Solubility of Water in a Benzene−Cyclohexane Mixture[†]

Sudha Dorairaj,[‡] Jonggu Jeon,[‡] and Hyung J. Kim*

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213-2683

Received: June 30, 2005; In Final Form: November 11, 2005

The solubility of a water molecule in a binary mixture of nonpolar cyclohexane and quadrupolar benzene is studied with the ab initio method. A novel self-consistent reaction field theory that properly accounts for benzene quadrupole moments in the continuum solvent framework is used to describe the solvation effects of the solvent mixture. The free energy of transfer from pure cyclohexane to the mixture solvent is obtained with the neglect of nonelectrostatic contributions. A reasonable agreement with experiments indicates that the theoretical method presented here provides a promising approach to electronic structure calculations in quadrupolar solvents and their mixtures with nonpolar solvents.

1. Introduction

It has been well-known that nondipolar or nearly nondipolar solvents with large molecular quadrupolar moments, hereafter referred to as quadrupolar solvents, offer a significantly polar medium for chemical processes. Examples include benzene, toluene, dioxane, dense carbon dioxide, etc. Despite their small dielectric constant, i.e., $\epsilon_0 \sim 2$ under liquid conditions, their empirical polarity scales, e.g., $E_T(30)$ and π^*, are comparable to those of weakly or moderately dipolar solvents with $\epsilon_0 \approx 4-8$, such as diethyl ether and tetrahydrofuran.[1] Also the quadrupolar solvents show substantive outer-sphere reorganization and solvation stabilization for many charge-transfer reactions[2−7] and significant spectral diffusion in various time-resolved spectroscopies.[8−10] Thus, the characteristics of their solvation free energetics and dynamics are very similar to those of conventional dipolar solvents.

Recently, Jeon and Kim have constructed a novel continuum theory with account of solvent quadrupole moments.[11−13] To be specific, they extended the conventional dielectric continuum description of dipolar solvents to include solvation effects arising from solvent quadrupole moments by treating the quadrupole density as an explicit field variable. Hereafter, this formulation is referred to as the continuum quadrupolar solvent (CQS) theory. Its applications to several charge-transfer systems[14,15] show that solvent quadrupoles play an important role in equilibrium and nonequilibrium reaction free energetics and dynamics, consonant with molecular theory predictions.[16−18] Also, through minor modifications of existing self-consistent reaction field (SCRF) quantum chemistry algorithms,[19] CQS allows ab initio electronic structure calculations for solute molecules under equilibrium solvation conditions in quadrupolar solvents.[11] In ref 11, this similarity to SCRF was used extensively to analyze solvation of small molecules with the Hartree−Fock (HF) and complete active space self-consistent field (CASSCF) methods in the point dipole approximation of the solute charge distributions.

In this article, we apply the CQS description to study solvation in binary mixtures of nonpolar[20] and quadrupolar solvents. It has been found that quadrupolar solvents, when mixed with nonpolar solvents[20] of comparable dielectric constants, enhance the effective polarity of the medium considerably even at small concentrations, analogous to the effect produced by dipolar solvents.[21,22] One well studied example is kinetics of Menshutkin reactions.[22] When benzene is added as a cosolvent to cyclohexane, the reaction rate between, e.g., triethylamine and iodomethane in the mixture increases rapidly with the mole fraction of benzene. Its rate constant in pure benzene is larger than that in pure cyclohexane by nearly 4 orders of magnitude.[22] Another example is the solubility of water, which was found to increase with the benzene concentration in the binary mixture of benzene and cyclohexane.[21] In the present study, we investigate the free energy of transfer of a water molecule from pure cyclohexane to benzene-cyclohexane mixture using ab initio methods in the CQS description. Higher 2^l-multipole moments of the solute charge distribution up to $l = 6$ are included in the electronic structure calculations.

The outline of this paper is as follows: In section 2, we briefly review the CQS formulation of pure quadrupolar solvents[11−13] and extend it to describe binary mixtures of nonpolar and quadrupolar solvents. Its application to solvation of a water molecule in benzene-cyclohexane mixtures is considered in section 3. There the free energy of transfer from neat cyclohexane to the mixtures is obtained as a function of the benzene mole fraction at the HF and CASSCF levels and compared with measurements.[21] Concluding remarks are offered in section 4.

2. Continuum Quadrupolar Solvent Theory

2.1. Hamiltonian. In the CQS formulation of refs 11−13, a polarizable, nondipolar but quadrupolar solvent is characterized by quadrupolarization Q, defined as the density of solvent quadrupole moments, and the usual dipolarization $\mathbf{P}_{\rm el}$ arising from the induced solvent dipole moments.[12] The total Hamiltonian $\hat{H}$ for a solute placed in a cavity immersed in the solvent medium is (see ref 12 for details)

[†] Part of the special issue “Donald G. Truhlar Festschrift”.

* To whom all correspondence should be addressed.

[‡] Present address: Department of Chemistry, University of California, Davis, CA 95616.

10.1021/jp053578+ CCC: $33.50

$$\hat{H} = \hat{H}^0 + \frac{1}{2\chi_{\mathrm{el}}}\int^V \mathrm{d}\mathbf{r}\, |\mathbf{P}_{\mathrm{el}}(\mathbf{r})|^2 + \frac{1}{2}\int^V \mathrm{d}\mathbf{r}\int^V \mathrm{d}\mathbf{r}'\, \mathbf{P}_{\mathrm{el}}(\mathbf{r})\cdot\left[\nabla\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\cdot\mathbf{P}_{\mathrm{el}}(\mathbf{r}') - \int^V \mathrm{d}\mathbf{r}\, \mathbf{P}_{\mathrm{el}}(\mathbf{r})\cdot\hat{\epsilon}(\mathbf{r}) + \frac{1}{6C_{\mathrm{Q}}}\int^V \mathrm{d}\mathbf{r}\, Q(\mathbf{r}) :\ Q(\mathbf{r}) + \frac{1}{3}\int^V \mathrm{d}\mathbf{r}\int^V \mathrm{d}\mathbf{r}'\, \mathbf{P}_{\mathrm{el}}(\mathbf{r})\cdot\left[\nabla\nabla'\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] :\ Q(\mathbf{r}') + \frac{1}{18}\int^V \mathrm{d}\mathbf{r}\int^V_{\mathbf{r}'\neq\mathbf{r}} \mathrm{d}\mathbf{r}'\, Q(\mathbf{r}) : \left[\nabla\nabla\nabla'\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right] : Q(\mathbf{r}') - \frac{1}{3}\int^V \mathrm{d}\mathbf{r}\, Q(\mathbf{r}) :\ \nabla\hat{\epsilon} \quad (1)$$

