Aqueous Hydration of Benzene

G. Ravishanker, P. K. Mehratra, M. Mezei, and D. L. Beveridge*

Contribution from the Hunter College of the City University of New York,
New York, New York 10021. Received October 12, 1993

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Abstract: A (T, V, N) ensemble Monte Carlo computer simulation has been performed on a dilute aqueous solution of benzene at 25 °C. The calculation employs intermolecular pairwise potential functions determined from quantum mechanical calculations. The results are analyzed by means of the proximity criterion, which permits the hydration to be described on a solute atom and steric attributes. Results are discussed in comparison with recent simulation studies of alkyl groups.

In view of the importance of the hydrophobic effect in structural biochemistry, a knowledge of the details of the hydrophobic hydration of prototype apolar species at the molecular level is quite desirable. Recent research studies from this laboratory have employed liquid-state computer simulations to study the structure and energetics of dilute aqueous solutions of CH₄,

\[A_{	ext{CH}}(n) = \gamma A + A^*\]

\[U_0(R + \Delta R) = \gamma A^* = (\gamma + \Delta \gamma)(A + \Delta A) = \gamma A + \gamma \Delta A + \Delta A\]

Following the ideas of Benson and Shuttleworth, one may estimate this contribution to be <1 kJ/mol. The other part, which may be viewed as the difference in relaxation energy between the cluster model and an infinite system, can be estimated in a continuum approximation, and it is found to be negligible (<1 kJ/mol).

Thus, we find that neither a change in the water density nor simple continuum corrections in the cluster model are able to explain the discrepancy between the different solvation energies found in this model and the model with periodic boundary conditions.

The dependence on the structure in pure water of boundary conditions has earlier been investigated by Pangali et al. In a comparison between a cubic and a spherical cutoff with periodic boundary conditions, they found that the number of hydrogen bonds was larger in the latter case. They also found that the structure was heavily dependent on the cutoff distance. Thus, from their and our studies, it seems crucial to use the same boundary conditions when making comparative investigations, although still effects from the boundary conditions may not be negligible.

Conclusions

The benzene–water pair potential shows a rather strong orientation dependence mainly due to the dipole–quadrupole interaction. This preferential orientation is also reflected in the orientation of water molecules in the first hydration shell of benzene. The water structure is only slightly perturbed by the presence of the benzene molecule, although both a first and a second hydration shell are discernable.

However, the main observation from our simulations is that different boundary conditions may lead to quite different results. This is certainly true for global properties like the solvation energy and maybe to a lesser extent for more local properties like the benzene–water distribution functions, confined to the first hydration shell. Neither of the two models considered is able to reproduce experimental results for the solvation energy, and there does not seem to be any obvious choice of model. Further methodological studies are certainly warranted.

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Thermalodynamic study of benzene-water interactions was carried out on $[\text{C}_6\text{H}_6]_{\text{aq}}$ using a modified statistical thermodynamic approach (1). The thermodynamic cycle for benzene-water interactions involves the calculation of the free energy change for the hydration of benzene. The calculations were carried out using a modified Monte Carlo method (2). The results were compared with experimental data (3) and showed good agreement. The calculated free energy of hydration was found to be $-5.33$ kcal/mol and $\Delta S = -15.7$ cal/(deg-mol) as quoted by Edsall and Koshland (4). Evidence for specific benzene-water interactions comes from studies by Backx and Goldman (5), who observed nonclassical rotational behavior of $\text{D}_2\text{O}$ in water/benzene solutions and anticipated a weak hydrogen bond between $\text{H}_2\text{O}$ and the benzene $\pi$-electron cloud. Though there has been experimental work on the hydrophobic interaction of benzene molecules, there is little known at the molecular level about the nature of benzene hydration. To explore the aqueous hydration of the phenyl group and to determine the nature of the hydrophobic and hydrophilic effects in this system, we have extended our computer simulation studies to $[\text{C}_6\text{H}_6]_{\text{aq}}$ at 25 $^\circ$C.

While this work was in progress, Karlström et al. (6) reported a new theoretical determination of an intermolecular potential function for the benzene-water interactions using quantum mechanical calculations. A novel means of correcting for the basis set superposition error was introduced. Comparison of the Karlström et al. results with those of the potential function used for our study gives an indication of the sensitivity of calculated interaction energies to basic assumptions in the theoretical methodology.

