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Toward a COSMO equation-of-state model of fluids and their mixtures*

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Abstract: The basic objective of this work is the development of an approximate, yet coherent and consistent equation-of-state model of fluids, which will benefit from recent developments in the successful COnductor-like Screening MOdel (COSMO)-type group-contribution models with their quantum-mechanical description of fluids. The development is done within our recent non-random hydrogen-bonding (NRHB) equation-of-state framework. In contrast to NRHB, the new model will not need any new parameters for the strong specific interactions, such as hydrogen bonds, since they will be provided by its COSMO component and the associated quantum-chemistry calculations. The bridge between COSMO and NRHB is the non-randomness factors as calculated by the quasi-chemical treatment of the non-random distribution of molecular entities in the system. Analytical expressions are provided for all basic thermodynamic quantities, including expressions for the cavitation and charging components of the solvation Gibbs energy. The new equation-of-state model is tested against experimental data for vapor pressures, heats of vaporization, and liquid densities of pure fluids and on phase equilibria of mixtures. The strength and perspectives of the new model are critically discussed.

Keywords: COSMOtherm; COSMO-SAC; free volume; high pressure.

INTRODUCTION

Solution thermodynamics has benefited very much in the last few years from osmosis with quantum chemistry and its dielectric continuum solvation models [1–9]. In particular, the extension of COnductor-like Screening MOdel, or COSMO, with a thermodynamic treatment of the molecular interactions led to the recent development of the COSMO-RS or COSMOtherm group-contribution model by Klamt and co-workers [4–7] and, subsequently, of the COSMO-SAC model by Sandler and co-workers [8]. These developments were, doubtlessly, a significant step forward in solution thermodynamics. We will refer to these models by the general term *COSMO models*. Their key characteristic is a refined mixture of a remarkable distillate of hard-core quantum mechanics and ab initio calculations with a group-contribution thermodynamic framework, identical to the relatively old but still widely used quasi-chemical framework [10]. It is this mixture of quantum-chemical ab initio solvation calculations and group-contribution thermodynamic treatments that 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 [4–9].

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One key limitation of the COSMOtherm model is its inadequacy for the gaseous state. From the quantum-mechanical and conductor-screening point of view, the gaseous state is fundamentally different from the liquid state. 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 in order to minimize the interaction energy with their neighbors, but this is not easy to account for by keeping the COSMOtherm picture of molecules solvated by other molecules without non-contacting surface segments. The consequence is the inability of COSMO models to account for high-temperature and -pressure vapor–liquid equilibria, for the supercritical state, and for volume changes on mixing. Thus, an ever-increasing interest is found in the recent literature for the extension of COSMO-type models to equation-of-state models [9,11–15]. In this work, we will present such an alternative extension to a COSMO equation-of-state model, but, in order to more clearly present our approach, a couple of pertinent concepts will be recalled, first, from the open literature.

Guggenheim's quasi-chemical theory [10] is an elegant approach to non-randomness in solutions and has been widely used over the last few decades. The introduction of non-randomness factors in early 1980s [16] and their calculation through the quasi-chemical theory, gave a physical meaning to the widely used "group-activity coefficients" by various group-contribution models of the excess thermodynamic properties of multicomponent mixtures, such as the ASOG [17] or the UNIFAC [18] models. It was shown that in group-contribution formalism, the group-activity coefficient for group k is identical to the non-randomness factor, Γ_{kk}, for the interaction k–k, as calculated by the quasi-chemical theory [10]. In an entirely similar manner, the surface "segment activity coefficient" of the COSMO-SAC model [8] was proved to be intimately related to the same non-randomness factors [9,15]. The segment-activity-coefficient approach as implemented in the COSMO-SAC model [8] is in many ways an excellent bridge between quantum-chemists and thermodynamicists for understanding and utilizing the COSMO models. In fact, this analogy between group-activity coefficients and segment-activity coefficients was the stimulus for the development of the COSMO equation-of-state model of this work.