where the carat means an operator, $\int^V$ indicates that the integrations are restricted to the volume outside the cavity and the colon denotes contraction over two indices of the tensor quantities involved. The first term on the right-hand side of eq 1 is the Hamiltonian $\hat{H}^\circ$ for the isolated solute. The next three terms there represent, in sequence, free energy cost for inducing $\mathbf{P}_{\mathrm{el}}$, interactions between $\mathbf{P}_{\mathrm{el}}$ at different positions in the medium, and interaction of $\mathbf{P}_{\mathrm{el}}$ with the electric field $\hat{\epsilon}$ arising from the solute charge distribution. They describe the effects of the solvent induced dipole moments in the continuum description. We note that there are no contributions from the solvent permanent dipole moments because the solvent is nondipolar. The rest of the terms in eq 1 which involve Q describe the additional contribution arising from the quadrupolar nature of the solvent. They are, respectively, the free energy cost for inducing Q, interactions between $\mathbf{P}_{\mathrm{el}}$ and Q, interactions between Q at different points in the medium, and interaction of Q with the solute electric field gradient $\nabla\hat{\epsilon}$. C_{Q} is a quadrupolar susceptibility which gauges the degree of quadrupolarization, analgous to the dielectric susceptibility χ_{el} associated with $\mathbf{P}_{\mathrm{el}}$. The optical dielectric constant ϵ_∞ and χ_{el} are related by $\epsilon_\infty = 1 + 4\pi\chi_{\mathrm{el}}$. We note that the short-range orientational and positional correlations between the solvent molecules are not reflected in eq 1 just like the conventional dielectric continuum descriptions. Also the short-range solute−solvent interactions are not included in $\hat{H}$ although account of quantum correlations[23] between the solute electronic degrees of freedom and solvent electronic polarization $\mathbf{P}_{\mathrm{el}}$ lead to their dispersion interactions.[13,24,25]

2.2. Equilibrium Free Energy. The free energy G for the solute−solvent system can be obtained via the expectation value of $\hat{H}$ in eq 1 with the solute wave function Ψ, i.e., $G = \langle\Psi|\hat{H}|\Psi\rangle$.[26−29] Since $\mathbf{P}_{\mathrm{el}}$ and Q are arbitrary, the free energy thus obtained describes a general nonequilibrium situation. In the special case of equilibrium solvation, both Q and $\mathbf{P}_{\mathrm{el}}$ become equilibrated to the solute charge distribution. This is effected via the free energy minimization with respect to $\mathbf{P}_{\mathrm{el}}$ and Q, viz., $\partial G/\mathbf{P}_{\mathrm{el}} = 0$ and $\partial G/\partial Q = 0$. The resulting solutions determine equilibrium solvation with free energy G_{eq}. In the special case of a spherical cavity for the solute, G_{eq} is given by

$$G_{\mathrm{eq}} = \langle\Psi|\hat{H}^0|\Psi\rangle + \Delta G^{\mathrm{P}}_{\mathrm{eq}} + \Delta G^{\mathrm{Q}}_{\mathrm{eq}}; \quad \Delta G^{\mathrm{P}}_{\mathrm{eq}} = -\frac{1}{2}\sum_{lm} R^{(l)}_{\mathrm{P}}\, |\varphi_{lm}|^2; \quad \Delta G^{\mathrm{Q}}_{\mathrm{eq}} = -\frac{1}{2}\sum_{lm} R^{(l)}_{\mathrm{Q}}\, |\varphi_{lm}|^2 \quad (2)$$

where φ_{lm} is the expectation value of the 2^l-multipole tensor operator $\hat{\varphi}_{lm}$

$$\varphi_{lm} = \langle\Psi|\hat{\varphi}_{lm}|\Psi\rangle; \quad \hat{\varphi}_{lm} \equiv \sqrt{\frac{4\pi}{2l+1}}\int \mathrm{d}\mathbf{x}\, x^l\, \hat{\rho}_0(\mathbf{x})\, Y^*_{lm}(\theta_x,\phi_x) \quad (3)$$

associated with the solute charge density operator $\hat{\rho}_0$ and spherical harmonics Y_{lm} and the reaction field factors $R^{(l)}_{\mathrm{P}}$ and $R^{(l)}_{\mathrm{Q}}$

$$R^{(l)}_{\mathrm{P}} = \frac{(l+1)(\epsilon_\infty - 1)}{(l+1)\epsilon_\infty + l}\,\frac{1}{a^{2l+1}}; \quad R^{(l)}_{\mathrm{Q}} = \frac{4\pi(l+1)(l+2)(2l+1)}{3\epsilon_\infty[(l+1)\epsilon_\infty + l]}\,\frac{\kappa^2 C_{\mathrm{Q}}}{S_l} F_l(\kappa a)\,\frac{1}{a^{2l+1}} \quad (4)$$

characterize respective strengths of $\mathbf{P}_{\mathrm{el}}$ and Q responses to φ_{lm} of the solute located at the center of the cavity of radius a. $\Delta G^{\mathrm{P}}_{\mathrm{eq}}$ and $\Delta G^{\mathrm{Q}}_{\mathrm{eq}}$ in eq 2 are, respectively, the contributions from equilibrated $\mathbf{P}_{\mathrm{el}}$ and Q to solvation free energy ΔG_{solv} defined as the difference between G_{eq} and the solute ground-state energy E° in a vacuum

$$\Delta G_{\mathrm{solv}} = G_{\mathrm{eq}} - E^0 \quad (5)$$

We point out that nonelectrostatic contributions to G_{eq}, e.g., cavitation free energy and short-range solute−solvent interactions,[19] are not included in eq 5.

In eq 4, κ determined by

$$\kappa^2 C_{\mathrm{Q}} = \frac{3}{32\pi}[(35 - 12\eta) + \sqrt{1225 - 280\eta + 144\eta^2}]; \quad \eta = \left(1 - \frac{1}{\epsilon_\infty}\right)^{-1} \quad (6)$$

measures the extent of screening of the solute electric field by Q equilibrated to the solute charge distribution, the S_l factor being given by

$$S_l = \frac{1}{(2l+1)\epsilon_\infty}\left[(l+1)\epsilon_\infty + l + \frac{4\pi}{3} l\,(l-1)\kappa^2 C_{\mathrm{Q}}(\kappa a)^l \beta_l(\kappa a)\, k_{l-1}(\kappa a) + \left(1 - \frac{16\pi}{35}\kappa^2 C_{\mathrm{Q}}\right) l(\kappa a)^{l+1}\beta_l(\kappa a)\, k_l(\kappa a)\right] \quad (7)$$

