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Solvation Thermodynamics and Non-Randomness. Part I: Self-Solvation[†]

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The central theme in this series of papers is the development of a coherent and consistent equation-of-state model of fluids in the frame of solvation thermodynamics. Two main ingredients will be used for this purpose: the first will be the successful conductor-like screening model (COSMO) type group-contribution models with their quantum-mechanical description of fluids, and the second, our recent nonrandom hydrogen-bonding (NRHB) equation-of-state framework. The bridge between the two is the quasi-chemical treatment of the nonrandom distribution of molecular entities in the system, a treatment used by Henry Kehiaian in his DISQUAC group-contribution model. In this first part we develop the solvation formalism of NRHB and propose a first approach for turning the COSMO model into an equation-of-state model in a straightforward and consistent manner. Although the formalism is general, the focus is on the self-solvation of fluids. This development permits the calculation of the various components of solvation Gibbs energy, such as the cavitation and charging components or the enthalpic and the entropic ones. It permits, in particular, their study over a broad range of external conditions. The strength of the intermolecular forces and its role on the variation of these components, as well as their interdependence, are critically discussed.

Introduction

Henry V. Kehiaian has developed, among others, one of the most successful group-contribution models, the well-known DISQUAC,[1,2] which is widely used for the prediction of phase equilibria and related properties. DISQUAC is an extended quasi-chemical[3] group contribution model and belongs to the broader family of incompressible-lattice models of the liquid state. Over the years, a large number of functional groups have been considered, and their group-interaction parameters have been determined by Kehiaian and his co-workers. DISQUAC is applicable to systems consisting of groups with known interaction parameters. Kehiaian was alert, however, for a cautious use of these parameters, since changes of the functional group properties may occur due to the intermolecular environment of the group (push−pull effect or proximity effect).

More recently, a significant step forward in solution thermodynamics was doubtlessly the development of the COSMO-RS or COSMOtherm group-contribution model by Klamt and co-workers[4−8] and, subsequently, of the COSMO-SAC model by Sandler and Lin.[9] In these COSMO models, a remarkable distillate of hard-core quantum mechanics and ab initio calculations was succinctly mixed with a group-contribution thermodynamic framework identical again to the quasi-chemical framework.[10] The backbone of the COSMO models allocates them into the broader family of dielectric continuum solvation models. COSMO, then, stands for COnductor-like Screening MOdel. Extension of this backbone approach with a thermodynamic treatment of the molecular interactions led to the COSMO for Realistic Solvation (COSMO-RS) model or to the COSMOtherm model, a truly predictive tool for phase equilibria and related thermodynamic calculations. Particularly important for understanding and utilizing the COSMO models was the segment-activity-coefficient approach as implemented in the COSMO-SAC model.[9] This later approach was another excellent bridge between quantum-chemists and thermodynamicists, especially chemical engineers.

An ever-increasing interest is found in recent literature for the extension of COSMO-type models to equation-of-state models.[10−14] In these attempts, the solvation thermodynamics is combined with widely used equations of state to calculate or even predict phase equilibria and related thermodynamic properties over a relatively extended range of external conditions. As already mentioned, however, an intrinsic component of the COSMO approach is nonrandomness as treated and expressed by the quasi-chemical model. The key question then is: are these equation-of-state extensions fulfilling the basic rules of any consistent nonrandom theory of mixtures?

A first attempt to incorporate in a consistent manner the quasi-chemical theory[3] in an equation-of-state model had appeared in early 1980s[15−17] and is known as the PV model. A preliminary attempt to cast the COSMO approach into a quasi-chemical + equation-of-state framework has also appeared recently.[10] Solvation thermodynamics, however, is not widely used by chemical engineers, although in recent years there is an increasing interest in it, especially in predicting the charging component of the solvation Gibbs energy.[18,19]

The purpose of this work is two-fold: first, to develop a coherent equation-of-state solvation model encompassing the quasi-chemical approach, and second, to compare calculations for both cavitation and charging energy of solvation with the corresponding quantities calculated by a simple but consistent COSMO + equation-of-state model. The first task will involve the derivation of the key solvation equations from NRHB (nonrandom hydrogen-bonding),[20,21] a recent equation-of-state model rooted in the PV model.[17] The second task will involve the derivation of the corresponding solvation equations from a COSMO + equation-of-state model rooted in a recent analogous model.[10] Since we want to perform calculations and make comparisons up to the critical point, we will focus in this first part in the self-solvation of a number of representative fluids.

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The Model

Before proceeding to the solvation formalism, let us recall the main elements of the NRHB model.[20,21] Let us consider a system of N_1 molecules of type 1, N_2 molecules of type 2, ..., N_t molecules of type t, and N_0 empty sites or voids of no screening charge, whose number depends on the external temperature, T, and pressure, p. Each molecule of type i is considered to be divided in r_i equal segments of size υ_i^* (set equal to 9.75 $\text{cm}^3\cdot\text{mol}^{-1}$),[17,20,21] and is characterized by two scaling constants, the hard-core density, $\rho_i^* = 1/\upsilon_{\text{sp},i}^*$, and the average per segment interaction energy, ε_i^*. If M_i is the molar mass of component i, the above constants are related through the equation:

$$r_i\upsilon_i^* = M_i\upsilon_{\text{sp},i}^* = \frac{M_i}{\rho_i^*} \tag{1}$$

The scaling temperature and pressure are related through the equations:

$$p_i^*\upsilon_i^* = kT_i^* = \varepsilon_i^* \tag{2}$$

k being the Boltzmann's constant. The corresponding reduced quantities are defined as the following:

$$\tilde{T}_i = \frac{T}{T_i^*} \qquad \tilde{p}_i = \frac{p}{p_i^*} \tag{3}$$

while for the volume or density of pure component i the following relation holds:

$$\tilde{\upsilon}_i = \frac{1}{\tilde{\rho}_i} = \frac{V_i}{V_i^*} = \frac{r_iN_i + N_0}{r_iN_i} \tag{4}$$

The holes of equal size (the reference size υ^*) are assumed to be noncollapsible. The molecular segments and holes are arranged on a quasi-lattice of coordination number z, set here equal to 10. It is further assumed that an encounter of two segments of empty sites or of one molecular segment and one empty site lead to a zero energy change.

In the case of a mixture, equations analogous to eqs 1 through 4 are obtained by applying the appropriate mixing and combining rules. Quantities pertinent to mixture will be indicated without subscript i. The composition of the mixture may be represented either by the mole fraction

$$x_i = \frac{N_i}{N_1 + N_2 + ... + N_t} = \frac{N_i}{N} \tag{5}$$

or the segment (or volume) fraction

$$\phi_i = \frac{r_iN_i}{r_1N_1 + r_2N_2 + ... + r_tN_t} = \frac{r_iN_i}{rN} \tag{6}$$

or the (contact) surface area fraction

$$\theta_i = \frac{q_iN_i}{q_1N_1 + q_2N_2 + ... + q_tN_t} = \frac{q_iN_i}{qN} \tag{7}$$

where zq_i is the total number of external contacts per molecule i. A measure of the sphericity or compactness of the molecule is obtained through Stavermann's parameter,[22] defined by the equation:

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \tag{8}$$

When the molecule is linear, $l_i = 0$. In NRHB the intermolecular interactions are divided into physical and chemical or hydrogen-bonding interactions.

By adopting the picture and nomenclature of Ben-Naim[23] for the solvation process, we may write for the chemical potential of component i in our mixture

$$\mu_i(T, P, \{N\}) = \mu_i^*(T, P, \{N\}) + kT\ln(\rho_i\Lambda_i^3) \tag{9}$$

The first term at the right-hand side of this equation is the so-called "pseudo-chemical" potential of molecule i at a fixed location in the mixture. The second term is the "liberation" free-energy, namely, the work gained after releasing the molecule from its fixed location. ρ_i in eq 9 is the number density (N_i/V) and Λ_i the de Broglie's wavelength of component i. $\{N\} = N_1, N_2, ..., N_t$ is a concise description of the constitution of the mixture. The solvation Gibbs energy is then given by:[18,23]

$$\begin{aligned}\Delta G_i^{*S}(T, P, \{N\}) = \mu_i^*(T, P, \{N\}) - \mu_i^{*\text{IG}}(T, P) = \\ RT\ln(\Phi_iZ) = \mu_i(T, P, \{N\}) - \mu_i^{\text{IG}}(T, P, \{N\}) + RT\ln Z\end{aligned} \tag{10}$$