Calculations

Statistical thermodynamic calculations were carried out on $[\text{C}_6\text{H}_6]_{\text{aq}}$ with use of a modified Metropolis procedure (7) incorporating the force bias method (8) and preferential sampling (9) for convergence acceleration. The system for study was comprised of 216 rigid particles, one benzene molecule, and 215 water molecules. The simulation was performed at a temperature of 25 $^\circ$C and a density determined from the experimentally observed partial molar volume of water and benzene. The condensed-phase environment of the system was provided by means of face centered cubic periodic boundary conditions, which provide in excess of two complete hydration shells for the solute. Convergence characteristics and statistical error bounds on each of the calculated quantities were monitored by control functions based on the method of batch means. Full details of the Monte Carlo methodology are given in a recent article by Mehrora et al. (10).

The N-particle configurational energies of the system were calculated under the assumption of pairwise additivity in intermolecular interactions with use of potential functions determined from $\text{ab initio}$ quantum mechanical calculations. For the water-water interactions we continue to use the MCY-CI(2) potential (11) developed by Matsuoka et al. and representative of moderately large configuration interaction calculations on the water dimer. For the calculation of benzene-water interactions, a potential function was constructed from the 12-6-1 functional (12) used in simulations based on Clementi's basis set in the GAUSSIAN-80 system of programs. The performance of the MCY-CI(2) water-water potential is now well documented. Simulations based on this potential are well-known to underestimate the internal energy of liquid water by 12%, about the amount expected by the neglect of cooperative effect in assuming pairwise additivity. A wide range of thermodynamic, structural, and dynamical properties of liquid water are well described in simulations based on this potential. Particularly excellent agreement is obtained with experiment on the

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Figure 1. Isoenergy contour surface for benzene-water dimer in the molecular plane of benzene. Lower energy is labeled A and corresponds to $-2.9$ kcal/mol. Each successive contour increases in energy by 1.0 kcal/mol.
Results

The calculated internal energies and related quantities for \([C_6H_6]_{aq}\) are collected in Table I. The quantities entered here are the mean energy \(U\) of the system \((N_S = 1, N_W = 215)\), the oxygen-oxygen radial distribution function, indicating essential structural elements of the system are well accommodated. The principal problem with the potential is the curvature in the region of equilibrium water-water separations, which leads to an inordinately high calculated pressure. The general position of Monte Carlo simulations on the liquid water problem is described in a recent review article by Beveridge et al. The convergence profile for the force-bias, preferential sampling augmented Monte Carlo simulation on \([C_6H_6]_{aq}\). Mean energy is denoted as \(U\), and mean energy for batches of size 50K is denoted as \(U_{50}\).

![Isoenergy contour surface for benzene-water dimer in the plane perpendicular to the molecular plane of benzene. Lowest energy is labeled A and corresponds to \(-2.9\) kcal/mol. Each successive contour increases in energy by \(1.0\) kcal/mol.](image)

Figure 2. Isoenergy contour surface for benzene-water dimer in the plane perpendicular to the molecular plane of benzene. Lowest energy is labeled A and corresponds to \(-2.9\) kcal/mol. Each successive contour increases in energy by \(1.0\) kcal/mol.

The calculated partial molar internal energy of transfer for \([C_6H_6]_{aq}\) from water, and finally \(U_s\) and \(U_{sol}\) to the solute-water and solvent-solute contributions to \(U\). Each of these is formally defined in eq 1-12 and Figure 4 of a previous paper from this laboratory by Swaminathan et al. The calculated molecular distribution functions and analysis thereof for \([C_6H_6]_{aq}\) at 25 °C follow. The analysis formalism follows that described by Mehrotra and Beveridge, except where noted. The results are displayed first on a solute-atom-by-atom basis, then developed in terms of C-H and C\(_\text{C}\) fragments, and finally extended to indices referred to the entire \(C_6H_6\) solute molecule. The interpretation and implications of the results are discussed in the following section.

The solute atom-solvent water radial distribution functions are described in the following paragraphs. Two forms of these functions are presented for each atom: (a) a "total" solute atom-water radial distribution function, \(g_{AW}^{10}(r)\), conventionally defined, and (b) a solute atom-water \(g_{AW}^{11}(r)\), describing only those solvent water molecules designated "primary" to the solute atom based on the proximity criterion, i.e., those waters closer to the solute atom than to any other. This \(g(r)\) is renormalized to the volume element of the truncated spherical shell of the Voronoi polyhedron associated with the primary region of the solute atom. The \(g_{AW}^{10}(r)\) and \(g_{AW}^{11}(r)\) are collected for each solute atom on a single graph, together with the corresponding running coordination numbers.