describes the cavity boundary effect, and $F_l(\kappa a)$ defined as

$$F_l(y) \equiv 1/y^2 + [y^l/(2l+1)]\, \beta_l(y)\, k_{l+1}(y); \quad \zeta \equiv 1 - \frac{16\pi}{105}\kappa^2 C_{\mathrm{Q}} \quad (8)$$

gauges the short-range effect of the solute−quadrupole interactions, compared to solute-dipole interactions. Here $k_l(z)$, $k^d_l(z)$, and $\beta_l(z)$ are related to modified Bessel functions $K_n(z)$

$$k_l(z) = \sqrt{\frac{2}{\pi z}} K_{l+1/2}(z); \quad k^d_l(z) = \frac{l}{z}k_l(z) - k_{l+1}(z); \quad \beta_l(z) = (l+1)(l+2)z^{-(l+3)}\left[\frac{l+1}{2l+1}k^d_{l+1}(z) + \frac{l}{2l+1}k^d_{l-1}(z) + \frac{16\pi}{105}\kappa^2 C_{\mathrm{Q}} k_l(z)\right]^{-1} \quad (9)$$

We note that $R^{(l)}_{\mathrm{Q}}$ varies not only with C_{Q} but also with ϵ_∞. For a detailed derivation of the results in eqs 2−9, the reader is referred to ref 12.

2.3. Self-Consistent Field Method. In the dielectric continuum approach, the solute electronic structure in solution is often determined via the SCRF method. Briefly, the nonlinear Schrödinger equation obtained through variational minimization of the equilibrium free energy with respect to the solute wave function Ψ is solved in a self-consistent fashion.[19] An analogous approach applied to CQS at equilibrium, i.e., eq 2, yields a similar nonlinear Schrödinger equation[11,12]

$$\hat{H}^0|\Psi\rangle - \frac{1}{2}\sum_{lm}(R_{\mathrm{P}}^{(l)}(\epsilon_\infty) + R_{\mathrm{Q}}^{(l)}(\epsilon_\infty, C_{\mathrm{Q}}))[\langle\Psi|\hat{\varphi}_{lm}^\dagger|\Psi\rangle\,\hat{\varphi}_{lm}|\Psi\rangle + \langle\Psi|\,\hat{\varphi}_{lm}|\Psi\rangle\,\hat{\varphi}_{lm}^\dagger|\Psi\rangle] = E_{\mathrm{eq}}|\Psi\rangle \quad (10)$$

which we refer to as self-consistent quadrupolar reaction field (SCQRF) theory of solute electronic structure. In ref 11, Jeon and Kim introduced an apparent dielectric constant ϵ_{app} for quadrupolar solvents as

$$R_{\mathrm{P}}^{(1)}(\epsilon_{\mathrm{app}}) \equiv R_{\mathrm{P}}^{(1)}(\epsilon_\infty) + R_{\mathrm{Q}}^{(1)}(\epsilon_\infty, C_{\mathrm{Q}}) \quad (11)$$

to gauge their capability of solvating dipolar solutes in a spherical cavity, viz., solvent influence arising from both $\mathbf{P}_{\mathrm{el}}$ and Q on $l = 1$ components of φ_{lm}. With eq 11, one can rewrite eq 10 for $l = 1$ as

$$\hat{H}^0|\Psi\rangle - \frac{1}{2}(R_{\mathrm{P}}^{(1)}(\epsilon_\infty) + R_{\mathrm{Q}}^{(1)}(\epsilon_\infty, C_{\mathrm{Q}}))\sum_m[\langle\Psi|\hat{\varphi}_{1m}^\dagger|\Psi\rangle\hat{\varphi}_{1m}|\Psi\rangle + \langle\Psi|\hat{\varphi}_{1m}|\Psi\rangle\hat{\varphi}_{1m}^\dagger|\Psi\rangle] = \hat{H}^0|\Psi\rangle - \frac{1}{2}R_{\mathrm{P}}^{(1)}(\epsilon_{\mathrm{app}})\sum_m[\langle\Psi|\hat{\varphi}_{1m}^\dagger|\Psi\rangle\hat{\varphi}_{1m}|\Psi\rangle + \langle\Psi|\,\hat{\varphi}_{1m}|\Psi\rangle\hat{\varphi}_{1m}^\dagger|\Psi\rangle] = E_{\mathrm{eq}}|\Psi\rangle \quad (12)$$

which can then be solved using the existing SCRF algorithms[19] without any additional modifications.[11]

To include the effects of solute multipole moments, we generalize eq 11 to higher l

$$R_{\mathrm{P}}^{(l)}(\epsilon_{\mathrm{app}}^{(l)}) \equiv R_{\mathrm{P}}^{(l)}(\epsilon_\infty) + R_{\mathrm{Q}}^{(l)}(\epsilon_\infty, C_{\mathrm{Q}}) \quad (13)$$

$\epsilon_{\mathrm{app}}^{(l)}$ in eq 13 defines an effective dielectric constant of quadrupolar solvents, measuring their solvating power of solutes whose charge distributions are characterized by 2^{l}-multipole moments. With $\epsilon_{\mathrm{app}}^{(l)}$, we recast SCQRF eq 10 as

$$\hat{H}^0|\Psi\rangle - \frac{1}{2}\sum_{lm}R_{\mathrm{P}}^{(l)}(\epsilon_{\mathrm{app}}^{(l)})[\langle\Psi|\hat{\varphi}_{lm}^\dagger|\Psi\rangle\hat{\varphi}_{lm}|\Psi\rangle + \langle\Psi|\hat{\varphi}_{lm}|\Psi\rangle\hat{\varphi}_{lm}^\dagger|\Psi\rangle] = E_{\mathrm{eq}}|\Psi\rangle \quad (14)$$

We note that except for the l dependence of $\epsilon_{\mathrm{app}}^{(l)}$, the structure of eq 14 is identical to that of the conventional SCRF theory in the multipole expansion approach.[19] Thus, we can perform SCQRF calculations, in principle, to arbitrary order in l by modifying SCRF algorithms to account for the l-dependent apparent dielectric constants. In section 3 below, we will extensively utilize this near isomorphism between the SCRF and SCQRF to do electronic structure calculations for a water molecule solvated in cyclohexane−benzene mixtures.

We note that the importance of solvent quadrupoles in solubility was recognized in a previous SCRF study.[30] There it was effected by scaling down the solute cavity size. This strengthens in effect the solute−solvent electrostatic interactions and thus mimics the additional stabilization arising from solvent quadrupole moments. By contrast, the effective solvent polarity is enhanced in the CQS theory, so that electrostatic interactions of the solute charge distributions with solvent quadrupoles are directly accounted for in our approach.