The superscript IG stands for ideal gas state, while Φ_i is the fugacity coefficient of component i and Z is the compressibility factor

$$Z = \frac{pV}{NRT} \tag{11}$$

The NRHB model may provide with the expressions for the chemical potential in the mixture, or:

$$\begin{aligned}\frac{\mu_i}{RT} = \ln\frac{\phi_i}{\omega_ir_i} - r_i\sum_j\frac{\phi_jl_j}{r_j} + \ln\tilde{\rho} + \\ r_i(\tilde{\upsilon} - 1)\ln(1 - \tilde{\rho}) - \frac{z}{2}r_i\left[\tilde{\upsilon} - 1 + \frac{q_i}{r_i}\right]\ln\left[1 - \tilde{\rho} + \frac{q}{r}\tilde{\rho}\right] + \\ \frac{zq_i}{2}\left[\ln\Gamma_{ii} + \frac{r_i}{q_i}(\tilde{\upsilon} - 1)\ln\Gamma_{00}\right] + r_i\frac{\tilde{P}\tilde{\upsilon}}{\tilde{T}} - \frac{q_i}{\tilde{T}_i} + \frac{\mu_{i,\text{H}}}{RT}\end{aligned} \tag{12}$$

where ω_i is a characteristic quantity for each fluid that takes into account the flexibility and the symmetry of the molecule, and Γ_{ii} and Γ_{00} are the nonrandomness factors[17,20,21] for the distribution of molecular segment i around a central segment i and for the distribution of an empty site around a central empty site, respectively. The hydrogen-bonding contribution to the chemical potential is given by:

$$\frac{\mu_{i,\mathrm{H}}}{RT} = r_i\nu_\mathrm{H} - \sum_{\alpha=1}^{m} d_\alpha^i \ln\frac{\nu_\mathrm{d}^\alpha}{\nu_{\alpha0}} - \sum_{\beta=1}^{n} a_\beta^i \ln\frac{\nu_\mathrm{a}^\beta}{\nu_{0\beta}} \qquad (13)$$

where ν_H is the total number of hydrogen bonds per segment, $d_\alpha{}^i$ is the number of donors of type α in molecule i, $a_\beta{}^i$ is the number of acceptors of type β in molecule i, $\nu_\mathrm{d}{}^\alpha$ the number of donors of type α per segment, $\nu_\mathrm{a}{}^\beta$ the number of acceptors of type β per segment, and

$$\nu_{i0} = \nu_\mathrm{d}^i - \sum_{j=1}^{n} \nu_{ij} \qquad (14)$$

$$\nu_{0j} = \nu_\mathrm{a}^j - \sum_{i=1}^{m} \nu_{ij} \qquad (15)$$

ν_{ij} being the number of hydrogen bonds between donor i and acceptor j per segment.

The chemical potential for the ideal gas is given by:

$$\frac{\mu_i^\mathrm{IG}}{RT} = \left(l_i - r_i\frac{l}{r} - \ln\omega_i^\mathrm{IG} + \ln\frac{v^*}{RT}\right) + \ln x_iP = \frac{\mu_i^{0,\mathrm{IG}}(T)}{RT} + \ln x_iP \qquad (16)$$

and the compressibility factor by:

$$Z = \frac{PV}{NRT} = r_i\frac{\tilde{P}\tilde{v}}{\tilde{T}} = r_i\left[\tilde{v}\left(\frac{z}{2} - 1\right)\ln(1-\tilde{\rho}) + \frac{l}{r} - \nu_\mathrm{H} - \frac{z}{2}\tilde{v}\ln\theta_0\Gamma_{00}\right] \qquad (17)$$

The last equation is the NRHB equation of state.[20,21] The above equations provide, then, with the full expression for the Gibbs energy of solvation of component i in the mixture. In the case of pure component i, this expression becomes:

$$\frac{\Delta G_{i/i}^{*\mathrm{S}}}{RT} = \frac{\Delta G_{i/i}^{*\mathrm{CAV}}}{RT} + \frac{\Delta G_{i/i}^{*\mathrm{CHR}}}{RT} \qquad (18)$$

where

$$\frac{\Delta G_{i/i}^{*\mathrm{CAV}}}{RT} = -r_i\ln(1-\tilde{\rho}) + \frac{z}{2}(r_i - q_i)\ln\left[1 - \tilde{\rho} + \frac{q}{r}\tilde{\rho}\right] \qquad (19a)$$

or, equivalently

$$\frac{\Delta G_{i/i}^{*\mathrm{CAV}}}{RT} = -\ln(1-\tilde{\rho}_i) - (r_i - 1)\ln(\theta_0\Gamma_{00}) + l\ln\frac{1-\tilde{\rho}_i}{\theta_0\Gamma_{00}} \qquad (19b)$$

and

$$\frac{\Delta G_{i/i}^{*\mathrm{CHR}}}{RT} = \frac{zq_i}{2}\ln\frac{\Gamma_{ii}}{\Gamma_{00}} - \frac{q_i}{\tilde{T}_i} - \left(d_i\ln\frac{d_i}{d_i - r_i\nu_{\mathrm{H},i}} + a_i\ln\frac{a_i}{a_i - r_i\nu_{\mathrm{H},i}}\right) \qquad (20)$$

d_i and a_i are the number of proton-donor and proton-acceptor groups, respectively, in pure i (when one type of hydrogen bonds is present).

It is worth rewriting eq 20 in terms of the "segment" activity coefficients,[9,10] Γ_i, defined by:

$$\Gamma_{ij} = \Gamma_i\Gamma_j\exp\left(-\frac{\varepsilon_{ij}}{kT}\right) \qquad (21)$$

or

$$\frac{\Delta G_{i/i}^{*\mathrm{CHR}}}{RT} = zq_i\ln[\Gamma_i - \Gamma_0] - \left(d_i\ln\frac{d_i}{d_i - r_i\nu_{\mathrm{H},i}} + a_i\ln\frac{a_i}{a_i - r_i\nu_{\mathrm{H},i}}\right) \qquad (22)$$

This equation may act as bridge between COSMO and NRHB approaches. The solvation equations for the COSMO approach are derived in the Appendix.

To appreciate the meaning of each term in eqs 19 and 20 or 22, it is worth writing them in the limit of the plain LFHB model,[24] where $q = r$ and where there is no nonrandomness ($\Gamma_{ij} = 1$), or

$$\frac{\Delta G_{i/i}^{*\mathrm{CAV}}}{RT} = -r_i\ln(1-\tilde{\rho}_i) \quad (\mathrm{LFHB}) \qquad (23)$$

and

$$\frac{\Delta G_{i/i}^{*\mathrm{CHR}}}{RT} = -r_iz\frac{\varepsilon_{ii}}{\tilde{v}_ikT} - \left(d_i\ln\frac{d_i}{d_i - r_i\nu_{\mathrm{H},i}} + a_i\ln\frac{a_i}{a_i - r_i\nu_{\mathrm{H},i}}\right) \quad (\mathrm{LFHB}) \qquad (24)$$

From an alternative point of view of the solvation process,[23] the work of cavitation may be obtained from the probability π_i to find a cavity of a volume r_iv^* in the system that will host the guest molecule i, or:

$$\frac{\Delta G_{i/i}^{*\mathrm{CAV}}}{RT} = -\ln\pi_i \qquad (25)$$

By comparing eqs 23 and 25 we obtain:

$$\pi_i = (1-\tilde{\rho}_i)^{r_i} \quad (\mathrm{LFHB}) \qquad (26)$$

Since $(1 - \tilde{\rho}_i)$ is the probability to find an empty site in the system, eq 26 simply says that the probability to find a cavity appropriate for the guest molecule i, which consists of r_i

segments of volume v^* each, is equal to the combined probability to find r_i empty sites in a series.

Let us now return to eq 19b for NRHB. This equation says that the probability to find a cavity appropriate for the guest molecule i consists of three contributions given by its three terms: The first term gives the probability to find an empty site to place the first segment of the guest molecule. Once we locate one empty site, the probability to find one empty site in its immediate neighborhood is $\theta_0\Gamma_{00}$. Thus, the second term in eq 19b gives the probability to find the remaining $r_i - 1$ consecutive empty sites required to host the guest molecule. This is, however, true if the molecule is a linear one. The last term in eq 19b corrects for the nonlinearity or compactness of the molecule. As already mentioned, the factor l in this term is a measure of this compactness. Finally, by setting $\Gamma_{00} = 1$ in eq 19b, one may obtain from the difference the influence of the charging process to the work of cavitation.

Let us now turn to eq 24. The first term in this equation is the contribution of the dispersive interactions to the charging Gibbs energy of solvation. According to this term, each of the r_i segments of the guest molecule interacts with its z neighbors with a van der Waals type energy, $(\varepsilon_{ii}/\tilde{v}_i)$, which is scaled with the thermal energy kT. The second and third terms are the hydrogen-bonding contributions to the charging Gibbs energy.

Compared to eq 24, eq 20 has an extra term, the first term. This term accounts for the contribution of nonrandomness in the distribution of the host molecules (and empty sites) around the guest molecule. It is the contribution for the rearrangement of solvent in the neighborhood of the guest molecule upon charging the molecules of the system (allowing for nonzero intermolecular interactions).

