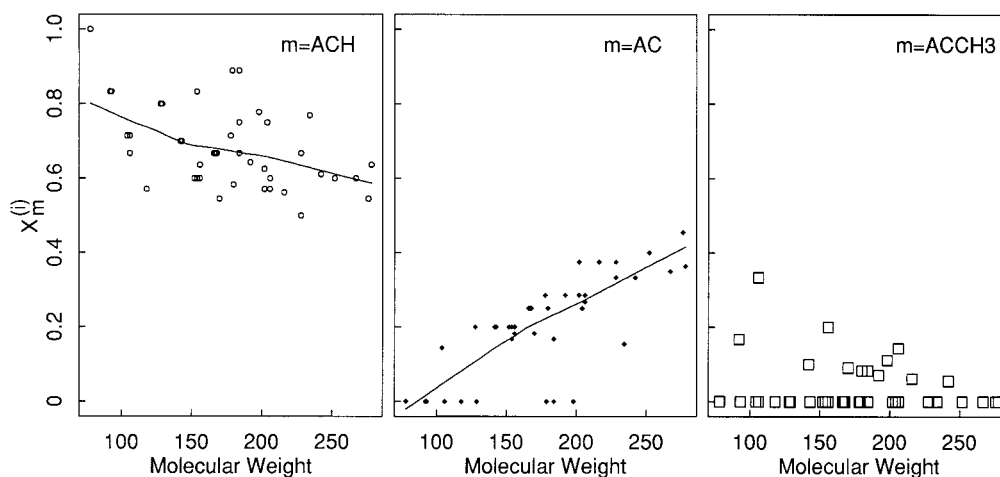


Fig. 1. Functional group fractions versus molecular weight for tar constituent compounds.

is likely to have 20 to 21 carbons because 258 is between the W_i s of benzo[a]pyrene ($C_{20}H_{12}$, $W = 252$) and picene ($C_{22}H_{14}$, $W = 278$). One compound with 21 carbons is dibenzofluorene, with $W_i = 266$. Its functional group representation is 60% ACH, 35% AC, and 5% $ACCH_2$, which is very similar to the regression results for the Stroudsburg UF.

Activity coefficient predictions

The UNIFAC-predicted NAPL phase activity coefficients are shown in Table 3. The predicted γ_i values for hydrocarbon compounds range from 0.81 for benzene (Stroudsburg and site 4) to 1.27 for ethylbenzene (site 5). Nearly ideal behavior is predicted for the majority of the compounds and especially for compounds whose molecular weights are nearer to the mixture average. This is consistent with experimental findings of Raoult's Law behavior for PAH constituents of coal tar and diesel fuel NAPLs [9–11] and for synthetic PAH-containing NAPLs [3]. Where there is deviation from ideality, whether it be slightly positive or negative, the deviations are largely attributable to deviations from unity in the combinatorial activity coefficients (not shown). A negative deviation in γ_i^c , which is predicted for benzene and naphthalene, suggests that these molecules have favorable size and shape characteristics in the mixture that result in excess solvation tendencies. Slight positive deviations from ideality result for ethyl PAHs and multialkylated PAHs, suggesting self-association tendencies.

Comparison across the four tars indicates that some compounds demonstrate consistent deviation from ideality. For example, benzene, naphthalene, and acenaphthene have consistently low γ_i values. Ethylbenzene, styrene, and the xylenes have consistently high γ_i values. Quinoline and acridine, present in small quantities in the site 1, 4, and 5 tars, have consistently low γ_i values of roughly 0.1 and 0.6, respectively. The deviations are due almost entirely to the γ_i^r values, predicting favorable interactions with the compounds in the mixture and thus excess solvation tendencies. Consistent negative deviations are also observed for 2-naphthylamine and carbazole, although to a lesser extent. Two of the other heterocyclic compounds, methyl dibenzothiophene and dibenzofuran, exhibit slight negative deviation from ideality.

It is interesting to note how these results differ from the conclusions drawn by Lee et al. [9] from a UNIFAC analysis of gasoline and diesel fuel. For gasoline, which is primarily composed of alkanes and monocyclic aromatic hydrocarbons,

it was observed that compounds with increasing aromaticity and that are solids in their pure form are predicted to have negative deviation from ideality. In contrast, for diesel fuel, which is largely aromatic but with as much as 56% naphthalenes, Lee et al. found that the largest PAH in the mixture, fluoranthene, demonstrated the largest deviation from ideality ($\gamma_i^N = 1.16$). For the tars analyzed here, the more aromatic, higher molecular weight PAHs demonstrated the least deviation from ideality. It is not surprising that a compound such as benzo[a]pyrene (60% ACH and 40% AC) is predicted to have nearly ideal behavior in tars because its molecular characteristics are similar to those of the overall mixtures. Conversely, benzene (100% ACH) and quinoline (80% ACH, 20% C_5H_3N) are quite different from the overall mixture and are predicted to deviate from ideality.

Sensitivity to values for UF

For each of the seven $X_m^{(UF)}$, found to represent the UF of the Stroudsburg tar, lower and upper bounds were estimated, based on regression statistics and on the standard deviations of the X_m^0 data sets. The set of upper and lower bounds, together with the constraint that $\sum X_m^{(UF)} = 1$, represents a six (i.e., $N - 1$) dimensional joint uncertainty region in which to select values for $X_m^{(UF)}$ to evaluate the sensitivity of UNIFAC model predictions. The number of extreme vertices, enumerated using the Crosier algorithm [12], was found to be 49, and the coordinates of these vertices were determined using the algorithm of McLean and Anderson [12]. Using these coordinates, 49 sets of UNIFAC predictions of γ_i^N for each of the 44 compounds in the Stroudsburg tar were generated. For each compound, the standard deviation of γ_i^N was computed. It was found that the mean standard deviation was 0.018, and the maximum standard deviation was 0.045. These values imply that uncertainty in the molecular structure of the UF contributes ~2% error in the UNIFAC estimates of γ_i^N and that this error is not likely to go above 5%.