A first quasi-chemical equation-of-state model had appeared in the early 1980s [19,20] 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 [9,15]. In parallel, an alternative quasi-chemical equation-of-state model was developed recently [21,22], which treats separately the strong specific interactions in the system, such as the hydrogen bonds, as quasi-chemical reactions at equilibrium. By applying mass-action law in these quasi-reactions, their equilibrium constant turns to be directly proportional to the density of the system. This idea may be generalized for multiple and simultaneous hydrogen bonds through the Veytsman statistics [23,24], leading to a comprehensive treatment of hydrogen-bonded systems, including complex systems of three-dimensional networks of hydrogen bonds. The derived equation-of-state model treats the nonrandom distribution of all other interacting sites and of the free volume by Guggenheim's quasi-chemical theory [10] and, thus, it is called the nonrandom hydrogen-bonding (NRHB) model [21,22]. This is a versatile and successful model of fluids but requires the knowledge of the enthalpy and the entropy change upon formation of each type of hydrogen bond present in the system, and this is not always simple.

The aim of this work is to develop an equation-of-state model, which will have all qualifications of the NRHB model but will not need any hydrogen-bonding parameters. This will be done by replacing the hydrogen-bonding component (partition function factor) of the NRHB model by the corresponding component of the COSMO models and, thus, all needed information will be provided by the associated *cosmo* files. These files can be obtained today either from commercially [25] or freely [26] available *cosmo* databases, or they can be created from easily accessible software [27–29].

THEORY

In this section, we will summarize, first, the essentials of the NRHB model and the group-contribution/quasi-chemical features of the COSMO models, and then we will proceed to their combination.

The NRHB model

Let us consider a multicomponent 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 noncollapsible voids, at temperature, T, and external pressure, p. Each molecule of type i is considered to consist of r_i equal segments of size v_i^* (set equal to 9.75 $\text{cm}^3\cdot\text{mol}^{-1}$) [20–22], and is characterized by two scaling constants, the hard-core density (or, equivalently, the hard-core specific volume), $\rho_i^* = 1/v_{sp,i}^*$, 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

$$r_i v_i^* = M_i v_{sp,i}^* \tag{1}$$

The scaling temperature and pressure are related through the equations

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

with k being the Boltzmann's constant. Having defined the scaling temperature, pressure, and density, the corresponding reduced quantities are defined as follows:

$$\tilde{T}_i = \frac{T}{T_i^*}, \tilde{p}_i = \frac{p}{p_i^*}, \tilde{v}_i = \frac{1}{\tilde{\rho}_i} = \frac{\rho_i^*}{\rho_i} = \frac{V_i}{V_i^*} = \frac{r_i N_i + N_0}{r_i N_i} \tag{3}$$

The molecular segments and holes are assumed to be 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. A key assumption in NRHB is the division of intermolecular interactions into physical and chemical or hydrogen-bonding interactions. We will come back to this assumption after we make some further definitions.

In the case of a mixture, one has to apply 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

$$x_i = \frac{N_i}{N_1 + N_2 + \ldots + N_t} = \frac{N_i}{N} \tag{4}$$

or the segment (or volume) fraction

$$\varphi_i = \frac{r_i N_i}{r_1 N_1 + r_2 N_2 + \ldots + r_t N_t} = \frac{r_i N_i}{rN} \tag{5}$$

or the (contact) surface area fraction

$$\theta_i = \frac{q_i N_i}{q_1 N_1 + q_2 N_2 + \ldots + q_t N_t} = \frac{q_i N_i}{qN} \tag{6}$$

zq_i is the total number of external contacts per molecule i. We may have a measure of the compactness or sphericity of the molecule through Stavermann's l parameter [30], defined by the equation

$$l_i = \frac{z}{2}\left(r_i - q_i\right) - \left(r_i - 1\right) \tag{7}$$

The higher the value of l the more compact is the molecule. When the molecule is linear, $l_i = 0$.

