Chemical Potential of Aromatic Compounds in Pure *n*-Alkanes Using Expanded Ensemble Monte Carlo Simulations

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The chemical potential of benzene and naphthalene in pure *n*-alkane fluids at infinite dilution (μ_{ex}^{∞}) is calculated using expanded ensemble Monte Carlo simulations. Simulations are carried out in an isobaric−isothermal ensemble at 1 atm pressure. The effect of temperature and carbon number of the solvent on μ_{ex}^{∞} is studied. The results indicate that, within the statistical uncertainty of the simulations, there is no strong dependence of the chemical potential of benzene and naphthalene on the carbon number of the solvent between C_6 and C_{24}. However, the chemical potential changes substantially with the temperature and the size of the solute. Good qualitative agreement is found between the simulation results and experiments.

1. Introduction

Knowledge of the chemical potential is important in many chemical processes such as phase separation and purification. For environmental pollutants, the chemical potential, which provides a measure of the solubility of a solute, is important in determining the fate and transport of pollutants in various media, such as air, particulates, and soil. The chemical potential can be obtained by measuring the activity coefficient by experiments, or by calculating it via equation of state or group contribution methods such as UNIFAC. Molecular simulations provide an alternative route for the calculation of the chemical potential, which can be very sensitive to fine structural details in the solute. Determining the chemical potential of aromatics by molecular simulation is notoriously difficult due to the large size and rigidity of these molecules. In this work, we demonstrate the use of Monte Carlo (MC) molecular simulations to calculate the chemical potential of aromatic compounds in organic liquids. Here we report results for relatively simple systems, benzene and naphthalene in pure *n*-alkanes (C_6−C_{24}). Benzene can be viewed as a building block for an important set of environmental pollutants, the polycyclic aromatic hydrocarbons (PAHs), while naphthalene is the smallest PAH compound. PAH compounds are formed during incomplete combustion processes and are present in different phases in the environment. *n*-Alkanes are representative of the oily organic phase associated with soils and airborne particulates. The method introduced here can be readily extended to more complicated combinations of solutes and mixed solvents without loss of rigor.

In Widom's particle insertion method,[1] the chemical potential is calculated by inserting a test particle into a simulation volume and measuring the potential energy interaction, u_t, of the test particle with the other particles in the system. The excess chemical potential, $\mu_{ex} = \mu - \mu_{ig}$, is then determined as

$$\beta\mu_{ex}(N,V,T) = -\ln\frac{Q(N+1,V,T)}{Q(N,V,T)} = \ln\langle\exp(-\beta u_t)\rangle_{NVT} \quad (1)$$

where μ is the chemical potential, μ_{ig} is the chemical potential

of an ideal gas, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature, $Q(N,V,T)$ is the partition function for a canonical ensemble of N molecules in a fixed volume V, and the brackets $\langle\cdot\rangle$ denote an ensemble averaged property. In the isobaric−isothermal (NPT) ensemble, the excess chemical potential is given by

$$\beta\mu_{ex} = -\ln\frac{Q(N+1,P,T)}{Q(N,P,T)} = $$
$$\ln\left\langle\frac{PV}{(N+1)k_B T}\exp(-\beta u_t)\right\rangle_{NPT} \quad (2)$$

where P is the pressure of the system. For a dense system, or for a solute of complex molecular shape, random insertion attempts often result in particle overlaps, giving a very large potential energy ($u_t \to \infty$) and no contribution to the ensemble average. For these conditions, Widom's particle insertion method becomes statistically inefficient. To overcome this difficulty, different simulation techniques have been devised, such as umbrella sampling,[2] thermodynamic integration,[3−5] and the expanded ensemble method.[6−9] In this work, we have used the expanded ensemble method (EEM), which is particularly suitable for calculating the chemical potential of molecular solutes at moderately high solvent densities.

The paper is organized as follows. Simulation details and a description of the force fields are given in sections 2 and 3, respectively. Results and discussions are presented in section 4.