The calculated solute-water radial distribution functions of the benzene carbon and hydrogen atom in \([C_6H_6]_{aq}\) are shown in Figure 4. All solute atoms-water radial distribution functions refer to the center of mass of water molecules unless otherwise noted. The total \(g_{W}(r)\) and the \(g_{C}^{11}(r)\) for carbon, symmetry averaged over the six carbon atoms, and the corresponding running

Table I. Calculated Internal Energies for the Dilute Aqueous Solution of Benzene at 25 °C in kcal/mol*

<table>
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<tr>
<th>(N_W)</th>
<th>(N_S)</th>
<th>(U_{AW})</th>
<th>(U_w)</th>
<th>(U_{sol})</th>
<th>(U_{sol})</th>
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<tr>
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<td>(-1.86)</td>
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</tr>
</tbody>
</table>

*See ref 1 for definition of these terms. 
Results from simulation as described in Calculations. 
Results from simulation based on benzene-water potential with the attractive region set everywhere to 0.

energy \(U_w\) of 215 water molecules in \([H_2O]_{aq}\) at 25 °C. \(U_w\), the corresponding energy of solvent water in \([C_6H_6]_{aq}\), \(U_s\), the calculated partial molar internal energy of transfer for \(C_6H_6\) into water, and finally \(U_{sol}\) and \(U_{sol}\) to the solute-solvent and solvent-solute contributions to \(U\). Each of these is formally defined in eq 1-12 and Figure 4 of a previous paper from this laboratory by Swaminathan et al. The calculated molecular distribution functions and analysis thereof for \([C_6H_6]_{aq}\) at 25 °C follow. The analysis formalism follows that described by Mehrotra and Beveridge, except where noted. The results are displayed first on a solute atom-by-atom basis, then developed in terms of C-H and C\(_\text{C}\) fragments, and finally extended to indices referred to the entire \(C_6H_6\) solute molecule. The interpretation and implications of the results are discussed in the following section.

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Figure 4. Calculated total (—) and primary (—-) solute-solvent radial distribution functions and the corresponding running coordination numbers on an atom-by-atom basis in [C₆H₆]aq. These distributions are symmetry averaged over six carbon atoms (a) and six hydrogen atoms (b) of benzene.

Figure 5. Calculated symmetry-averaged QCDF for primary solute-solvent coordination number on an atom-by-atom basis in [C₆H₆]aq. Coordination numbers are given in Figure 4a. The total g_CW(r) shows two peaks, each relatively broad, since both in-plane and out-of-plane solvent molecules are included together. The g_CW(r) for carbon, by virtue of the proximity criterion, describes mainly those water molecules above and below the C₆ hexagon in benzene. A well-defined first shell with a maximum value at 3.2 Å is evident. Integrating this shell up to r = 4.5 Å gives a value of 0.37 water molecules per carbon atom in this region.

The total and primary radial distribution functions and running coordination number for the benzene hydrogen atom, also symmetry averaged, are shown in Figure 4b. The g_HW(r) is of most interest and shows a maximum at 2.2 Å. The peak decays slowly to a minimum at 4.0 Å. The area under the curve indicates 3.42 waters are included in the first shell for each hydrogen. Here a composite of in-plane and out-of-plane solvation is reflected even in the g_HW(r).

We turn now to an atom-by-atom analysis of the primary solvation of the carbon and hydrogen atoms of benzene in aqueous solution by means of quasicomponent distribution functions. This analysis is based on the g_CW(r) and the R_C values discussed above. The distribution x_C(K) of primary coordination numbers K for benzene carbon and hydrogen atoms is shown in Figure 5. For the carbon atom, Figure 5a, the distribution ranges from zero to two with a average K = 0.39. For hydrogen, Figure 5b, the distribution ranges from two to five, with three and four being the maximum contributors, and R = 3.23.

The distribution x_p(ε) of binding energies for water molecules primary to the benzene atoms in [C₆H₆]aq is shown in Figure 6. For the carbon atom, Figure 6a, the distribution ranges from -4.5 to -0.5 kcal/mol with ε = -1.07 kcal/mol. For hydrogen the range is from -14.0 to -4.0 kcal/mol with 6 = -9.46 kcal/mol.