The Gibbs energy of solvation may be broken down to its enthalpic and entropic components through the equation

$$\Delta G_i^{*S} = \Delta H_i^{*S} - T\Delta S_i^{*S} \tag{27}$$

In the case of self-solvation, the entropic component is given by the following equation (subscript i is omitted for clarity):

$$\begin{aligned} -\Delta S_{i/i}^{*S} = {} & R\left[(l-1)\ln(1-\tilde{\rho}) - (l+r-1)\ln\theta_0 + \right. \\ & \left. \frac{zq}{2}\ln\Gamma_{rr} - \frac{zr}{2}\ln\Gamma_{00}\right] - q\varepsilon_s^* - R\left[d\ln\frac{d}{d-r\nu_H} + \right. \\ & \left. a\ln\frac{a}{a-r\nu_H}\right] + \frac{z}{2}rRT\left[\frac{q/r}{\Gamma_{rr}}\left(\frac{\partial\Gamma_{rr}}{\partial T}\right)_{\tilde{\rho}} - \frac{1}{\Gamma_{00}}\left(\frac{\partial\Gamma_{00}}{\partial T}\right)_{\tilde{\rho}}\right] + \\ & \alpha\tilde{\rho}RT\left[\frac{l-1}{1-\tilde{\rho}} - \frac{l+r-1}{(q/r)\theta_0}\left(\frac{\theta_r}{\tilde{\rho}}\right)^2 - \frac{zq}{2\Gamma_{rr}}\left(\frac{\partial\Gamma_{rr}}{\partial\tilde{\rho}}\right)_T + \right. \\ & \left. \frac{zr}{2\Gamma_{00}}\left(\frac{\partial\Gamma_{00}}{\partial\tilde{\rho}}\right)_T\right] - RTr\left[\frac{d}{d-r\nu_H} + \frac{a}{a-r\nu_H}\right] \times \\ & \left[\left(\frac{\partial\nu_H}{\partial T}\right)_{\tilde{\rho}} - \alpha\tilde{\rho}\left(\frac{\partial\nu_H}{\partial\tilde{\rho}}\right)_T\right] \end{aligned} \tag{28}$$

where

$$\begin{aligned} \left(\frac{\partial\Gamma_{r0}}{\partial\tilde{\rho}}\right)_T &= \Gamma_{r0}\left(\frac{\theta\Gamma_{r0}}{\tilde{\rho}}\right)^2\frac{(1-A)(\theta_0-\theta)}{(q/r)(2-\Gamma_{r0})} \\ \left(\frac{\partial\Gamma_{rr}}{\partial\tilde{\rho}}\right)_T &= \frac{r}{q}\frac{\theta}{\tilde{\rho}^2}(\Gamma_{r0}-\Gamma_{rr}) - \frac{\theta_0}{\theta}\left(\frac{\partial\Gamma_{r0}}{\partial\tilde{\rho}}\right)_T \\ \left(\frac{\partial\Gamma_{00}}{\partial\tilde{\rho}}\right)_T &= \frac{\theta}{\theta_0}\left[\frac{r}{q}\frac{\theta}{\theta_0\tilde{\rho}^2}(1-\Gamma_{r0}) - \left(\frac{\partial\Gamma_{r0}}{\partial\tilde{\rho}}\right)_T\right] \\ \left(\frac{\partial\Gamma_{r0}}{\partial T}\right)_{\tilde{\rho}} &= \frac{2A\theta\theta_0}{zT\tilde{T}\sqrt{K}}\Gamma_{r0}{}^2 \\ \left(\frac{\partial\Gamma_{rr}}{\partial T}\right)_{\tilde{\rho}} &= -\frac{2A\theta_0^2}{zT\tilde{T}\sqrt{K}}\Gamma_{r0}{}^2 \\ \left(\frac{\partial\Gamma_{00}}{\partial T}\right)_{\tilde{\rho}} &= -\frac{2A\theta^2}{zT\sqrt{K}}\left[\frac{1}{\tilde{T}} - \frac{\varepsilon_s^*}{R}\right]\Gamma_{r0}{}^2 \end{aligned} \tag{29}$$

and

$$\begin{aligned} \sqrt{K} &= \frac{2-\Gamma_{r0}}{\Gamma_{r0}} \\ A &= \exp\left(\frac{2\varepsilon^*}{zRT}\right) \\ \Gamma_{rr} &= \frac{1-\theta_0\Gamma_{r0}}{\theta} \end{aligned} \tag{30}$$

The derivatives from the hydrogen bonding term are:

$$\begin{aligned} \left(\frac{\partial\nu_H}{\partial\tilde{\rho}}\right)_T &= \frac{r\nu_H}{\tilde{\rho}^2K_HD} \\ \left(\frac{\partial\nu_H}{\partial T}\right)_{\tilde{\rho}} &= \frac{r\nu_H(H_H+PV_H)}{\tilde{\rho}K_HDRT^2} \end{aligned} \tag{31}$$

where

$$\begin{aligned} K_H &= \exp\left(-\frac{H_H+PV_H-TS_H}{RT}\right) \\ D &= d + a + \frac{r\tilde{v}}{K_H} - 2r\nu_H \end{aligned} \tag{32}$$

The thermal expansion coefficient is given by:

$$\alpha\tilde{\rho}T = \frac{-\dfrac{\tilde{P}}{\tilde{T}} + \tilde{\rho}T\left(\dfrac{\partial\nu_H}{\partial T}\right)_{\tilde{\rho}} + \dfrac{z}{2}\dfrac{T}{\Gamma_{00}}\left(\dfrac{\partial\Gamma_{00}}{\partial T}\right)_{\tilde{\rho}}}{\nu_H + \tilde{\rho}\left(\dfrac{\partial\nu_H}{\partial\tilde{\rho}}\right)_T + \dfrac{z}{2\Gamma_{00}}\left(\dfrac{\partial\Gamma_{00}}{\partial\tilde{\rho}}\right)_T + \dfrac{1}{\tilde{\rho}-1} - \dfrac{l}{r} - \dfrac{z\theta}{2\tilde{\rho}}\left(1-\dfrac{r}{q}\right)} \tag{33}$$

The enthalpic component is, then, obtained from eq 27 as:

$$\Delta H_i^{*S} = \Delta G_i^{*S} + T\Delta S_i^{*S} \tag{34}$$

Let us now turn to mixtures to complete the solvation formalism. In an earlier version of NRHB[21] the nonrandom distribution of molecular segments was considered to be due, primarily, to the hydrogen-bonding interactions, while the remaining van der Waals interactions were considered the main cause for the nonrandom distribution of free-volume in the system. The advantage of this approach is its simplicity as it leads to analytical expressions for many systems of practical interest. In this case and for a binary mixture, the equation for the chemical potential is given by:

$$\frac{\mu_1}{RT} = \ln \frac{\phi_1}{\omega_1 r_1} - r_1 \frac{x_1 l_1 + x_2 l_2}{r} + \ln \tilde{\rho} + r_1(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - \frac{z}{2} r_1 \left[\tilde{v} - 1 + \frac{q_1}{r_1}\right] \ln\left[1 - \tilde{\rho} + \frac{q}{r}\tilde{\rho}\right] + \frac{zq_1}{2}\left[\ln \Gamma_{rr} + \frac{r_1}{q_1}(\tilde{v} - 1)\ln \Gamma_{00}\right] - \frac{q_1}{\tilde{T}} - 2q_1\theta_r\Gamma_{rr}\Theta_2 \frac{\varepsilon_1^* - \varepsilon_{12}^* - \Theta_2 RTX_{12}}{RT} + r_1 \frac{\tilde{P}\tilde{v}}{\tilde{T}} \frac{v_1^*}{v^*} \tag{35}$$

where

$$\Theta_i = \frac{N_i q_i}{\sum_k N_k q_k} \tag{36}$$

On the basis of eqs 16 and 35, and disregarding the contribution from factors ω, we obtain for the solvation Gibbs energy:

$$\frac{\Delta G_1^{*S}(T,P,\{N\})}{RT} = \frac{\mu_1(T,P,\{N\}) - \mu_1^{IG}(T,P,\{N\})}{RT} + \ln Z = r_1\frac{l}{r} - l_1 - r_1\ln(1 - \tilde{\rho}) - \frac{z}{2}[q_1 - r_1]\ln\left[1 - \tilde{\rho} + \frac{q}{r}\tilde{\rho}\right] + \frac{zq_1}{2}\ln \Gamma_{rr} - \frac{zr_1}{2}\ln \Gamma_{00} - \frac{q_1}{\tilde{T}} - 2q_1\theta_r\Gamma_{rr} \times \Theta_2 \frac{\varepsilon_1^* - \varepsilon_{12}^* - \Theta_2 RTX_{12}}{RT} - \sum_{\alpha=1}^{m} d_\alpha^i \ln \frac{\nu_d^\alpha}{\nu_{\alpha 0}} - \sum_{\beta=1}^{n} a_\beta^i \ln \frac{\nu_a^\beta}{\nu_{0\beta}} \tag{37}$$

From this equation we may obtain the equation of self-solvation (eq 18) by setting $x_1 = 1$. We may also obtain the equation for the solvation Gibbs energy of component 1 in solvent 2 by taking eq 37 in the limit of pure 2. Thus,

$$\frac{\Delta G_{1/2}^{*S}}{RT} = r_1\left(\frac{l_2}{r_2} - \frac{l_1}{r_1}\right) - r_1\ln(1 - \tilde{\rho}_2) - \frac{z}{2}[q_1 - r_1] \times \ln\left[1 - \tilde{\rho}_2 + \frac{q_2}{r_2}\tilde{\rho}_2\right] + \frac{zq_1}{2}\ln \Gamma_{rr,2} - \frac{zr_1}{2}\ln \Gamma_{00,2} - \frac{q_1}{\tilde{T}_2} - 2q_1\theta_2\Gamma_{rr,2}\frac{\varepsilon_{12}^* - \varepsilon_2^*}{RT} - \left\{\sum_{\alpha=1}^{m} d_\alpha^i \ln \frac{\nu_d^\alpha}{\nu_{\alpha 0}} + \sum_{\beta=1}^{n} a_\beta^i \ln \frac{\nu_a^\beta}{\nu_{0\beta}}\right\}_{x_1=0} \tag{38}$$

The activity coefficient at infinite dilution of component 1 in solvent 2 is then obtained from the relation

$$\frac{\Delta G_{1/2}^{*S} - \Delta G_{1/1}^{*S}}{RT} = \frac{\mu_1(T,P,x_1 \to 0) - \mu_1^{IG}(T,P,x_1 \to 0)}{RT} - \frac{\mu_1^0(T,P) - \mu_1^{0,IG}(T,P)}{RT} + \ln Z(x_1 \to 0) - \ln Z(x_1 = 1) = \ln \gamma_{1/2}^\infty + r_1\frac{l}{r} - l_1 + \ln\frac{r_2}{r_1} + \ln\frac{\tilde{\rho}_1}{\tilde{\rho}_2} \tag{39}$$