2. Simulation Details

2.1. Calculation of Chemical Potential. In the expanded ensemble method (EEM),[6] an additional parameter λ is defined, and its value is varied continuously during a single simulation. The partition function Ω for the expanded ensemble is given by

$$\Omega(\mathbf{q}^N,\lambda) = \sum_{n=0}^{M}\exp(\eta_n)\,Q(N,P,T;\lambda_n) \quad (3)$$

where $\mathbf{q}^N$ represents the translational and rotational position

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vectors of the N-particle system, η_n, is a bias function, M is the total number of λ states, and $Q(N,P,T;\lambda_n)$ is the partition function of the isothermal−isobaric ensemble at $\lambda = \lambda_n$. In this formalism, M, the total number of λ states, are defined a priori. λ can also be varied continuously over a range from 0 to 1, and the partition function can be written as[10]

$$\Omega(\mathbf{q}^N,\lambda) = \int_0^1 d\lambda \, \exp(\eta) \, Q(N,P,T;\lambda) \qquad (4)$$

For the calculation of the chemical potential, λ can be varied such that it controls the coupling between the solute and the solvent. For $\lambda = 0$, the solute is completely decoupled from the solvent and the system corresponds to an N-particle system. For $\lambda = 1$, the solute and the solvent are fully interactive, and this condition corresponds to an $(N + 1)$-particle system. To control the coupling between the solute and solvent, we varied the Lennard-Jones molecular diameter (σ), well depth (ϵ), and bond length (L) parameters of the solute particle linearly with λ. The partition function $Q(N,P,T;\lambda)$ can then be written as

$$Q(N,P,T;\lambda) \propto \int dV \exp(-\beta PV) \int d\mathbf{q}^N d\mathbf{q}_{N+1} \times$$
$$\exp(-\beta u_N(\mathbf{q}^N)) \exp(-\beta u_t(\mathbf{q}^N,\mathbf{q}_{N+1};\lambda)) \quad (5)$$

where $\mathbf{q}_{N+1}$ is the position vector of the partially inserted $(N + 1)$th particle, u_N is the potential energy of the N-particle system, and u_t is the potential energy of the $(N + 1)$th particle due to its interaction with the other N particles. The probability of visiting a state λ is proportional to

$$p(\lambda) \propto \exp(\eta) \, Q(N,P,T;\lambda) \qquad (6)$$

The ratio of the partition functions for any two coupling parameter values λ_1 and λ_2 is given by

$$\frac{Q(N,P,T,\lambda_1)}{Q(N,P,T,\lambda_2)} = \frac{p(\lambda_1) \exp(-\eta_1)}{p(\lambda_2) \exp(-\eta_2)} \qquad (7)$$

Substituting eq 7 in eq 2 yields

$$\beta\mu_{ex} = -\ln\frac{Q(N,P,T,\lambda=1)}{Q(N,P,T,\lambda=0)} = \ln\frac{p(\lambda=0)}{p(\lambda=1)} + \eta_{\lambda=1} - \eta_{\lambda=0} \quad (8)$$

The weighting function or bias, η, is introduced to facilitate transition of the system over the range of λ space. The intermediate steps are nonphysical states, and they are not used in the calculation of the free energy or chemical potential. Nonetheless, they are important, as they provide a path between the initial and the final states.