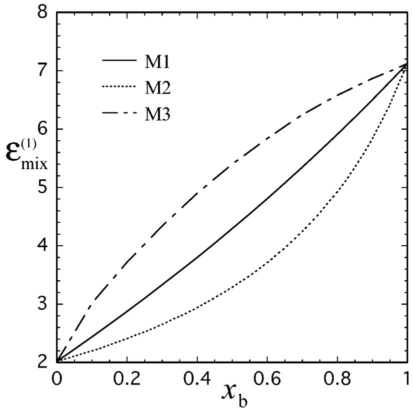

Figure 1. Apparent dielectric constant $\epsilon_{\mathrm{mix}}^{(l)}$ ($l = 1$) of mixture as a function of benzene mole fraction x_{b}: M1 (method 1); M2 (method 2): M3 (method 3). The cavity radius employed in the calculations is $a = 2.4$ Å.

2.4. SCQRF for Mixtures. Theoretical analyses of solvation in binary mixtures of nonpolar and polar liquids via a dielectric continuum description are not as extensive as those in pure solvents although the former offer attractive properties, e.g., tunability of medium polarity by merely varying their composition. One of the key issues is the determination of an appropriate dielectric constant ϵ_{mix} for the solvent mixture. One widely used relation is [see, e.g., ref 31]

$$\epsilon_{\mathrm{mix}} = \upsilon_{\mathrm{n}}\epsilon_{\mathrm{n}} + \upsilon_{\mathrm{p}}\epsilon_{\mathrm{p}} \quad (15)$$

where ϵ_{p} and ϵ_{n} are the static dielectric constants of the polar and nonpolar solvent components of the binary mixture, respectively, and υ_{p} and υ_{n} their volume fractions. Recognizing that polarization is defined as the density of solvent dipoles, we can introduce a mild extension of eq 15 as

$$\bar{\upsilon}_{\mathrm{mix}}\epsilon_{\mathrm{mix}} = \bar{\upsilon}_{\mathrm{n}}x_{\mathrm{n}}\epsilon_{\mathrm{n}} + \bar{\upsilon}_{\mathrm{p}}x_{\mathrm{p}}\epsilon_{\mathrm{p}} \quad (16)$$

where $\bar{\upsilon}_{\mathrm{n}}$, x_{n} and $\bar{\upsilon}_{\mathrm{p}}$, x_{p} are the molar volume and mole fraction of the nonpolar and polar neat solvent components, respectively, while $\bar{\upsilon}_{\mathrm{mix}}$ is the molar volume of their mixture. We note that eqs 15 and 16 would become identical if mixing of solvents would not incur any volume changes. A different approach developed by Suppan and co-workers[32,33] posits an ideal mixing of two continuum solvents according to the combination rule

$$R_{\mathrm{P}}^{(1)}(\epsilon_{\mathrm{mix}}) = x_{\mathrm{n}}R_{\mathrm{P}}^{(1)}(\epsilon_{\mathrm{n}}) + x_{\mathrm{p}}R_{\mathrm{P}}^{(1)}(\epsilon_{\mathrm{p}}) \quad (17)$$

and deviations from eq 17 are interpreted as preferential solvation due to dielectric enrichment near the solute molecules. While this method has been applied to solvent spectral shifts for various chromophores with success,[32−36] the definition of ideal mixing, viz., eq 17, is empirical in a strict sense [cf. Figure 1 below]. Therefore, dielectric enrichment couched in terms of deviations from eq 17 and related preferential solvation seem rather arbitrary. It should be noted that eqs 15 and 17 yield considerably different results for ϵ_{mix} for the mixtures [see Figure 1 below].[32]

In the absence of a firm continuum framework for binary mixtures—even for those involving dipolar solvents, we employ analogues of eqs 16 and 17 to study solvation in the mixture of

TABLE 1: $\epsilon^{(l)}_{\rm app}$ for Pure Benzene

l	1	2	3	4	5	6
$a = 2.2$ Å	7.634	8.112	8.231	8.258	8.290	8.296
$a = 2.4$ Å	7.127	7.509	7.592	7.608	7.622	7.624

TABLE 2: Apparent Dielectric Constant $\epsilon^{(l)}_{\rm mix}$ of Mixture for $l = 1$: M1 (Method 1), M2 (Method 2), and M3 (Method 3)[a]

x_b	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
M1	2.02	2.44	2.88	3.33	3.80	4.30	4.81	5.35	5.91	6.50	7.13
M2	2.02	2.20	2.41	2.65	2.94	3.29	3.71	4.24	4.92	5.84	7.13
M3	2.02	3.02	3.72	4.34	4.90	5.40	5.84	6.25	6.58	6.87	7.13

[a] Cavity radius: $a = 2.4$ Å.

nonpolar cyclohexane and quadrupolar benzene. Specifically, we first determine apparent dielectric constants $\epsilon^{(l)}_{\rm b}$ of pure benzene from eq 13 and substitute the resulting values into

$$\bar{v}_{\rm mix}\epsilon^{(l)}_{\rm mix} = \bar{v}_{\rm c}x_{\rm c}\epsilon_{\rm c} + \bar{v}_{\rm b}x_{\rm b}\epsilon^{(l)}_{\rm b} \quad \text{(method 1)} \tag{18}$$

$$R^{(l)}_{\rm P}(\epsilon^{(l)}_{\rm mix}) = x_{\rm c}R^{(l)}_{\rm P}(\epsilon_{\rm c}) + x_{\rm b}R^{(l)}_{\rm P}(\epsilon^{(l)}_{\rm b}) \quad \text{(method 2)} \tag{19}$$

to obtain the effective l-dependent dielectric constants $\epsilon^{(l)}_{\rm mix}$ for the mixture. Here subscripts c and b denote the cyclohexane and benzene components, respectively. The results are then used in eq 14 for SCQRF electronic structure calculations.

In addition to methods 1 (eq 18) and 2 (eq 19) above, we also consider a linear scaling of the benzene quadrupolar susceptibility $C_{\rm Q,b}$ with $x_{\rm b}$

$$\bar{v}_{\rm mix}C_{\rm Q,mix} = \bar{v}_{\rm b}x_{\rm b}C_{\rm Q,b} \quad \text{(method 3)} \tag{20}$$

where $C_{\rm Q,mix}$ is the quadrupolar susceptibility of the mixture.[37] This is similar to eq 16 in spirit in that the quadrupolarization is given by the local density of solvent quadrupoles.[38] As for the optical dielectric constant of the mixture needed in the evaluation of $R^{(l)}_{\rm Q}$ (see eq 4), we employ a linear combination of the cyclohexane and benzene values analogous to eq 18.