Substituting from eqs 18 and 39 we obtain

$$\ln \gamma_{1/2}^\infty = \ln \frac{r_1\tilde{\rho}_2}{r_2\tilde{\rho}_1} - r_1 \ln\frac{(1 - \tilde{\rho}_2)}{(1 - \tilde{\rho}_1)} - \frac{z}{2}[q_1 - r_1]\ln \frac{[1 - \tilde{\rho}_2 + \frac{q_2}{r_2}\tilde{\rho}_2]}{[1 - \tilde{\rho}_1 + \frac{q_1}{r_1}\tilde{\rho}_1]} + \frac{zq_1}{2}\ln\frac{\Gamma_{rr,2}}{\Gamma_{rr,1}} - \frac{zr_1}{2}\ln\frac{\Gamma_{00,2}}{\Gamma_{00,1}} - 2q_1\theta_2\Gamma_{rr,2}\frac{\varepsilon_{12}^* - \varepsilon_2^*}{RT} + \frac{q_1}{\tilde{T}_1} - \frac{q_1}{\tilde{T}_2} - \left\{\sum_{\alpha=1}^{m} d_\alpha^1 \ln \frac{\nu_d^\alpha}{\nu_{\alpha 0}} + \sum_{\beta=1}^{n} a_\beta^1 \ln \frac{\nu_a^\beta}{\nu_{0\beta}}\right\}_{x_1=0} + \left\{\sum_{\alpha=1}^{m} d_\alpha^1 \ln \frac{\nu_d^\alpha}{\nu_{\alpha 0}} + \sum_{\beta=1}^{n} a_\beta^1 \ln \frac{\nu_a^\beta}{\nu_{0\beta}}\right\}_{x_1=1} \tag{40}$$

Sometimes, it is more practical to use the activity coefficient based on the weight fraction rather than the mole fraction. Their relation at infinite dilution is:

$$\Omega_{1/2}^\infty = \gamma_{1/2}^\infty\left(\frac{r_2\rho_2^*}{r_1\rho_1^*}\right) \tag{41}$$

Henry's law constant is also obtained from γ_1^∞ by the equation:

$$\ln \frac{k_{H,1}}{P_1^0(T)} = \ln \gamma_1^\infty(T,P) \tag{42}$$

The infinite dilution partition coefficient of component 1 between solvent 2 and solvent 3 is obtained as the ratio $\gamma_{1/2}^\infty/\gamma_{1/3}^\infty$.

With the above equations one may easily calculate the solubility of solid 1 in solvent 2 by adopting the procedure proposed by Kramer and Thodos,[25] or

$$y_1 = \frac{1}{\gamma_{1/2}^\infty}\left(\frac{f_1^{0S}}{f_1^{0L}}\right) \tag{43}$$

The term in parentheses is the ratio of the fugacity coefficients of component 1 in the pure solid and the pure liquid state, and it can be approximated by:

$$\ln\left(\frac{f_1^{0S}}{f_1^{0L}}\right) = \frac{\Delta H_1^m}{RT}\left(\frac{T}{T_1^m} - 1\right) \tag{44}$$

where $\Delta H_1{}^m$ is the enthalpy of fusion of component 1 and $T_1{}^m$ its melting point.

The last equations are indicative of the large range of applications of our treatment. However, in the present work we will confine ourselves to the study of solvation of vapors in their own liquids or the self-solvation of pure fluids. This is essential for the development of a consistent COSMO-type equation-of-state framework.

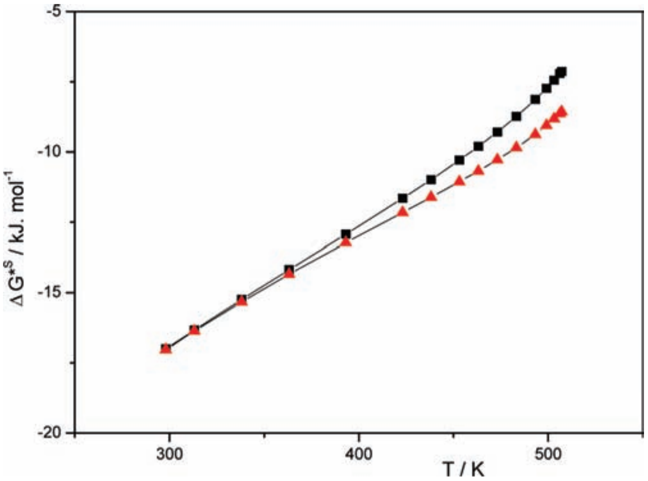

Figure 1. Gibbs energy of self-solvation of hexane as calculated by eq 18 (triangles) and the approximate eq 47 (squares).

Applications

In this approach, each pure fluid is characterized by the two NRHB scaling constants,[20,21] the specific hard-core volume, υ^*_{sp} (or the hard-core density, $\rho^* = 1/\upsilon^*_{\mathrm{sp}}$), and the average per segment interaction energy, ε^*. A weak variation with temperature is allowed for both constants, through the equations:

$$\varepsilon^* = \varepsilon^*_{\mathrm{h}} + \varepsilon^*_{\mathrm{s}}(T - 298.15\ \mathrm{K}) \tag{44a}$$

and

$$\upsilon^*_{\mathrm{sp}} = \upsilon^*_{\mathrm{sp},0} + \upsilon^*_{\mathrm{sp},1}(T - 298.15\ \mathrm{K}) \tag{45}$$

In the case of hydrogen-bonded fluids, the free-energy change upon formation of the hydrogen bond may be analyzed into an enthalpic and an entropic component and is given by

$$\Delta G_{\mathrm{H}} = \Delta H_{\mathrm{H}} - T\Delta S_{\mathrm{H}} \tag{46}$$

The NRHB scaling constants are available in the literature[20,21] and were obtained from vapor pressure, heat of vaporization, and density data.[26,27] We do not need any other data for our solvation calculations.

It is a common practice in the literature[18,28] to approximate the self-solvation Gibbs energy by the equation:

$$\Delta G^{*\mathrm{S}} = RT \ln \frac{p^0(T)M}{\rho RT} \tag{47}$$

where p^0, M, and ρ are the vapor pressure, the molar mass, and the density, respectively, of the liquid. As shown in Figure 1, this is a good approximation for relatively low temperatures (or vapor pressures), but there are significant deviations as the critical point is approached. Symbols in Figures 1 to 8 are calculations based on vapor pressure, density, and heat of vaporization data from DIPPR Compilation.[26]

In Figure 2 are shown the two main components of self-solvation Gibbs energy of hexane and their variation with temperature along the saturation line. As shown, the charging component is sufficiently negative to overcome the work of cavitation and turn negative (favorable) the self-solvation Gibbs energy along the equilibrium line.

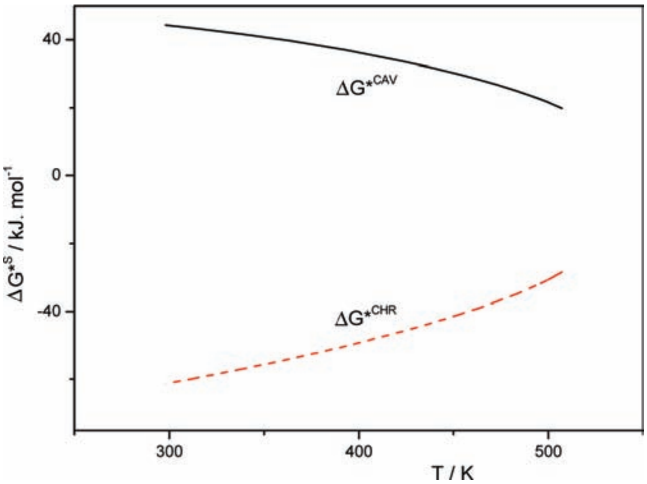

Figure 2. Components of the Gibbs energy of self-solvation of hexane as calculated by eq 22 (dashed line) for the charging energy and by eq 19a or 19b (solid line) for the cavitation energy.

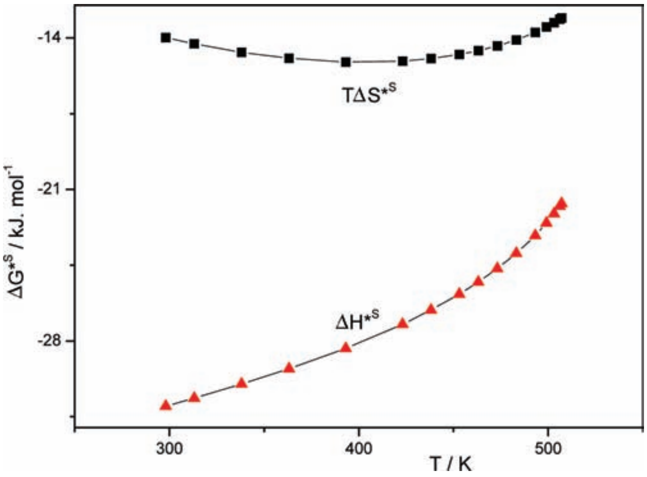

Figure 3. Components of the Gibbs energy of self-solvation of hexane as calculated by NRHB: the solvation enthalpy $\Delta H^{*\mathrm{S}}$ (squares) and the solvation entropy (circles), $T\Delta S^{*\mathrm{S}}$, obtained from eq 28.