The bias function η is adjusted through a series of short runs such that we get a uniform distribution over all of the λ values. The bias function needed to achieve a certain distribution requires a priori knowledge of the chemical potential itself. This problem can be solved approximately in an iterative way.[8] A few simulations with a small number of MC cycles are performed, and the bias function is updated by comparing the calculated distribution with the desired target distribution:

$$\eta_i^{new} = \ln\left[\left(\frac{p(\lambda_i)}{p(\lambda_0)}\right)^{calc}\left(\frac{p(\lambda_0)}{p(\lambda_i)}\right)^{tar}\right] + \eta_i^{old} \qquad (9)$$

where the superscripts "calc" and "tar" refer to the calculated and target distributions, respectively. For a uniform distribution of probability density, the term $(p(\lambda_0)/p(\lambda_i))^{tar}$ is equal to unity. In our modified EEM with continuous variation of λ, a histogram

of probability density (with bin size ≈ 0.05) is created, and the bias function is calculated at the midpoint of each bin. For λ values other than the bin midpoints, the value of $\eta(\lambda)$ is obtained by linear interpolation of the η values at the neighboring bin midpoints.

2.2. Monte Carlo Moves. Simulations are performed in the isobaric−isothermal (NPT) ensemble at 1 atm pressure and for three different temperatures (300, 323, and 373 K). A series of n-alkane solvents ranging from C_6 (n-hexane) to C_{24} (n-tetracosane) are used to evaluate the effect of the solvent on the chemical potential of aromatic solutes. A cubic simulation volume is used with periodic boundary conditions. Interparticle interactions are truncated at a distance equal to half the simulation box length and long-range corrections are applied to the energy and chemical potential calculations, assuming a uniform pair correlation function beyond the cutoff radius. Each simulation cell contains 20 alkane chains and a partially grown solute particle. The configurational space of each chain molecule is sampled using the continuum configurational bias (CCB)[11,12] method. In the CCB method, several chain units are removed from one end of the chain and the chain is regrown (on the same side) by replacing the units one by one. The regrowth of the chain is biased by selective placement of chain units over a limited range of torsional angles, such that a configuration of low potential energy is generated. This bias is then removed in the final acceptance criterion of the CCB move. In addition to the CCB move, individual sites on the alkane chain are randomly displaced so as to sample the bond length and bond angle distributions. Rigid displacement (i.e., keeping the internal chain coordinates constant) is also applied in translational sampling of the alkane chains. The configuration space of the partially inserted solute molecule is sampled using translational and rotational moves.[13] To maintain constant pressure, a volume change move is attempted in every Monte Carlo cycle.[13] The value of the coupling parameter λ is also sampled over a range between 0 and 1. The probability of accepting a λ-change move is

$$p_{\lambda_o \to \lambda_n}^{acc} = \min\left[1, \frac{p_{n \to o}^{att} \exp(\eta_n) \exp(-\beta u_t(\lambda_n))}{p_{o \to n}^{att} \exp(\eta_o) \exp(-\beta u_t(\lambda_o))}\right] \quad (10)$$

where $p_{i \to j}^{att}$ is a probability of attempting a transition from $\lambda = \lambda_i$ to λ_j.

$$p_{i \to j}^{att} = \frac{1}{\lambda_{range}} \qquad (11)$$

where

$$\lambda_{range} = \min(1, \lambda_i + \Delta\lambda) - \max(0, \lambda_i - \Delta\lambda) \qquad (12)$$

and $\Delta\lambda$ is the maximum step size used for a λ move.

Each Monte Carlo cycle consists of one CCB and one rigid displacement move for each alkane chain, a single site displacement move for each alkane chain unit, and one translation and one rotation move for the solute particle. The maximum step sizes for the volume change, translational, and rotational moves are adjusted so as to achieve approximately 50% acceptance rate. The maximum step size of a λ change move is approximately 0.05, and is adjusted to get an 80% acceptance rate. The initial configuration is generated by adding units to chains using CCB-type moves. After an initial equilibration run, a small number of short runs (typically three to five runs with 2×10^4