The SCQRF calculations for a water molecule in a spherical cavity were carried out in the aug-cc-pVDZ basis set[39,40] using ab initio HF and CASSCF levels of theory at all mixture compositions with the DALTON[41] program. For both HF and CASSCF calculations, we used the water geometry optimized in the solution phase via the HF method. We employed 12 active space orbitals and 8 active space electrons in the CASSCF calculations as in ref 11. The ϵ_∞ values used in the calculations are 2.02 and 2.24 for pure cyclohexane and benzene, respectively. We employed $C_{\rm Q,b} = 3.56$ Å^2 for pure benzene.[37] We considered two different cavity radii, 2.2 and 2.4 Å. While these values are greater than those commonly used for aqueous solvation,[30,42−45] there is evidence that cavity size for solvation in liquid hydrocarbons is generally larger than in water.[30] For instance, according to the cavity scaling regime of ref 30 (Table 2 there), $a \approx 2.03$ and 2.10 for a water molecule in benzene and cyclohexane, respectively, whereas $a \approx 1.55$ Å in water. In addition, though their parametrizations are well tested with the ab initio and semiempirical methods, most of the existing prescriptions for a are essentially on an ad hoc basis, so that different recipes for evaluations of, e.g., cavitation and/or solute−solvent repulsion and dispersion contributions to solvation could lead to somewhat different cavity radii. Perhaps the most important is that qualitative and even semiquantitative aspects of our results are not influenced by minor uncertainties in the cavity size; i.e., the basic solvation trends we obtained are essentially the same between $a = 2.2$ and 2.4 Å (see below). This seems to indicate that unless the actual cavity size is considerably different from the values employed in the present study, our analysis is robust.

3. Results and Discussion

We begin by considering the apparent dielectric constants of pure benzene and mixture. In Table 1, $\epsilon^{(l)}_{\rm b}$ ($l = 1−6$) determined via eqs 4 and 13 are summarized for two different values of the cavity radius. Because of the short-range nature of electrostatic interactions with solvent quadrupoles, $\epsilon^{(l)}_{\rm b}$ increases with the solute multipole character l and decreases with the cavity size a. This means that as the solute electric field becomes shorter in range, the solvent quadrupolarization plays an increasingly more important role.[12] We point out that in the presence of small cavities, effective polarity of pure benzene ($\epsilon^{(l)}_{\rm b} \sim 7−8$) is comparable to that of moderately dipolar solvents, e.g., tetrahydrofuran ($\epsilon = 7.6$) and dichloromethane ($\epsilon = 8.9$).

The results for the $l = 1$ apparent dielectric constants of the cyclohexane−benzene mixture obtained with three different recipes, eqs 18−20, are compared in Table 2 and exhibited in Figure 1. As noted above, the three methods yield rather different trends for the solvent polarity with the mixture composition. $\epsilon^{(1)}_{\rm mix}$ determined via method 1 (M1) shows a near linear increase with the benzene mole fraction. By contrast, method 2 (M2)[32,33] yields $\epsilon^{(1)}_{\rm mix}$ which is sublinear in $x_{\rm b}$ for small $x_{\rm b}$ but becomes superlinear as $x_{\rm b}$ approaches 1. The behavior of $\epsilon^{(1)}_{\rm mix}$ obtained with method 3 (M3) is opposite of that with M2.

The free energy of transfer $\Delta\Delta G_{\rm tr}$ from pure cyclohexane to benzene-cyclohexane mixture is calculated via

$$\Delta\Delta G_{\rm tr} = \Delta G_{\rm solv,mix} - \Delta G_{\rm solv,c} \tag{21}$$

where $\Delta G_{\rm solv}$ is the solvation free energy introduced in eq 5 above. Since benzene and cyclohexane are “similar” in molecular composition and structure, we would expect that the nonelectrostatic contributions, e.g., cavitation and short-range solute−solvent interactions, to solvation free energy are canceled to a large extent in eq 21 between $\Delta G_{\rm solv,mix}$ and $\Delta G_{\rm solv,c}$.[11] Our SCQRF results obtained with the neglect of nonelectrostatic contributions should be interpreted only in this context, i.e., to understand the *difference* in solubility of water in cyclohexane and in mixture. In view of the fact that $\mathbf{P}_{\rm el}$ solvation strengths are nearly the same for cyclohexane and benzene (recall that their respective ϵ_∞ values are 2.02 and 2.24), solvation stabilization arising from electrostatic interactions with Q present only in pure benzene and mixture solvent is mainly responsible for $\Delta\Delta G_{\rm tr}$.[37]

With this in mind, we consider the results of ab initio SCQRF calculations to multipole order $l = 6$ for a water molecule in the mixture solvent compiled in Tables 3−5. It should be mentioned that the convergence is attained at the $l = 6$ level in the SCQRF calculations with the HF method, so that the inclusion of 2^7-multipole moments or higher has little effect on the numerical results. Regardless of the recipes used to determine the polarity of mixture, solvation free energy $-\Delta G_{\rm solv}$ shows a significant increase with $x_{\rm b}$. For example, with M1, the HF results for $-\Delta G_{\rm solv}$ increase from 1.18 kcal mol^{-1} in pure cyclohexane to 2.11 kcal mol^{-1} in the 50−50 mixture of benzene and cyclohexane. This would correspond to an enhancement of water solubility by a factor of ∼5 in the mixture at room temperature, compared to pure cyclohexane. M3 yields a somewhat bigger increase, 1.16 kcal mol^{-1}, while a 0.6 kcal mol^{-1} increase results from M2. As mentioned above, the

TABLE 3: Solvation Free Energy ΔG_{solv} of Water in Benzene-cyclohexane Mixture and Its Free Energy of Transfer $\Delta\Delta G_{\mathrm{tr}}$ from Cyclohexane to Binary Mixture (HF=Hartree−Fock, CAS=CASSCF)[a,b]

x_b	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$-\Delta G_{\mathrm{solv}}^{\mathrm{HF}}$	1.18	1.47	1.68	1.85	2.00	2.11	2.21	2.30	2.37	2.43	2.49
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{HF}}$	0.00	0.28	0.50	0.67	0.81	0.93	1.03	1.11	1.19	1.25	1.31
$-\Delta G_{\mathrm{solv}}^{\mathrm{CAS}}$	1.11	1.38	1.60	1.77	1.91	2.02	2.12	2.20	2.27	2.34	2.39
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{CAS}}$	0.00	0.28	0.49	0.66	0.80	0.91	1.01	1.09	1.17	1.23	1.29
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{exp}}$	0.00	0.11	0.30	0.44	0.61	0.77	0.88	1.05	1.17	1.30	1.44

[a] The cavity size employed for water is $a = 2.4$ Å and apparent dielectric constants of solvent mixture are determined via method 1. Non- electrostatic contributions to the solvation free energy are ignored in the calculations as explained in the text. Since the solute concentration is fixed in the calculations regardless of the composition of the mixture, $\Delta\Delta G_{\mathrm{tr}}^{\mathrm{exp}}$ is corrected by adding $RT\ \ln(\bar{v}_{\mathrm{mix}}/\bar{v}_{\mathrm{c}})$ to the experimental data,[30] where R and T are the gas constant and temperature. [b] Units for free energy: kcal mol^{-1}.