Equally illuminating is Figure 3, which shows that the enthalpic component overcomes the entropic one and turns negative the self-solvation Gibbs energy. It is important for the subsequent discussion to point out that both the enthalpic and the entropic component for hexane increase with temperature as the critical point is approached. Hexane is a typical nonpolar compound, and the variation of its solvation components, as exhibited in Figures 1 to 3, is rather smooth and expected. It is of interest to see the corresponding behavior of a hydrogen-bonded fluid.

Figure 4 shows the range of conditions where eq 47 is a good approximation for the calculation of the self-solvation Gibbs energy of the hydrogen-bonded ethanol. Figure 5 shows that the variation of the cavitation and charging components for ethanol along its saturation line is also rather smooth. However, as shown in Figure 6, the variation of the corresponding enthalpic and entropic component exhibits a drastically different profile. The increase in temperature facilitates the breaking of hydrogen bonds, but it appears that this solvation process amounts to a drastic variation of the enthalpic and the entropic component near the critical point, although their interplay leads finally to a smooth variation of the overall self-solvation Gibbs

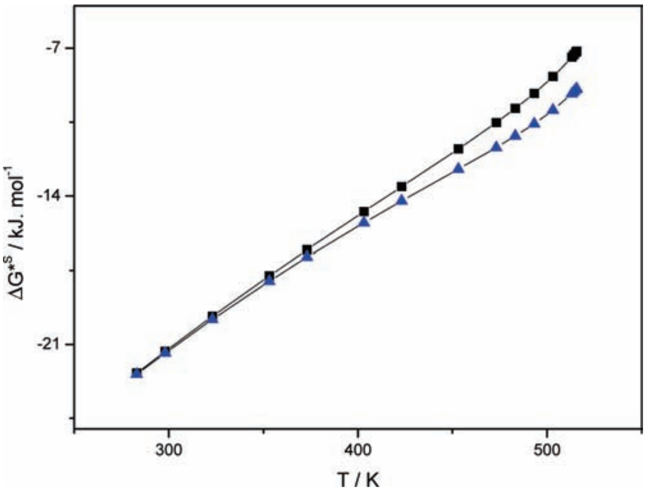

Figure 4. Gibbs energy of self-solvation of ethanol as calculated by eq 18 (triangles) and the approximate eq 47 (squares).

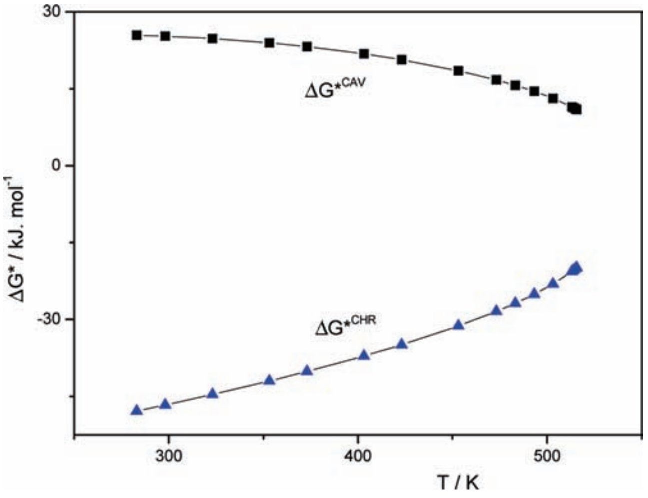

Figure 5. Components of the Gibbs energy of self-solvation of ethanol as calculated by eq 22 (triangles) for the charging energy and by eq 19 (squares) for the cavitation energy.

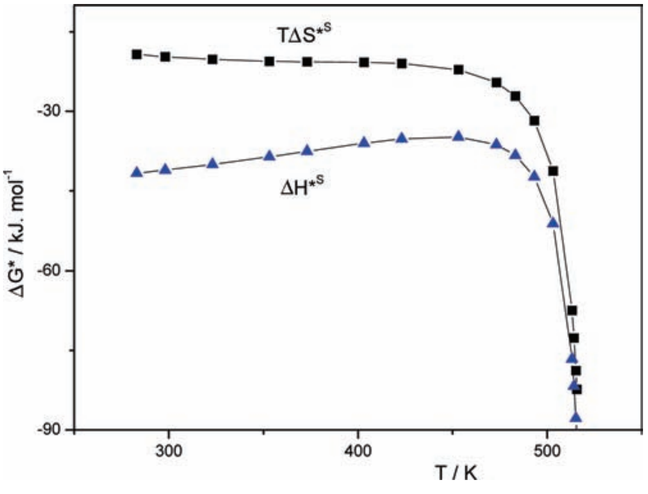

Figure 6. Components of the Gibbs energy of self-solvation of ethanol as calculated by eqs 28 and 34.

energy. It is worth then exploring whether this drastically different behavior is observed in other fluids.

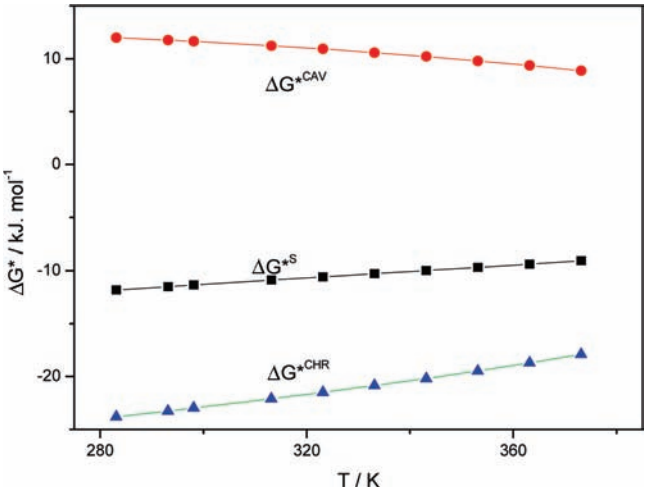

Figure 7. Gibbs energy of self-solvation of ammonia (squares) and its components as calculated by eq 22 (triangles) for the charging energy and by eq 19 (circles) for the cavitation energy.

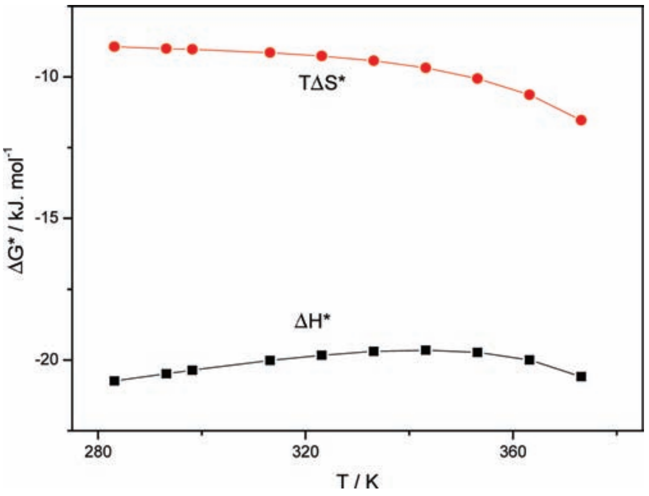

Figure 8. Components of the Gibbs energy of self-solvation of ammonia as calculated by eq 34 (circles) for the solvation enthalpy and by eq 28 (squares) for the solvation entropy $T\Delta S^*$.

In Figure 7 the rather smooth variations along the saturation line of the self-solvation Gibbs energy and its cavitation and charging components for ammonia are shown. In Figure 8 the corresponding variations for the enthalpic and the entropic component of ammonia are shown. As shown, although not as abrupt as in ethanol, here also both components decrease with temperature, and this is enhanced as the critical point is approached. This common behavior of the two hydrogen-bonded fluids (ethanol and ammonia) is in contrast with the corresponding behavior of the nonpolar hexane. A systematic study along these lines of other representative fluids with varying strength of intermolecular forces would shed light into the prevailing mechanism of the solvation process and could contribute in understanding other related phenomena such as the enhanced solvation at (super)critical conditions.

One potentially important source of information regarding the solvation process could be the quantum mechanics calculations as embodied in the COSMO approach. COSMO models could tell us about the solvation at high temperatures and pressures if they were applicable to such conditions. As mentioned earlier, this would amount to the development of a consistent COSMO equation-of-state model. As a first step toward this goal, such a model is presented in the Appendix and is referred to as COSMO-V1 model (an alternative variation of it, called NRCosmo, will be presented in a forthcoming manuscript along with calculations for mixtures).