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TABLE 1: Density of *n*-Alkane and Chemical Potential of Benzene and Naphthalene at Infinite Dilution at 1 atm

solvent	$\rho_{solv}^{expt\ a}$	ρ_{solv}^{sim}	$\beta\mu_{ex,benz}^{\infty}$	λ cycles	$\beta\mu_{ex,naph}^{\infty}$	λ cycles
			Temperature = 300 K			
n-hexane	0.655	0.66 ± 0.03	-7.0 ± 0.2	77	-11.2 ± 0.4	36
n-nonane	0.714	0.73 ± 0.02	-6.3 ± 0.4	55	-10.7 ± 0.4	30
n-dodecane	0.745	0.76 ± 0.02	-6.3 ± 0.3	50	-10.8 ± 0.5	23
n-pentadecane	0.765	0.78 ± 0.02	-6.9 ± 0.3	44	-10.7 ± 0.6	18
			Temperature = 323 K			
n-hexane	0.633	0.64 ± 0.03	-5.6 ± 0.5	66	$-8.8 + 0.6$	46
n-nonane	0.694	0.71 ± 0.02	-5.9 ± 0.3	68	-9.4 ± 0.2	35
n-dodecane	0.728	0.74 ± 0.02	-5.7 ± 0.2	64	-8.9 ± 0.4	23
n-pentadecane	0.748	0.77 ± 0.02	-5.5 ± 0.2	51	-9.9 ± 0.6	17
n-octadecane	0.762	0.78 ± 0.02	-5.5 ± 0.3	51	-9.3 ± 0.8	19
			Temperature = 373 K			
n-nonane	0.653	0.67 ± 0.03	-4.4 ± 0.1	118	-7.4 ± 0.6	56
n-dodecane	0.691	0.71 ± 0.02	-4.5 ± 0.4	91	-7.2 ± 0.5	38
n-pentadecane	0.713	0.73 ± 0.02	-4.2 ± 0.4	76	-7.4 ± 0.4	33
n-octadecane	0.729	0.75 ± 0.02	-4.6 ± 0.7	71	-7.5 ± 0.6	38
n-henicosane		0.76 ± 0.01	-4.7 ± 0.5	57	-7.6 ± 0.3	23
n-tetracosane	0.748	0.77 ± 0.01	-4.4 ± 0.2	61	-7.5 ± 0.6	21

a Reference 26.

MC cycles) are used to adjust the bias function. The final production runs consist of 2×10^5 MC cycles.

3. Force Fields

We have used the NERD united atom force field for modeling *n*-alkane chains.[14] The CH_2 and the CH_3 units, represented by spherical sites, interact with a Lennard−Jones (LJ) potential.

$$u_{ij} = 4\epsilon((\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6) \tag{13}$$

Interactions between units that are on the same chain and separated by more than three bond lengths are also represented by eq 13. The LJ parameters are $\sigma_{CH_3} = 3.91$ Å, $\sigma_{CH_2} = 3.93$ Å, $\epsilon_{CH_3}/k_B = 104.0$ K, and $\epsilon_{CH_2}/k_B = 45.8$ K. The bond stretching potential $U(r)$ is given by

$$U(r)/k_B = \frac{K_r}{2}(r - r_{eq})^2 \tag{14}$$

where r is the bond length, $K_r = 96\ 500$ K/Å², and $r_{eq} = 1.54$ Å. The bond bending potential $U(\theta)$ is given by

$$U(\theta)/k_B = \frac{K_\theta}{2}(\theta - \theta_{eq})^2 \tag{15}$$

where θ is the angle between two successive bonds, $K_\theta = 62\ 500$ K/rad², and $\theta_{eq} = 114°$. The torsional potential energy, U_{tor}, is given by

$$U_{tor}(\phi)/k_B = V_0 + V_1(1 + \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 + \cos 3\phi) \tag{16}$$