TABLE 4: ΔG_{solv} and $\Delta\Delta G_{\mathrm{tr}}$ Obtained with Method 2[a]

x_b	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$-\Delta G_{\mathrm{solv}}^{\mathrm{HF}}$	1.18	1.29	1.41	1.53	1.66	1.79	1.92	2.05	2.19	2.34	2.49
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{HF}}$	0.00	0.11	0.23	0.35	0.48	0.60	0.74	0.87	1.01	1.16	1.31
$-\Delta G_{\mathrm{solv}}^{\mathrm{CAS}}$	1.11	1.22	1.33	1.45	1.57	1.70	1.83	1.96	2.10	2.24	2.39
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{CAS}}$	0.00	0.11	0.23	0.34	0.47	0.59	0.73	0.86	0.99	1.14	1.29

[a] Same as in Table 3 except for the method used to determine the apparent dielectric constants.

TABLE 5: ΔG_{solv} and $\Delta\Delta G_{\mathrm{tr}}$ Obtained with Method 3[a]

x_b	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$-\Delta G_{\mathrm{solv}}^{\mathrm{HF}}$	1.18	1.80	2.03	2.17	2.27	2.34	2.39	2.42	2.46	2.48	2.49
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{HF}}$	0.00	0.62	0.85	0.99	1.09	1.16	1.21	1.25	1.27	1.29	1.31
$-\Delta G_{\mathrm{solv}}^{\mathrm{CAS}}$	1.11	1.72	1.95	2.09	2.18	2.25	2.30	2.33	2.36	2.38	2.40
$-\Delta\Delta G_{\mathrm{tr}}^{\mathrm{CAS}}$	0.00	0.61	0.84	0.98	1.08	1.14	1.19	1.23	1.26	1.28	1.29

[a] Same as in Table 3 except for the method used to determine the apparent dielectric constants.

quadrupole moments of benzene in the mixture is mainly responsible for this increase in $-\Delta G_{\mathrm{solv}}$ with x_b. This clearly exposes the role played by solvent quadrupole moments in stabilizing solute molecules through Coulombic interactions.[11] Though not presented here, the ab initio results with $a = 2.2$ Å show the same trend as those with $a = 2.4$ Å in Tables 3−5. The only difference between the two is that solvation stabilization is somewhat larger for the former than for the latter. For instance, the respective $-\Delta G_{\mathrm{solv}}$ values in pure cyclohexane and pure benzene at the HF level are 1.65 and 3.53 kcal mol^{-1} with $a = 2.2$ Å, whereas they are 1.18 and 2.49 kcal mol^{-1} with $a = 2.4$ Å.

In Figure 2, the HF results with $a = 2.4$ Å for $\Delta\Delta G_{\mathrm{tr}}$ obtained with M1, M2, and M3 are compared. The CASSCF results are nearly the same as the HF results and thus are not shown. The main reason for the good agreement between HF and CASSCF is that their difference in solvation free energy ΔG_{solv} is largely canceled in the free energy of transfer in eq 21 between cyclohexane and mixture. The experimental results by Goldman and Krishnan[21] are also presented in Figure 2. We notice that their measured value for $-\Delta\Delta G_{\mathrm{tr}}$ at $x_b = 1$ is slightly larger than the corresponding SCQRF result. While exact agreement between the two can be obtained by reducing the cavity size in the calculations (by 0.07 Å or so), we refrain from doing this here because it does not influence the qualitative and semiquantitative aspects of our analysis (see above).

We observe that $\Delta\Delta G_{\mathrm{tr}}$ decreases with increasing x_b; i.e., a water molecule becomes better stabilized as the benzene mole fraction of the solvent mixture grows. As mentioned above, this arises from electrostatic interactions between the water charge distribution and benzene quadrupole moments in our description. This again demonstrates the importance of solvent quadrupole moments in solvation phenomena. We notice that experimental results for $\Delta\Delta G_{\mathrm{tr}}$ decrease almost linearly with x_b. By contrast, ab initio results with three different recipes for $\epsilon_{\mathrm{mix}}^{(1)}$ show a varying degree of nonlinearity in the $\Delta\Delta G_{\mathrm{tr}}$ trend. To be specific, among the three methods, M3 yields the most nonlinear behavior in $\Delta\Delta G_{\mathrm{tr}}$, showing a rather pronounced deviation from near linear experimental results. For example, the difference in $\Delta\Delta G_{\mathrm{tr}}$ between M3 and experiments is about 0.6 kcal mol^{-1} for $x_b = 0.2-0.3$. This means that in this x_b range, the M3 prediction for Henry's law constant for water would be about 3 times larger than experiments under ambient conditions. In view of the approximate nature of M3,[38] this is not surprising. The nonlinear behavior of $\Delta\Delta G_{\mathrm{tr}}$ is considerably weaker for M1 and M2 than that for M3. Therefore, while M1 and M2 tend to over- and underestimate the solvation stabilization for mixture, respectively, they both show decent agreement with experiments. The maximum deviation of the M1 results for $\Delta\Delta G_{\mathrm{tr}}$ from measurements is about 0.23 kcal mol^{-1} when $x_b = 0.3$. The largest discrepancy between M2 and experiments is 0.17 kcal mol^{-1} at $x_b = 0.5$. Considering various assumptions invoked in the development the SCQRF formulation[12] and also uncertainties involved in actual measurements, we feel that this level of agreement between theory and experiment is quite reasonable. It is interesting that M2 yields somewhat better agreement with measurements than M1 even though the former lacks theoretical justification. However, this state of affairs could change if cavity size alterations with the benzene concentration are included (see below).