Table 2. Components of the Gibbs Energy of Solvation (in $kJ\cdot mol^{-1}$) at 298.15 K as Calculated by the Plain NRHB Model and the COSMO-V1 Model

	NRHB		COSMO-V1	
	ΔG^{*CAV}	ΔG^{*CHR}	ΔG^{*CAV}	ΔG^{*CHR}
fluid	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
propane	18.62	−27.36	18.94	−27.63
butane	27.70	−39.33	25.85	−37.00
hexane	44.28	−61.31	48.55	−65.85
heptane	52.45	−72.23	57.43	−77.33
octane	60.27	−82.67	58.92	−81.37
decane	75.88	−103.56	84.43	−112.66
methanol	18.93	−39.50	17.53	−38.11
ethanol	25.27	−46.67	24.60	−45.84
1-propanol	32.73	−56.05	31.22	−54.43
1-butanol	40.48	−65.91	38.47	−64.03
1-pentanol	48.01	−75.56	44.94	−72.52
1-hexanol	55.47	−85.21	52.35	−82.36
1-octanol	71.56	−106.46	67.31	−102.15
ammonia	11.68	−22.98	8.59	−19.90
water	16.11	−42.42	10.91	−37.15
carbon dioxide	7.37	12.83	7.31	−12.82

In COSMO-V1, the segment−segment interaction energy consists of three contributions. The first two are the usual misfit term and hydrogen-bonding term of the COSMOtherm[4−8] or COSMO-SAC[9] models. The third contribution encompasses all other types of interactions and is collectively called the "dispersion" term. In this first attempt to use the formalism in the Appendix, we attribute one "dispersion" constant and one "specific volume" constant to each fluid. These constants for a number of common fluids are reported in Table 1 and are obtained as the scaling constants of the plain NRHB model.[20,21] The resulting model is a complete equation-of-state model and can be applied over an extended range of external conditions up to the critical point and beyond it.

In Table 2 the components of the solvation Gibbs energy at 25 °C as calculated by the plain NRHB model and the COSMO-V1 model of the Appendix are compared. As observed, the discrepancies are not negligible and sometimes are quite large. Water exhibits the largest percent discrepancy for its cavitation component, while decane exhibits the largest absolute difference for its charging component of the solvation Gibbs energy. An intermediate variation is shown in Figure 9a,b, where these calculations for ethanol as a function of temperature are compared.

A careful examination of the data in Table 2 reveals that the calculations of the Gibbs energy of solvation (sum of cavitation and charging components) by the two approaches are practically identical. The separate components, however, may differ as much as 35 %.

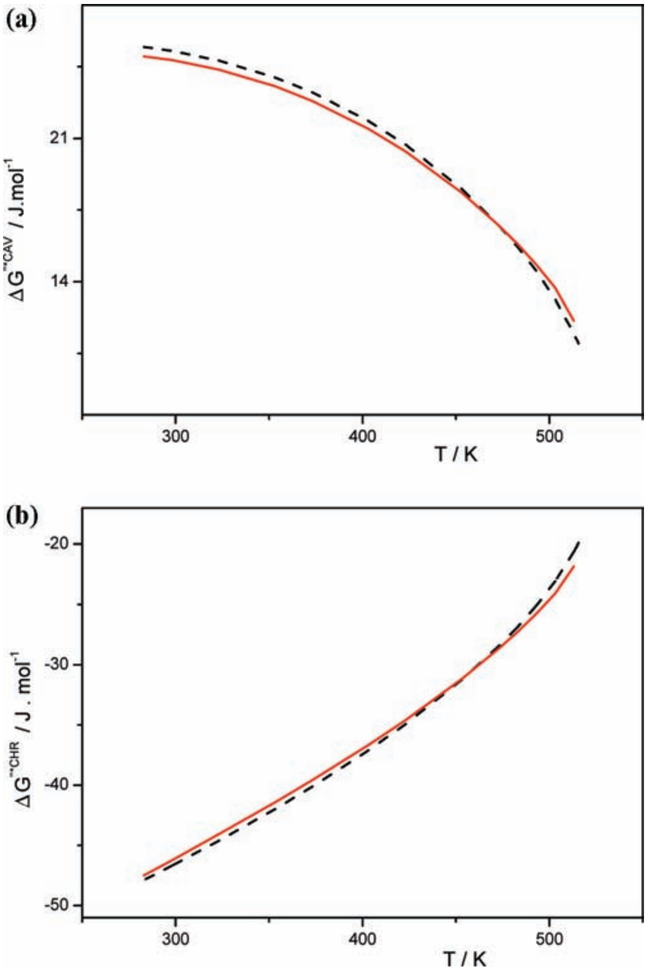

Figure 9. (a) The cavitation component of the Gibbs energy of self-solvation of ethanol as calculated by the plain NRHB model (dashed line) and by the COSMO-V1 model (solid line). (b) The charging component of the Gibbs energy of self-solvation of ethanol as calculated by the plain NRHB model (dashed line) and by the COSMO-V1 model (solid line).

Discussion and Conclusions

The calculations of the previous section raise a number of issues regarding solvation calculations. These issues cannot be overlooked if an equation-of-state model is to be developed in the frame of solvation thermodynamics. The first issue arises from Figures 1 and 4. As observed, the common approximation of eq 47 has a limited application and must be corrected before use at higher pressures (or temperatures). The second issue arises from the variation with temperature of the enthalpic and entropic component of the Gibbs energy of solvation. In hydrogen-bonded fluids these components are drastically affected by the hydrogen-bond interruption with an increase in temperature. The abrupt changes observed in Figure 6 arise from the hydrogen bonding constants that were adopted in the NRHB model.[20,21] This can be verified by comparing Figure 6 for ethanol with Figure 8 for ammonia where the individual hydrogen bonds are weaker than in ethanol. The reliability then of these calculations resides on the reliability of the hydrogen bonding constants. We should recall that, for simplicity, in this work we have used one constant to describe variation with temperature of the free energy change upon formation of a hydrogen bond. In addition, one single pair of constants was used for all hydrogen bonds of one type. Thus, for all alkanols we have used the pair of constants $\Delta H_H = -25.1\ kJ\cdot mol^{-1}$ and $\Delta S_H = -26.5\ J\cdot K^{-1}\cdot mol^{-1}$ for the OH−OH bonds in all alcohols.

In COSMO-V1 we have not introduced any change with temperature in the hydrogen-bonding term or in the misfit energy term. For lack of any other information, only the dispersion term was allowed to vary with temperature. It is not, then, unexpected that this difference will lead to the differences observed in the calculations of Table 2 and of Figure 9a,b. In view of this, a comparison of enthalpic and entropic components of solvation Gibbs energies is meaningful only when it is discussed in connection with the model that has been adopted for the interaction energies.

Another important issue is the interdependence of the cavitation and charging components of the solvation Gibbs energy. Our calculations were verified against reliable data on vapor pressures, equilibrium densities, and heats of vaporization over a broad range of external conditions. The separate components could vary, but their sum was imposed by the equilibrium data. This is essential when comparing different solvation models. Unfortunately, in their majority these comparisons are made at ambient conditions, and the above-mentioned interdependence is disregarded. Thus, caution should be exercised when adopting values for the charging and the cavitation components from different sources.

In conclusion, then, this work has provided with two different equation-of-state models for the calculation of the self-solvation Gibbs energy of fluids with varying strength of intermolecular interactions. The strength of these interactions dictates the local composition around a molecule or the nonrandom distribution of the various molecular entities in the system and, thus, their solvation. Both models use the quasi-chemical approach[3] for treating this nonrandomness in the distribution throughout the volume of the system. In both cases we have analytical equations with clear terms regarding their provenance and their meaning. Thus, in eqs 19b and 20 one may see how intermolecular forces, dispersive or hydrogen-bonding, and the concomitant nonrandomness influence solvation. This kind of analysis could shed light on the variation of these terms with temperature or pressure. Of course, intermolecular interactions dictate also the density of the system, and thus, there are no “inert” volumetric terms that can be discussed independently of the charging terms. It is hoped that the present work will contribute in understanding dissolution, preferential solvation or enhanced solvation phenomena at high temperatures or pressures where changes in densities play a dominant role.

Appendix

COSMO Equation-of-State Approach. The COSMOtherm model has attracted very much interest as been a most promising predictive tool for phase equilibria and related properties.[4−8] As already mentioned in the main text, in spite of the recent progress in the development of COSMO + equation-of-state models, much work remains to be done to consistently extend the COSMOtherm model and account for high temperature and pressure VLE, for the supercritical state, and for volume changes on mixing. In essence, as the critical state is approached, or in the transition from the liquid to the gas state, the molecules will continuously adjust their wave functions to minimize the interaction energy with their neighbors, but this is not easy to be accounted for by keeping the COSMOtherm picture of molecules solvated by other molecules without noncontacting surface segments. By letting noncontacting segments be parts of the surfaces of voids or empty sites, free volume enters the COSMOtherm picture of fluids.Scope of Our Approach. The present work, does not address the quantum mechanical problem. It attempts instead to augment the capacity of the surface−contact thermodynamic approach of COSMO models by incorporating free volume in the formalism and deriving an equation-of-state model applicable to the subcritical as well as supercritical state, able to account for density variations and volume changes, and potentially applicable to polymer systems.Key Assumptions. 1. The system contains k types of molecular surface segments, namely, n_i segments with charge density σ_i, which are distributed in N_1 molecules of type 1, N_2 molecules of type 2, ..., N_t molecules of type t.2. The dielectric continuum and continuum solvation picture of COSMO[4−8] holds here.3. The system contains n_0 segments of empty sites of no screening charge, whose number depends on the external T and p conditions. As in the main text, these holes are assumed to be of equal size (the reference size v^*), not collapsible, and, most importantly, they do not modify the mean geometrical characteristics of the molecules. The molecular segments and holes are arranged on a quasi-lattice of coordination number z set equal to 10 again.4. Any contact of two interacting segments m and n with charge densities σ_m and σ_n, respectively, is characterized by a pair interaction energy $\varepsilon_{\text{pair}}(\sigma_m, \sigma_n)$.5. Any encounter of a molecular segment with a “hole” segment will lead to a zero energy change.6. An encounter of two segments of empty sites will also lead to a zero energy change.Surface Segment Activity Coefficients. In our former treatment,[10] we have used the chemical potential of surface segments given by:[4−10]

$$\mu(\sigma_m) = -kT \ln\left\{\sum_{n=0}^{k} \exp\left[\frac{-\varepsilon_{\text{pair}}(\sigma_m, \sigma_n) + \mu(\sigma_n)}{kT}\right]\right\} + kT \ln p(\sigma_m) \quad \text{(A1)}$$

where $p(\sigma_m)$ is the probability of finding a segment with charge density σ_m in the system. In terms of the surface segment activity coefficients, eq A1 may, equivalently, be written in the following alternative way:

$$\Gamma(\sigma_m) = \Gamma_m = -\ln\left\{\sum_{n=0}^{k} p(\sigma_n)\Gamma_n \exp\left[\frac{-\varepsilon_{\text{pair}}(\sigma_m, \sigma_n)}{kT}\right]\right\} \quad \text{(A2)}$$