where ϕ is the torsional angle. The constants are $V_0 = 0.00$ K, $V_1 = 355.04$ K, $V_2 = -68.19$ K, and $V_3 = 701.32$ K. Benzene is modeled using a six-site united atom model,[15] with each site representing a −CH− unit. The LJ parameters for this model are $\sigma = 3.72$ Å and $\epsilon/k_B = 55.3$ K. The distance between the −CH− units is 1.41 Å. Naphthalene is modeled using a ten-site united atom model.[16] The LJ parameters are $\sigma = 3.395$ Å and $\epsilon/k_B = 67.1$ K. The LJ spheres representing outer −CH− units are positioned on the carbon−hydrogen bond while the spheres representing C atoms shared by two aromatic rings are positioned at the carbon position of the molecule. The distance between the centers of the two aromatic rings is set to 0.7236σ. The outer LJ spheres are located at a distance of 0.5σ from the center of the aromatic ring, while the shared units are located at a distance of 0.418σ. In both of these models, the aromatic molecules are assumed to be planar and rigid. The LJ interaction parameters between units of different types are calculated using the standard Lorentz−Berthelot mixing rules. We were motivated to use the united atom models, instead of explicit atom models, due to the computational cost of the chemical potential calculations. The use of an explicit atom model would increase the computational time as order N^2. Previous simulation results obtained for the chemical potential of pure liquid benzene have indicated the suitability of this rather simple model (i.e., united atom without quadrupole interaction)[10] for calculating the chemical potential of aromatic compounds. For simulations carried out at infinite dilution of the aromatic solute, the lack of quadrupole interactions will not affect the final results significantly.
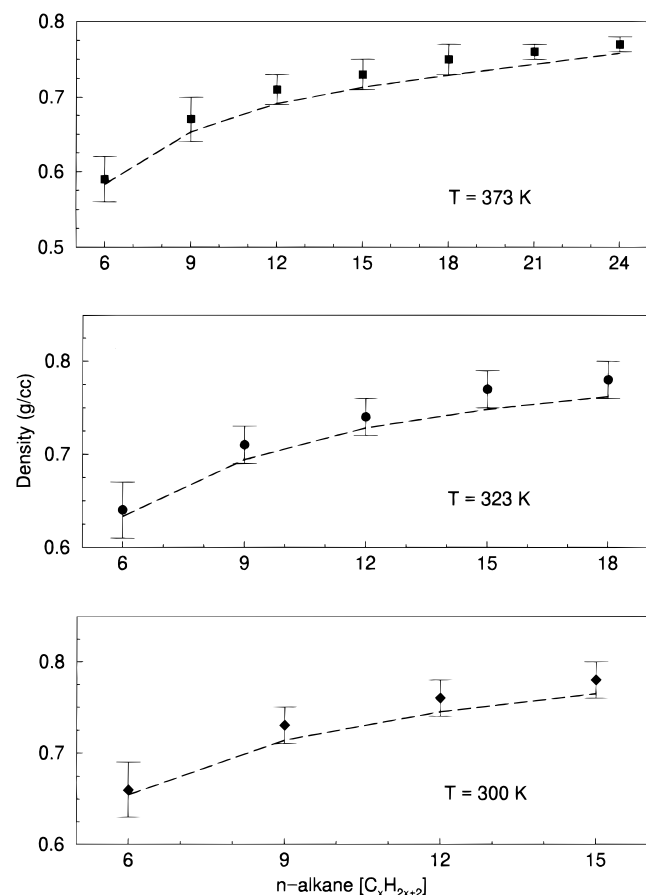
4. Results

Table 1 shows the results for the chemical potentials of benzene and naphthalene in pure *n*-alkane at 300 K and 1 atm. The average density of the system is also calculated and shown in the table. Due to the continuously changing size of the solute particle, it is not considered in the calculation of system density. The average density of the system compares well with experimental data (Figure 1). The liquid density of *n*-alkanes increases with the number of carbon atoms on the chain, and the calculation of the chemical potential becomes more difficult. This fact is apparent from the number of completed cycles over the λ space. At 300 K, simulations are performed for alkanes only up to C_{15}, as the melting temperatures for C_{18} and higher alkanes are above 300 K.