CONCLUSIONS

This work has demonstrated the utility of the UNIFAC group contribution method to predict the NAPL-phase activity coefficients of compounds in a complex mixture such as coal tar by simplifying it to a small number of functional groups. The uncharacterized fractions of four tar materials were carefully represented in terms of average molecular structure prop-

Table 3. UNIFAC-predicted nonaqueous phase liquid activity coefficients^a

Compound	γ_i			
	Strouds-burg	Site 1	Site 4	Site 5
Benzene	0.81	0.82	0.81	0.85
Toluene	0.94	0.98	0.94	1.02
Ethylbenzene	—	1.21	1.13	1.27
<i>m</i> -, <i>p</i> -Xylenes	1.01	1.08	1.03	1.13
<i>o</i> -Xylene	1.01	1.08	1.03	1.13
Styrene	—	1.18	1.11	1.23
Indan	—	0.99	0.96	—
Naphthalene	0.93	0.94	0.93	0.97
Quinoline	—	0.14	0.15	0.14
1-Methylnaphthalene	0.99	1.04	1.00	1.07
2-Methylnaphthalene	0.99	1.04	1.00	1.07
2-Naphthylamine	—	0.85	—	0.88
Acenaphthylene	0.99	0.89	0.94	0.89
Biphenyl	1.01	—	—	—
Acenaphthene	0.95	0.93	0.93	0.95
2-Ethyl-naphthalene	1.06	—	—	—
1-Ethyl-naphthalene	1.06	—	—	—
2,6-Dimethylnaphthalene	1.02	—	—	—
9H-Fluorene	0.98	0.98	0.97	1.00
1H-Phenalene	0.98	—	—	—
Carbazole	—	0.94	0.96	0.95
Dibenzofuran	—	0.92	0.94	0.94
Trialkylated naphthalenes	1.12	—	—	—
Phenanthrene	0.98	1.00	0.99	1.03
Anthracene	0.98	1.00	0.99	1.03
Acridine	—	0.55	0.58	0.56
Methyl-9H-fluorenes	0.98	—	—	—
4-Methyl-1,1'-biphenyl	1.06	—	—	—
Dibenzothiophene	1.01	—	0.98	0.99
3-Methylphenanthrene	1.00	—	—	—
2-Methylphenanthrene	1.00	—	—	—
2-Methylanthracene	1.00	—	—	—
9-Methylphenanthrene	1.00	—	—	—
1-Methylphenanthrene	1.00	—	—	—
Methyldibenzothiophene	0.94	—	—	—
Fluoranthene	1.01	0.98	0.99	0.99
Aceanthrylene	1.09	—	—	—
Pyrene	1.01	0.98	0.99	0.99
1-Phenylnaphthalene	1.01	—	—	—
2-Phenylnaphthalene	1.01	—	—	—
9-Ethylphenanthrene	1.03	—	—	—
2-Ethylphenanthrene	1.03	—	—	—
Dimethylphenanthrene	1.00	—	—	—
Methylpyrene	1.00	—	—	—
Benzo[a]anthracene	1.00	1.02	1.00	1.04
Acepyrene	1.04	—	—	—
Chrysene	1.00	1.02	1.00	1.04
Triphenylene	1.00	—	—	—
Methylchrysenes	0.99	—	—	—
Benzo[b]fluoranthene	—	1.00	1.01	1.00
Benzo[k]fluoranthene	—	1.00	1.01	1.00
Benzo[a]pyrene	1.03	1.00	1.01	1.00
Dibenzo[c,g]carbazole	—	1.01	1.02	1.01
Indeno[1,2,3-cd]pyrene	—	1.01	1.05	1.00
Benzo[g,h,i]perylene	—	1.01	1.05	1.00
Dibenz[a,h]anthracene	—	1.00	0.98	1.01
Picene (278)	0.98	—	—	—
UF	1.00	0.99	1.00	0.97

^a Dashes are shown for compounds that were not detected in the composition analyses.

erties, permitting thermodynamic modeling despite the lack of complete composition data for very high molecular weight compounds. The ability to describe the entire mixture by its functional group representation provides a useful characterization of the mixture, and deviations from ideality are readily explained with respect to this baseline. Despite the differences in the tars, the functional group representations are quite similar, with roughly two thirds of the mixture represented by the ACH group and one third represented by the AC group. Because a compound's behavior is determined by its similarity with the overall characteristics of the mixture, this results in similar behavior for particular compounds across tars.

For the four tar materials studied, the UNIFAC-predicted NAPL-phase activity coefficients range from 0.14 to 1.27. In general, slight positive deviations were consistently predicted for PAHs with alkyl groups, and negative deviations were predicted for molecules much smaller than the average and for nitrogen containing compounds. The vast majority of the constituents are predicted to have activity coefficients between 0.9 and 1.1, implying that, for PAH-containing NAPLs such as coal tar, one can apply the Raoult's law simplification with confidence of roughly $\pm 10\%$.

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