To establish the link between this COSMO terminology and the more widely used terminology of surface area fractions of the main text, we may express the probability $p(\sigma_m)$ as following:

$$p(\sigma_m) = \theta_m = \frac{Q_m n_m}{n_q} = \frac{n_m Q_m}{n_1 Q_1 + ... + n_k Q_k} \frac{n_1 Q_1 + ... + n_k Q_k}{n_0 + n_1 Q_1 + ... + n_k Q_k} = \Theta_m \theta \qquad m = 1, ..., k \quad \text{(A3)}$$

Θ_m in eq A3 is the surface area fraction of segments m in the compact system without empty sites. zQ_m is the number of external contacts of each segment m. The overall surface area fraction, θ, of molecular segments in the real system, containing n_0 empty sites, is given by

Table 1. Characteristic Constants of Pure Fluids (COSMO-V1)

fluid	ε_{cd1} $\text{J}\cdot\text{nm}^{-2}\cdot\text{mol}^{-1}$	ε_{cd2} $\text{J}\cdot\text{nm}^{-2}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$v_{\text{sp}} = 1/\rho$ $\text{cm}^3\cdot\text{g}^{-1}$	v_{sp1} $\text{cm}^3\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
methane	0.6962	0.0049	2.2200	−0.0003
ethane	0.8330	−0.0448	1.5987	−0.0003
propane	0.8937	0.0134	1.4273	−0.0003
butane	0.9201	0.0322	1.2950	−0.0003
hexane	0.9255	0.0752	1.2728	−0.0003
heptane	0.9289	0.0837	1.2460	−0.0003
octane	0.9372	0.0898	1.2170	−0.0003
decane	0.9464	0.0965	1.1980	−0.0003
methanol	1.6761	0.4979	1.0947	−0.0001
ethanol	1.7623	0.3824	1.0900	−0.0001
1-propanol	1.6615	0.3383	1.0740	−0.0001
1-butanol	1.5891	0.3024	1.0715	−0.0001
1-pentanol	1.4803	0.3145	1.0591	−0.0001
1-hexanol	1.4447	0.2928	1.0585	−0.0001
1-octanol	1.3719	0.2674	1.0572	−0.0001
1-decanol	1.3175	0.2469	1.0550	−0.0001
ammonia	2.8209	0.7012	1.3143	−0.0003
water	0.8853	0.7766	0.9343	−0.0001
carbon dioxide	1.4711	0.8284	0.7580	−0.0003

$$\theta = \frac{n_1Q_1 + ... + n_kQ_k}{n_0 + n_1Q_1 + ... + n_kQ_k} = \frac{Qn}{Qn + n_0} = \frac{Qn}{n_q} \qquad \text{(A4)}$$

If n_{ij} is the number of contacts between segments of type i and j, the total potential energy of our system is given by

$$E = \sum_{i=0}^{k}\sum_{j\geq i}^{k} n_{ij}\varepsilon_{\text{pair}}(\sigma_i, \sigma_j) = \sum_{i=0}^{k} n_{0i}\varepsilon_{\text{pair}}(0, i) + \sum_{i=1}^{k}\sum_{j\geq i}^{k} n_{ij}\varepsilon_{\text{pair}}(\sigma_i, \sigma_j) = E_0 + E_1 \qquad \text{(A5)}$$

Nonrandomness Factors. As in the main text (cf. eq 21), the link between the segment activity coefficients Γ_m and the nonrandomness factors Γ_{mn} for the distribution of a segment m around a central segment n is established by the equation:[9,10]

$$\Gamma_{mm} = \Gamma_m\Gamma_n \exp\left[\frac{-\varepsilon_{\text{pair}}(\sigma_m, \sigma_m)}{kT}\right] = \Gamma_m\Gamma_n\tau_{mn} \qquad \text{(A6)}$$

With these definitions, the number n_{mn} of contacts between segments m and n is given by the equation:

$$n_{mn} = znQ\Theta_m\theta_n\Gamma_{mn} = znQ\theta\Theta_m\Theta_n\Gamma_m\Gamma_n\tau_{mn} \qquad \text{(A7)}$$

and between segments m and m, by the equation:

$$n_{mm} = \frac{1}{2}znQ\Theta_m\theta_m\Gamma_{mm} = \frac{1}{2}znQ\theta\Theta_m{}^2\Gamma_m{}^2\tau_{mm} \qquad \text{(A8)}$$

The number of contacts 0−0 between empty sites in our system is given by:

$$n_{00} = \frac{1}{2}zn_0\theta_0\Gamma_{00} = \frac{1}{2}zn_0\theta_0\Gamma_0{}^2 \qquad \text{(A9)}$$

where $\theta_0 + \theta = 1$.Mass balance or conservation equations for the intersegmental contacts take, then, the form:

$$\sum_{n=0}^{k} n_{mn} = zn_mQ_m \quad \text{or} \quad \theta_0\Gamma_{m0} + \theta\sum_{n=1}^{k}\Theta_n\Gamma_{mn} = \Gamma_m\{\theta_0\Gamma_0 + \theta\sum_{n=1}^{k}\Theta_n\Gamma_n\tau_{mn}\} = 1 \qquad \text{(A10)}$$

which gives the working equation for calculating segment activity coefficients:

$$\Gamma_m = 1/\{\theta_0\Gamma_0 + \theta\sum_{n=1}^{k}\Theta_n\Gamma_n\tau_{mn}\} \qquad \text{(A11)}$$

This is the alternative way of writing eq A2 in terms of surface area fractions. As discussed previously,[10] eqs A2 and A11 reflect the quasi-chemical character of the COSMO model.[4−9]Having been convinced about the quasi-chemical character of this combined model, we may write the full form of the configurational partition function in its maximum term approximation in Guggenheim's terminology[3] as the following:[10,15−17]

$$Z = \Omega_{\text{R}}\frac{\prod_{m}(n^0_{mn}!)\prod_{n\neq m}\left[\left(\frac{1}{2}n^0_{mn}\right)!\right]^2}{\prod_{m}(n_{mn}!)\prod_{n\neq m}\left[\left(\frac{1}{2}n_{mn}\right)!\right]^2} \times \exp\left(-\frac{\sum_{m}\sum_{n\geq m} n_{mn}\varepsilon_{\text{pair}}(\sigma_m, \sigma_n)}{kT}\right) \qquad \text{(A12)}$$

Ω_{R} is the number of distinguishable configurations in the case of random distribution of segments in the system and E the potential energy of our system. Ω_{R} is assumed to be given by Staverman's combinatorial term[22] as in NRHB and in COSMOtherm. The superscript 0 in eq A12 indicates quantities pertinent to the case of random distribution of segments and empty sites in the system. The corresponding quantities in the case of nonrandomness are given by:

$$n_{mn} = n^0_{mn}\Gamma_{mn} = n^0_{mn}\Gamma_m\Gamma_n\tau_{mn} \qquad \text{(A14)}$$

Equation of State and the Chemical Potential of Molecular Species. As in the main text, we will consider each molecule i divided into r_i volume segments and having a total of zq_i external contacts. If N_r is the total number of segments, the total volume of the system is $V = N_r v^*$. Each molecule i consists of a multitude of interacting segments. Let ν_{mi} be the number of segments of type m in each molecule of type i. Since each such segment has zQ_m external contacts, the conservation equation gives:

$$zq_i = \sum_{m=1}^{k}\nu_{mi}zQ_m \qquad \text{(A15)}$$

and for each type of segments in the mixture we have:

$$n_m = \sum_{i=1}^{t}N_i\nu_{mi} \qquad \text{(A16)}$$

and

$$znQ = z\sum_{m=1}^{k}n_mQ_m = z\sum_{i=1}^{t}\sum_{m=1}^{k}N_i\nu_{mi}Q_m = zN\sum_{i=1}^{t}\sum_{m=1}^{k}x_i\nu_{mi}Q_m = zqN \qquad \text{(A17)}$$

Combining eqs A3, A4, A16, and A17, we obtain:

$$zn_mQ_m = zN\sum_{i=1}^{t}x_i\nu_{mi}Q_m = zqN\Theta_m = znQ\Theta_m \qquad \text{(A18)}$$

where x_i is the mole fraction of component i in the system. The equivalent of eq A18 in COSMO terminology is obtained by recalling that:

$$zq_i = \frac{A_i}{\alpha_{\text{eff}}} \qquad \text{(A19)}$$

and

$$A_i(\sigma_m) = A_i p_i(\sigma_m) \qquad \text{(A20)}$$

where A_i is the total surface area per molecule i, $A_i(\sigma_m)$ is the surface area of segments m in molecule i, and α_{eff} is the standard surface area per segment in the COSMO approach. The correspondence between the two terminologies is established through the equations:

$$p_i(\sigma_m) = \frac{A_i(\sigma_m)}{A_i} = \Theta_m^i = \frac{z\nu_{mi}Q_m}{zq_i} \qquad \text{(A21)}$$