The simulation results can be compared with experimental data, where available, using the activity coefficient (γ_i^∞) of a solute at infinite dilution. γ_i^∞ is related to Henry's constant, k_H, as

$$\gamma_i^\infty = \frac{f_i^L}{x_i f_i^0} = \frac{k_H}{f_i^0} \tag{17}$$

where x_i is the mole fraction and f_i^L is the fugacity of the solute i in the solution. f_i^0 is the fugacity of the solute at the reference state. The reference state for the solute is taken as a pure liquid at the same temperature and pressure of the solution.

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Figure 1. Liquid density of *n*-alkane at 1 atm. The simulation results are represented by filled points, and the experimental data (ref 26) are shown by the dotted line.

f_i^0 can be calculated using either an equation of state or molecular simulations. It can also be obtained from experimental data:

$$RT \ln \frac{f_i^0}{P} = \int_0^P \left(v_i - \frac{RT}{P}\right) dP \qquad (18)$$

where v_i is the molar volume of species *i*. Henry's constant (k_H), which is a measure of solubility of a solute, is related directly to the excess chemical potential at infinite dilution, μ_{ex}^∞:

$$k_H = \rho k_B T \exp(\beta\mu_{ex}^\infty) \qquad (19)$$

where ρ is the solvent density. Thus the chemical potential can be written in terms of the activity coefficient as

$$\exp(\beta\mu_{ex,i}^\infty) = \frac{\gamma_i^\infty f_i^0}{\rho k_B T} \qquad (20)$$

For pure benzene at room temperature and pressure, the liquid density (ρ_i^L) and the fugacity/pressure ratio (f_i^0/P) are 0.8786 g/cm³ and 0.13542, respectively.[17] Using these values and experimental data for the activity coefficients at infinite dilution,[18] the chemical potential of benzene in *n*-alkane is calculated and compared to the simulation values (Table 2). To our knowledge, there are no experimental data available for the fugacity and activity coefficient of naphthalene in *n*-alkane, so we use the Peng–Robinson equation of state (PR-EoS)[19] to obtain a fugacity ratio for pure naphthalene. The PR-EoS

TABLE 2: Comparison between Experimental and Simulation Chemical Potential of Benzene in *n*-Alkane at 300 K and 1 atm

solvent	mol wt	ρ_{liq}^{expt}	$\gamma_i^{\infty\ a}$	$\beta\mu_{ex,benz}^{\infty\ b}$	$\beta\mu_{ex,benz}^{\infty,sim}$
n-hexane	86.18	0.655	1.67	−6.72	−7.0 ± 0.2
n-nonane	128.26	0.714	1.46	−6.54	−6.3 ± 0.4
n-dodecane	170.34	0.745	1.29	−6.43	−6.3 ± 0.3
n-pentadecane	212.42	0.765	1.03	−6.40	−6.9 ± 0.3

a Data for the activity coefficients are taken from ref 18. *b* Excess chemical potential calculated using eq 20.
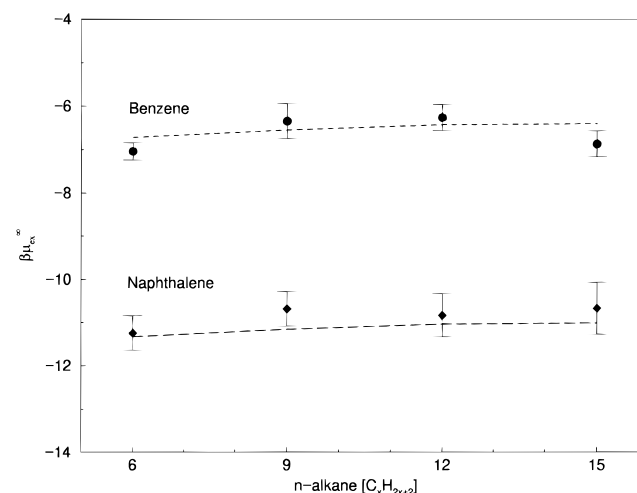
Figure 2. Chemical potentials of benzene and naphthalene in pure *n*-alkane at 300 K and 1 atm. The simulation results for benzene and naphthalene are shown by the filled circles and filled diamonds, respectively. The experimental results are shown by the dotted lines.