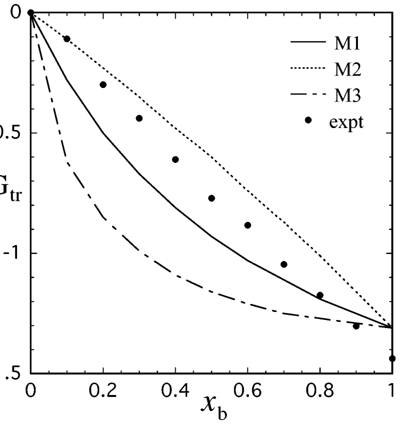

Figure 2. Free energy of transfer (units: kcal mol^{-1}) from cyclohexane to cyclohexane−benzene mixture as a function of benzene mole fraction. The SCQRF calculations are performed to $l = 6$ at the HF level with $a = 2.4$ Å: M1 (method 1); M2 (method 2): M3 (method 3). Experimental results (●) of ref 21 are also shown. The CASSCF results are nearly the same as the HF and thus are not presented here.

For perspective, we consider several aspects of solvation that are not included in our description. First, the cavity radius a is assumed to be fixed, so that its variations with the mixture composition is neglected in our calculations as noted above. Since benzene is denser than cyclohexane, the actual cavity size would be smaller in the former than in the latter.[30] To generalize this somewhat, we would expect that a in the mixture would decrease as x_b increases. In view of the a dependence in the reaction field factors (eq 4), this would have a nonnegligible effect on solvation free energy and its trend with x_b. Specifically, with account of cavity size variations, solvation stabilization would be, relatively speaking, enhanced for large x_b but reduced

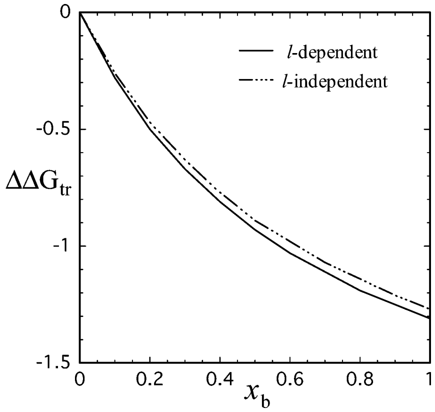

Figure 3. Comparison of $\Delta\Delta G_{tr}$ (in units of kcal mol^{-1}) obtained with *l*-dependent (−) and *l*-independent (- ··· -) apparent dielectric constants at the HF level. Method 1 is used to determine apparent dielectric constants of the mixture with $a = 2.4$ Å.

for small x_b, compared to the case of fixed *a*. This could further improve the agreement between measurements and SCQRF calculations in the $\Delta\Delta G_{tr}$ trend with x_b. On a related issue, the short-range solute−solvent interactions and cavitation ignored in the present study could make a nonnegligible contribution to $\Delta\Delta G_{tr}$, especially when the cavity size varies with x_b. Another aspect not included is preferential solvation.[32−36] However, a nearly linear increase in water solubility with the benzene concentration observed in the experiments[21] seems to imply that, at least for the present case, there is little preferential solvation; i.e., enrichment of benzene near water is not significant.

Before we conclude, we briefly consider the *l* dependence of the apparent dielectric constants for quadrupolar solvents. To gain insight into this, we calculated $\Delta\Delta G_{tr}$ by assuming that $\epsilon_{mix}^{(l)}$ does *not* vary with *l*. In Figure 3, the HF results thus obtained, i.e., by using the value of the $l = 1$ apparent dielectric constant for all $\epsilon_{mix}^{(l)}$ ($l = 1-6$) in eq 14, are compared with the accurate SCQRF predictions with *l*-dependent dielectric constants. While the latter yield better solvation stabilization of water in mixture and in pure benzene than the former due to the short-range character of quadrupolar interactions, their difference is numerically insignificant. The maximum discrepancy in $\Delta\Delta G_{tr}$ between the two methods is less than 0.1 kcal mol^{-1}. Since variations of apparent dielectric constants of benzene with *l* are not that substantial and multipole moments of water are not that large, the *l* dependence of $\epsilon_b^{(l)}$ does not have any significant numerical consequence for solvation of water.[46] This leads to an interesting possibility that one can perform ab initio calculations in quadrupolar solvents by treating them as regular dipolar solvents. The polarity of these effective dipolar solvents should be determined by eq 13, where *l* is the first nonvanishing multipole moment of solutes. In this case, one can employ any SCRF algorithms,[19] such as multipole expansions used in the present study or polarizable continuum model (PCM). This would provide an attractive avenue for electronic structure calculations in quadrupolar solvents.

4. Concluding Remarks

In this article, we extended the SCQRF formulation by Jeon and Kim[11] to include 2^l-multipole moments of the solute charge distribution in solvation calculations in quadrupolar solvents. This was effected via *l*-dependent apparent dielectric constants that measure the ability of quadrupolar solvents to solvate 2^l-multipoles. The resulting description is nearly identical to the existing SCRF theory[19] of electronic structure in polar solvents in the multipole expansion approach.

We applied the extended theory to study solvation of a water molecule in cyclohexane, benzene and their mixture via ab initio methods using the DALTON program.[41] The convergence in the SCQRF electronic structure calculations at the HF level was obtained at $l = 6$. By employing three different methods to determine the apparent dielectric constants for the mixture, we calculated the solvation free energy and related free energy of transfer from pure cyclohexane to mixture at the HF and CASSCF levels. We found that solvation free energy in the mixture increases with increasing benzene concentration. This is in good accord with measurements.[21] It was also found that the HF and CASSCF results for $\Delta\Delta G_{tr}$ are nearly the same because their difference in the solvation free energy results are largely canceled in the evaluation of free energy of transfer.

Our study here and an earlier investigation by Jeon and Kim[11] demonstrate that the SCQRF formulation couched in apparent dielectric constants provides a promising theoretical framework to perform ab initio calculations of solute electronic structure in quadrupolar solvents. Good agreement with solubility measurements found in this study, as well as previous successes in describing electron-transfer reaction free energetics and kinetics,[14,15] suggests that the apparent dielectric constants capture quantitatively the effective polarity of quadrupolar solvents and their binary mixtures with nonpolar solvents. Furthermore, since the *l* dependence of the apparent dielectric constants is of minor importance for solute molecules like water,[46] one can combine leading-order apparent dielectric constants determined via the CQS theory with any existing SCRF algorithms[19] to study solute electronic structure in benzene and its mixture with nonpolar solvents. It would thus be worthwhile in the future to study other solvent systems, such as supercritical CO_2, to further explore and test this possibility. If this is indeed borne out, it would be extremely desirable, though challenging, to extend the present CQS formulation to nonspherical cavities and implement it via SCRF algorithms, e.g., PCM. For accurate quantitation of solvation free energy and related solubility, the incorporation of the cavity size variations with the composition and inclusion of nonelectrostatic contributions to solvation free energy would also be worthy of efforts.

Acknowledgment. This work was supported in part by NSF Grant No. CHE-0098062.