From statistical thermodynamics, the pressure of the system is obtained from eq A12 as the following:

$$P = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} = kT\left(\frac{\partial \ln \Omega}{\partial V}\right)_{T,N} - \left(\frac{\partial E}{\partial V}\right)_{T,N} \qquad \text{(A22)}$$

Replacing from above, we obtain the equation of state of our system (cf. eq 17 of the main text):

$$\frac{Pv^*}{kT} + \ln(1 - \tilde{\rho}) - \frac{z}{2}\ln\left[1 + \frac{q}{r}\tilde{\rho} - \tilde{\rho}\right] - \tilde{\rho}l + z\ln\Gamma_0 = 0 \qquad \text{(A23)}$$

where

$$l = \sum_i \phi_i \frac{l_i}{r_i} = \sum_i \phi_i\left[\frac{z}{2}\left(1 - \frac{q_i}{r_i}\right) + \frac{1}{r_i} - 1\right] = \frac{z}{2}\left(1 - \frac{q}{r}\right) + \frac{1}{r} - 1 \qquad \text{(A24)}$$

For the chemical potential of component i we obtain:

$$\frac{\mu_i}{RT} = -\left(\frac{\partial \ln Z}{\partial N_i}\right)_{T,V,N_{j\neq i}} = \ln \tilde{\rho}\frac{\phi_i}{\omega_i r_i} - r_i l + r_i(\tilde{v} - 1)\ln(1 - \tilde{\rho}) - \frac{z}{2}r_i\left[\tilde{v} - 1 + \frac{q_i}{r_i}\right]\ln\left[1 - \tilde{\rho} + \frac{q}{r}\tilde{\rho}\right] + zr_i(\tilde{v} - 1)\ln\Gamma_0 + r_i\frac{P\tilde{v}v^*}{kT} + zq_i\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_m \qquad \text{(A25)}$$

The last term in eq A25 may be written in COSMO terms as

$$zq_i\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_m = \frac{A_i}{\alpha_{\text{eff}}}\sum_{m=1}^{k}p_i(\sigma_m)\ln\Gamma_m \qquad \text{(A26)}$$

Combination of eqs A23 and A25 leads to expressions for the components of the Gibbs energy of solvation. Of particular interest are these expressions for the self-solvation of pure components. Thus, the Gibbs energy of cavitation is identical to the corresponding expression for the plain NRHB model (cf. eq 19a of the main text), while the charging component of the Gibbs energy of solvation is given by

$$\frac{\Delta G_{i/i}^{*\text{CHR}}}{RT} = -zr_i\ln\Gamma_0 + zq_i\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_m = -zr_i\ln\Gamma_0 + \frac{A_i}{\alpha_{\text{eff}}}\sum_{m=1}^{k}p_i(\sigma_m)\ln\Gamma_m \qquad \text{(A27)}$$

Equation A27 should be compared with eq 22 of the main text for the plain NRHB model.All calculations in this work are done by using either the *Cosmotherm-C12* package of Cosmologic GmbH[29] or the Virginia Tech database of σ profiles,[30] while TURBOMOLE (distribution by Cosmologic GmbH) is used for obtaining the *cosmo* files. There are many possible combinations of NRHB and COSMO approaches, but here we will confine ourselves to just one, hereafter referred to as COSMO-V1. Apart from the misfit terms and the hydrogen-bonding interactions, in the COSMO approach there are three other types of interactions that are discussed in the frame of the solvation picture, but in the COSMO approach they are not considered to contribute to the nonrandom distribution of the interacting segments. The second type is the van der Waals or dispersion interactions. In the COSMO approach[4−9] these interactions are nonspecific and are considered proportional to the exposed surface of the atoms in the system. The third type of interactions is associated with the ideal solvation energy or the energy difference of solute between the ideal gas state and the ideal conductor state. The fourth type of interactions is the charging correction and accounts for the energy shift due to a charge averaging process. The last three types of interactions will be collectively called cosmo-dispersion or cd interactions. Thus, the "physical" interactions of the NRHB model correspond to the sum of the misfit and the cd interactions of the COSMO approach.As in NRHB, in the COSMO-V1 approach we consider that all intermolecular interactions do contribute to the nonrandom distribution of interacting segments and account for it through the quasi-chemical procedure. The cosmo-dispersion or cd-interaction *densities* (per unit area of interaction) for each component in the system are assumed to vary linearly with temperature, or

$$\varepsilon_{\text{cd}} = \varepsilon_{\text{cd1}} + \varepsilon_{\text{cd2}}\frac{T}{298.15\text{ K}} \qquad \text{(A28)}$$

Apart from this scaling constant, the equation-of-state model has a second constant, namely, the specific hard-core volume, v^*_{sp}, or the hard-core density, $\rho^* = 1/v^*_{\text{sp}}$. In Table 1 are presented the scaling constants for some representative common fluids.The calculations with this model are as good as the corresponding calculations with the plain NRHB model of the main text. In Figure A, as an example, are compared the experimental and calculated vapor pressures for methanol by the COSMO-V1 model. There are, however, additional features of the latter model. It should be stressed that the COSMO-V1 model offers the possibility to break down the σ profile into the contribution of each type of atom, as shown in Figure B for methanol. In addition, it offers the possibility to further break down the contribution of each type of atom into its components. As an example, in Figure C the components of the contribution of H atoms in methanol are shown. There are contributions from hydrogens bonded to C and from hydrogens bonded to O. The

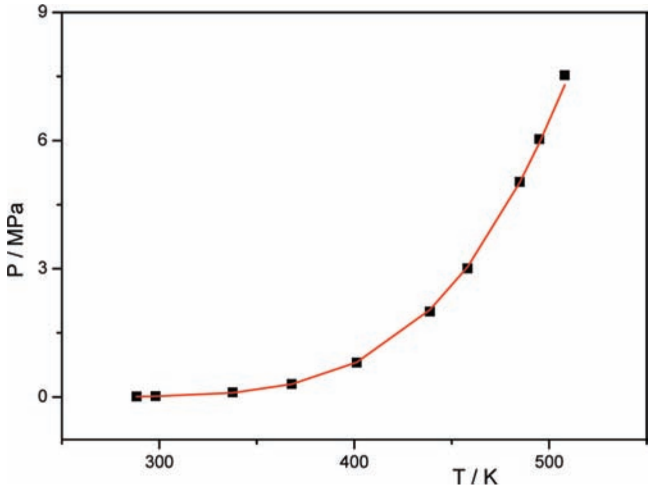

Figure A. Experimental[26] and calculated vapor pressures for methanol.

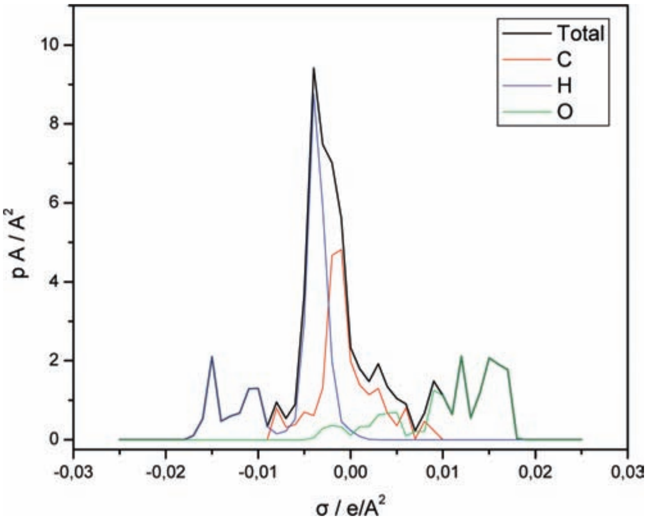

Figure B. Contributions of the various atom types to the σ profile of methanol.

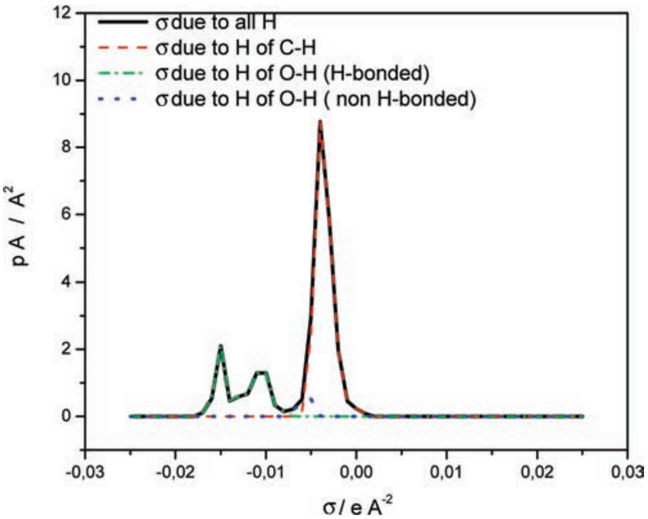

Figure C. Contribution of hydrogens to the σ profile of methanol.

latter are further broken down into those participating in hydrogen bonds and to the non-hydrogen-bonded ones.

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