predicts the density of naphthalene at room temperature and pressure to within 1% error (experimental density = 0.997 g/cm³ and PR-EoS density = 0.989 g/cm³). The solid state fugacity/pressure ratio, f_i^s/P, is 4.31×10^{-4}. The reference state liquid fugacity is calculated as
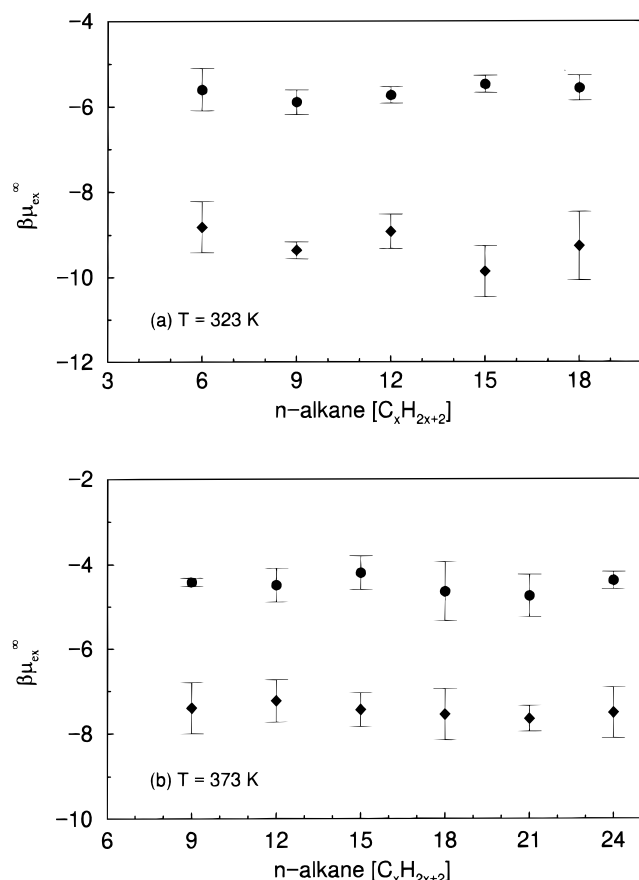
$$\ln \frac{f_i^s}{f_i^0} = \frac{-\Delta S_f}{R}\left(\frac{T_M}{T} - 1\right) = \frac{-\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_M}\right) \qquad (21)$$

where ΔS_f is the molar entropy of fusion, ΔH_f is the molar enthalpy of fusion, *R* is the gas constant, and T_M is the normal melting point. The molar enthalpy of fusion for naphthalene is 18.98 kJ/mol,[20] and its melting point is 353.4 K. From eq 20 the chemical potentials of two solutes at the same thermodynamic conditions can be written as

$$\beta\mu_{ex,N}^\infty = \beta\mu_{ex,B}^\infty + \ln \frac{\gamma_N^\infty f_N^0}{\gamma_B^\infty f_B^0} \qquad (22)$$

In eq 22, the subscripts B and N correspond to benzene and naphthalene respectively. Assuming γ^∞ of naphthalene to be the same as that of benzene, $\beta\mu_{ex}^\infty$ of naphthalene will be less than that of benzene by −4.607. The chemical potential of naphthalene obtained from the simulations compares well with the values suggested by eq 22. The experimental data suggest a weak trend of increasing values of chemical potential with increasing solvent carbon number (Figure 2). A similar weak trend for the chemical potential of methane in *n*-alkane has been reported from experiments[21] and confirmed by simulations.[22] However, even in the expanded ensemble employed here, the insertion of a C_6 or C_{10} aromatic solute into a dense liquid solvent is significantly more difficult than the insertion of

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Figure 3. Chemical potentials of benzene (filled circles) and naphthalene (filled diamonds) at 1 atm in *n*-alkanes.