The computed distribution functions x_p(ε) for solute-water interaction energy are given in Figure 7. For carbon, Figure 7a, the distribution ranges from -3.6 to 1.8 kcal/mol with the most probable ε value being -2.5 kcal/mol and with ε = 1.64 kcal/mol. For hydrogen, x_p(ε) ranges from -4 to 2.5 kcal/mol, with most probable ε value being -1.2 kcal/mol and ε = -1.02 kcal/mol.

The out-of-plane benzene-water interactions are slightly stronger energetically than the in-plane interactions.

The above results can be combined to produce a description of the local solution environment of benzene in [C₆H₆]aq in terms of the C-H group and the C₆ fragment and also the entire C₆H₆ molecule. The groupwise distributions for coordination numbers, binding energies, and pair interaction energies are shown in Figures 8, 9, and 10, respectively. Of particular interest is the C₆ coordination number distribution, with contributions from K = 0, 1, 2, and 3 and R = 2.34. This shows that essentially one water...
molecule above the plane and one below comprise the first hydration shell of the π cloud of benzene in [C₆H₆]₆, with a corresponding pair interaction energy placed on the average at -3 kcal/mol and a distribution favoring bound values.

The distribution of the various analysis quantities referred to the entire molecule is shown in Figures 11-14. The first hydration shell of benzene is seen to involve from 19 up to 26 water molecules, with \( K = 22.1 \). The average total binding energy for water molecules is -60.6 kcal/mol. The pair interaction energy extends from -3 to 0 kcal/mol, with the contribution at \( \epsilon = 0 \) coming from all the distant waters. The average pair energy is -1.08 kcal/mol.
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Figure 14. Calculated QCDF for solute-solvent pair energy and the running coordination number on a molecular basis in $[\text{C}_6\text{H}_6\text{aq.}]^{2}$.

Discussion

The essential structural feature of the aqueous hydration of benzene emerging from the simulation results is a first hydration shell consisting of 23 water molecules, shown in Figure 15. Twenty one of the first shell waters can be associated primarily with H-region hydration, and 2 are associated with hydration of the benzene ring above and below the carbon skeleton. Further insight into the nature of the calculated hydration can be obtained by examining details of the local hydration of the benzene ring C-H groups and $\pi$-electron cloud in individual structures contributing to the simulation. A stereoview of the computer-generated Dreiding model of the benzene hydration complex is shown in Figure 16; the “bonds” in the figure connect oxygen atoms of water molecules that are within hydrogen bonding distance. This figure reveals the cage-like features of the benzene hydration complex. Quite a few puckered pentagonal forms can be discerned but so can contributions from higher and lower order polygonal forms. The irregularity of the polygons is a natural consequence of thermal disorder in the system at ambient temperatures. For the in-plane interactions, the number of waters and the spatial extent of the hydration shell are consistent with previous examples of hydrophobic hydration found in simulations of dilute aqueous solutions of alkyl group containing molecules. The average pair interaction energy of water molecules primary to the CH groups at $-1.08 \text{ kcal/mol}$ turns out to be significantly closer to corresponding values computed for methane-water interactions in $[\text{CH}_4\text{aq.}]^{2}$, suggesting that the apolar solute–water interactions are quite similar in both cases and essentially hydrophobic.

The hydration complex above and below the molecular plane, Figure 17, features two water molecules, one on each side of the benzene ring, located one above and one below the center of the $\pi$-electron cloud. A hydrogen atom on each water molecule extends into the $\pi$-cloud, toward the center of the molecule, and a mean pair energy of $-1.64 \text{ kcal/mol}$ is associated with this structure. The single water molecules interact with a set of second shell waters which extend over the carbon atoms and articulate with the H-region waters completing the benzene hydration. It is interesting to note that the in-plane and out-of-plane potential minima in the pairwise interaction energy surface, both $3 \text{ kcal/mol}$, give rise to quite different hydration structures in the simulation. The $\pi$-cloud hydration structure is favored by both a weak hydrogen bonding interaction and by steric factors, since the hydrogen atom of water can be accommodated better than the oxygen in the $\pi$ cloud. The relative importance of these two effects is discussed below.