References and Notes

(1) See, e.g.: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Verlag Chemie: Weinheim, Germany, 1988.
(2) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080.
(3) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429.
(4) Chatterjee, S.; Davis, P. D.; Gottschalk, P.; Kurz, M. E.; Sauerwein, B.; Yang, X.; Schuster, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 6329.
(5) Asahi, T.; Ohkohchi, M.; Matsusaka, R.; Mataga, N.; Zhang, R. P.; Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1993**, *115*, 5665.
(6) Read, I.; Napper, A.; Kaplan, R.; Zimmt, M. B.; Waldeck, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 10976.
(7) Kauffman, J. F. *J. Phys. Chem. A* **2001**, *105*, 3433. Khajehpour, M.; Kauffman, J. F. *J. Phys. Chem. A* **2001**, *105*, 10316.
(8) Berg, M. *Chem. Phys. Lett.* **1994**, *228*, 317.
(9) Reynolds, L.; Gardecki, J. A.; Frankland, S. J. V.; Horng, M. L.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 10337.
(10) Larsen, D. S.; Ohta, K.; Fleming, G. R. *J. Chem. Phys.* **1999**, *111*, 8970.
(11) Jeon, J.; Kim, H. J. *J. Solution Chem.* **2001**, *30*, 849.
(12) Jeon, J.; Kim, H. J. *J. Chem. Phys.* **2003**, *119*, 8606.
(13) Jeon, J.; Kim, H. J. *J. Chem. Phys.* **2003**, *119*, 8626.
(14) Jeon, J.; Kim, H. J. *J. Phys. Chem. A* **2000**, *104*, 9812.
(15) Dorairaj, S.; Kim, H. J. *J. Phys. Chem. A* **2002** *106*, 2322.
(16) Perng, B.-C.; Newton, M. D.; Raineri, F. O.; Friedman, H. L. *J. Chem. Phys.* **1996**, *104*, 7177.

(17) Matyushov, D. V.; Voth, G. A. *J. Chem. Phys.* **1999**, *111*, 3630.

(18) Read, I.; Napper, A.; Zimmt, M. B.; Waldeck, D. H. *J. Phys. Chem. A* **2000**, *104*, 9385.

(19) For reviews, see: Tomasi, J.; Persico, M. *Chem. Rev.* **1994**, *94*, 2027. Rivail, J. L.; Rinaldi, D.; Ruiz-Lopez, M. F. In *Computational Chemistry: Review of Current Trends*; Lecszynsky, J., Ed.; World Scientific: Singapore, 1995. Cramer, C. J.; Truhlar, D. J. *Chem. Rev.* **1999**, *99*, 2161. Amovilli, C.; Barone, V.; Cammi, R.; Cancès, E.; Cossi, M.; Mennucci, B.; Pomelli, C. S.; Tomasi, J. *Adv. Quantum Chem.* **1998**, *32*, 227.

(20) We use the term "nonpolar" to describe solvents whose constituent molecules have vanishing dipole and quadrupole moments in a vacuum, e.g., cyclohexane.

(21) Goldman, S.; Krishnan, T. R. *J. Solution Chem.* **1976**, *5*, 693.

(22) Abbound, J. M.; Douhal, A.; Arín, M. J.; Diez, M. T.; Homan, H.; Guihéneuf, G. *J. Phys. Chem.* **1989**, *93*, 214.

(23) Kim, H. J.; Hynes, J. T. *J. Chem. Phys.* **1992**, *96*, 5088. Kim, H. J.; Bianco, R.; Gertner, B. J.; Hynes, J. T. *J. Phys. Chem.* **1993**, *97*, 1723.

(24) Amovilli, C. *Chem. Phys. Lett.* **1994**, *229*, 244. Amovilli, C.; Mennucci, B. *J. Phys. Chem. B* **1997**, *101*, 1051.

(25) Kim, H. J. *J. Chem. Phys.* **1996**, *105*, 6818.

(26) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966, 979; *Faraday Symp. Chem. Soc.* **1975**, *10*, 60.

(27) Felderhof, B. J. *J. Chem. Phys.* **1977**, *67*, 293.

(28) Calef, D. F.; Wolynes, P. G. *J. Phys. Chem.* **1983**, *87*, 3387.

(29) Lee, S.; Hynes, J. T. *J. Chem. Phys.* **1988**, *88*, 6853.

(30) Amovilli, C.; Floris, F. M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 363.

(31) Hirata, Y.; N. Mataga, M. *J. Phys. Chem.* **1984**, *88*, 3091.

(32) Suppan, P. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 495.

(33) Lerf, C.; Suppan, P. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 963.

(34) Kolling, O. W. *J. Phys. Chem.* **1991**, *95*, 3950; *Trans. Kansas Acad. Sci.* **1997**, *100*, 109.

(35) Cichos, F.; Willert, A.; Rempel, U.; Borczyskowski, C. *J. Phys. Chem. A* **1997**, *101*, 8179.

(36) Khajehpour, M.; Welch, C. M.; Kleiner, K. A.; Kauffman, J. F. *J. Phys. Chem. A* **2001**, *105*, 5372.

(37) Although a cyclohexane molecule can acquire an induced quadrupole moment, it will be considerably smaller in magnitude than the overall quadrupole moment of benzene. Furthermore, we expect that the major solvation stabilization in solvent cyclohexane is due to its induced dipole moments. We thus neglect the induced quadrupole moments of cyclohexane completely in the present study. As for the quadrupolar susceptibility of benzene, we use an empirically determined value that arises mainly from its permanent quadrupolar moment.[11,13.]

(38) Due to the neglect of, e.g., orientational and position correlation of molecules, the approximation that the quadrupolar susceptibility is proportional to the density of quadrupolar molecules provides only a rough estimate for C_Q, even for a pure quadrupolar solvent.[13]

(39) Dunning, J. T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(40) Basis sets were obtained from the Extensible Computational Chemistry Enviroment Basis Set Database as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratoratory, which is part of the Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the US Department of Energy. The Pacific National Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute of the US Department of Energy under contract DE-AC06-76RLO-1830. Contact David Feller or Karen Schuchardt for further information.

(41) Dalton, a molecular electronic structure program, Release 1.2 2001. See http://www.kjemi.uio.no/software/dalton/dalton.html.

(42) Rashin, A. A.; Namboodiri, K. *J. Phys. Chem.* **1987**, *91*, 6003.

(43) Chambers, C. C.; Hawkins, G. D.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem.* **1996**, *100*, 16385.

(44) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.

(45) Li, A.-J.; Nussinov, R. *Proteins* **1998**, *32*, 111.

(46) This also holds for solvation of other molecules, such as acetonitrile, formaldehyde and acetone. See: Dorairaj, S. Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA, 2005.