TABLE 3: Comparison between Experimental and Simulation Chemical Potential of Benzene in *n*-Alkane at 323 K and 1 atm

solvent	mol wt	$\rho_{\text{liq}}^{\text{expt}}$	γ_i^∞	$\beta\mu_{\text{ex,benz}}^\infty$ [a]	$\beta\mu_{\text{ex,benz}}^{\infty,\text{sim}}$
n-hexane	86.18	0.633	1.50[b]	−5.91	−5.6 ± 0.5
n-nonane	128.26	0.694	0.96[b]	−6.07	−5.9 ± 0.3
n-dodecane	170.34	0.728	1.04[c]	−5.75	−5.7 ± 0.2
n-pentadecane	212.42	0.748	0.79[c]	−5.84	−5.5 ± 0.2
n-octadecane	254.50	0.762	0.93[b]	−5.51	−5.5 ± 0.3

[a] Excess chemical potential calculated using eq 20. [b] Data for the activity coefficients are taken from ref 24. [c] The activity coefficients estimated using its temperature dependence (eq 23). $H_i^{\text{E},\infty}$ for benzene at 300 K in $C_{12}H_{26} = 7536.93$ J/mol and in $C_{15}H_{32} = 9234.96$ J/mol.[25]

Monte Carlo simulations have been used to calculate the chemical potentials of benzene and naphthalene at infinite dilution in several pure *n*-alkanes. Good agreement is found between the simulation results and experimental data. The simulation results indicate that the chemical potential of a low molecular weight aromatic compound does not depend strongly on the carbon number of the solvent. The change in the chemical potential with solvent temperature and solute type are also consistent with the trends suggested by experimental data and equations of state. Such agreement provides a degree of confidence for extending these simulations to more complicated solutes and to mixed solvent systems commonly found in the environment.

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methane. As a result, the statistical uncertainty here is too large to detect changes on the order of $\Delta\beta\mu_{\text{ex}}^\infty = 0.32$ as the solvent size is increased from C_6 to C_{15}. Significantly longer simulations would be needed to resolve trends of this magnitude.

Simulations were also performed at 323 K for *n*-alkanes ranging from C_6 to C_{18} and at 373 K for *n*-alkanes ranging from C_9 to C_{24}. The results for $\beta\mu_{\text{ex}}^\infty$ are shown in Figure 3. Comparison with experimental data is again made by using γ_i^∞ values obtained from the literature.[18] This comparison is shown in Table 3. For cases where there were no experimental data for γ_i^∞, we utilized the temperature dependence of γ_i^∞ given by

$$\frac{\partial \ln \gamma_i^\infty}{\partial T} = \frac{-H_i^{\text{E},\infty}}{RT^2} \qquad (23)$$

where $H_i^{\text{E},\infty}$ is the partial molar heat of mixing at infinite dilution. There is an increase in the chemical potential with increasing temperature. As for 300 K, no dependence of the chemical potential of the aromatic solutes on the solvent carbon number can be discerned at the higher temperatures. At 373 K, $\beta\mu_{\text{ex}}^\infty$ for benzene in C_{18} is calculated using the temperature dependence of γ_i^∞ given by eq 23. $H_i^{\text{E},\infty}$ of benzene in C_{18} is 3290 J/mol at 313 K.[23] Using eqs 20 and 23, the estimated value for $\beta\mu_{\text{ex}}^\infty$ is −4.72, which compares well with the simulation result (see Table 1).

In conclusion, this work demonstrates the use of molecular simulations for the calculation of the chemical potential of molecular solutes in solvents at liquid densities. Such simulation methods can be used to provide necessary thermodynamic information when experimental data or analytical equations of state are not readily available. In this work, expanded ensemble

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