Figure 15. Stereographic view of a significant molecular structure contributing to the statistical state of $[\text{C}_6\text{H}_6\text{aq.}]^{2}$.

Figure 16. Stereographic view of the Dreiding model of the first hydration shell of benzene taken from the Monte Carlo simulation described herein on $[\text{C}_6\text{H}_6\text{aq.}]$ at 25 °C. Water oxygens within 3.2 Å are bonded.
Partial molar internal energy of transfer for benzene calculated from simulation results comes out to be $-70.15 \text{ kcal/mol}$ with error bounds estimated to be $\pm 30.0 \text{ kcal/mol}$. This calculation used a value of $-8.65 \text{ kcal/mol}$ for the energy of water as calculated in a previous study. A recent, 3000K long run using the force-biased sampling scheme predicted a value of $-8.75 \text{ kcal/mol}$ for the energy of water. By use of this value, the partial molar internal energy of transfer of benzene is calculated to be $-48.6 \text{ kcal/mol}$, with the estimated error bound still about $\pm 30.0 \text{ kcal/mol}$. The calculated transfer energy also has a large error associated with it because it is a small quantity derived from the difference of two large numbers known only with a considerable degree of statistical uncertainty. This number can also be expected to be quite sensitive to the well depth of the benzene-water interaction energy in the in-plane region. The energy difference of 1 kcal/mol between the function used herein and that of Karlstrom et al. propagated over 20 in-plane interactions could change the calculated transfer energy by 30%. Experience with similar problems in liquid water system indicates that the calculated structural characteristics of the system are not highly sensitive to small changes in energetics, and thus the description of the essential nature of the benzene hydration complex set forth herein is expected to remain valid.

Finally, we pursued the question of sensitivity of results to choice of potential function, with an additional simulation, identical with that previously described, except that the attractive part of the benzene-water potential was everywhere set to 0. The complete simulation also involved 1700K configurations with ensemble averages formed over the last 1000K. The computed energetics are given in column B of Table 1. Here the transfer energy is reduced to $-1.86 \text{ kcal/mol}$, still with large error bounds. Thus, the attractive part of the benzene-water potential influences the transfer energy significantly, with the experimental value bracketed by the two simulation results reported herein. The structural indices turned out to be essentially insensitive to this change in benzene-water potential, which indicates the steric contribution to the structure of the $\pi$ cloud to be quite significant. Although a water hydrogen is proximal to the $\pi$ cloud in this model, the nature of the interactions is not exclusively hydrophilic.

Further studies are underway to improve the quality of energetics in the potential function and in the simulation results, and determination of a potential of mean force for the benzene-benzene interaction is in progress.

Registry No. Benzene, 71-43-2; water, 7732-18-5.

Reactive Scattering of O(3P) with Toluene

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Abstract: In a crossed molecular beam study, the reaction of O(3P) + toluene, at 9.7 kcal/mol collision energy, is shown to give primarily radical products, CH$_3$ + phenoxy and H + cresoxy, under single-collision conditions. There is no evidence of intersystem crossing to a stable singlet species, cresol, as was previously observed in the O + benzene reaction. The isotropic angular distributions of the products suggest that the mechanism involves formation of a long-lived triplet biradical intermediate.

The chemical reactions of oxygen atoms with aromatic hydrocarbons remain only poorly understood in spite of efforts directed at elucidating the reaction mechanisms by many workers in the field. Knowledge of the mechanism of the initial reactions of these systems is important for understanding many combustion processes, but the bulk reactions are sufficiently complex, with highly reactive primary radical products producing secondary products, that identification of the primary mechanism is difficult in multiconfiguration environments. For the prototypical reaction, O + benzene, the primary reaction channels were identified in a previous crossed molecular beam study in which two competing reactions were observed. One channel, with products H atom and phenoxy radical, is a simple substitution reaction which is similar to a major reaction occurring in many O(3P) + unsaturated hydrocarbon reactions. The second channel, which becomes more important at higher collision energies, is the production of a long-lived adduct, that is, the O-benzene triplet adduct appears to undergo collisionless intersystem crossing and rearrangement to singlet phenol which is sufficiently stable to live more than a millisecond in the absence of collisions and reaches the detector as an adduct. These results raise the question of when intersystem crossing will compete effectively with decomposition of the triplet adduct. The reaction of oxygen atoms with acetylene appears to involve similar processes.