The NRHB model [21,22] may provide the expressions for the chemical potential in the mixture, or

$$\begin{aligned}\frac{\mu_i}{RT} &= \ln\frac{\varphi_i}{\omega_i r_i} - r_i\sum_j\frac{\varphi_j l_j}{r_j} + \ln\tilde{\rho} + r_i(\tilde{v}-1)\ln(1-\tilde{\rho}) \\ &\quad - \frac{z}{2}r_i\left[\tilde{v}-1+\frac{q_i}{r_i}\right]\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right] \\ &\quad + \frac{zq_i}{2}\left[\ln\Gamma_{ii} + \frac{r_i}{q_i}(\tilde{v}-1)\ln\Gamma_{00}\right] + r_i\frac{\tilde{P}\tilde{v}}{\tilde{T}} - \frac{q_i}{\tilde{T}_i} + \frac{\mu_{i,\mathrm{H}}}{RT}\end{aligned} \tag{8}$$

where ω_i is a characteristic quantity for each fluid that takes into account the flexibility and the symmetry of the molecule, Γ_{ii} and Γ_{00} are the non-randomness 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

$$\frac{\mu_{i,\mathrm{H}}}{RT} = r_i\nu_{\mathrm{H}} - \sum_{\alpha=1}^{m} d_\alpha^i \ln\frac{\nu_d^\alpha}{\nu_{\alpha 0}} - \sum_{\beta=1}^{n} a_\beta^i \ln\frac{\nu_a^\beta}{\nu_{0\beta}} \tag{9}$$

where ν_{H} is the total number of hydrogen bonds per segment, d_α^i is the number of donors of type α in molecule *i*, a_β^i is the number of acceptors of type β in molecule *i*, ν_d^α the number of donors of type α per segment, ν_a^β the number of acceptors of type β per segment and

$$\nu_{i0} = \nu_d^i - \sum_{j=1}^{n}\nu_{ij} \tag{10}$$

$$\nu_{0j} = \nu_a^j - \sum_{i=1}^{m}\nu_{ij} \tag{11}$$

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

The NRHB equation of state is given by

$$Z = \frac{pV}{NRT} = r_i\frac{\tilde{p}\tilde{v}}{\tilde{T}} = r_i\left[\tilde{v}\left(\frac{z}{2}-1\right)\ln\left(1-\tilde{\rho}\right) + \frac{l}{r} - \nu_{\mathrm{H}} - \frac{z}{2}\tilde{v}\ln\theta_0\Gamma_{00}\right] \tag{12}$$

It is worth pointing out that the above equations, along with the equation for the chemical potential of the ideal gas

$$\frac{\mu_i^{IG}}{RT} = \left(l_i - r_i\frac{l}{r} - \ln\omega_i^{IG} + \ln\frac{v^*}{RT}\right) + \ln x_i p = \frac{\mu_i^{0,IG}\left(T\right)}{RT} + \ln x_i p \tag{13}$$

may be used to obtain the full expression for the Gibbs energy of solvation of component *i* through the equation [31,32]:

$$\Delta G_i^{*S}\,(T, P,\{N\}) = \mu_i\,(T, P,\{N\}) - \mu_i^{IG}\,(T, P,\{N\}) + RT\ln Z \tag{14}$$

as well as its cavitation and charging components.

The group- or segment-contribution formalism of COSMO models

Let us now focus on the alternative group-contribution or surface segment-contribution formalism, which will facilitate the extension of NRHB with the COSMO approach.

Let us consider that our system contains k types of molecular surface segments, namely, n_i segments with charge density σ_i, $i = 1,k$, which are distributed in the t types of molecules N_1, ..., N_t. For consistency of nomenclature, we will set the number n_0 of segments of voids of no screening charge equal to the number N_0 of voids in the system. The dielectric continuum and continuum solvation picture of COSMOtherm is assumed to hold here. 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 $\varepsilon_{\mathrm{pair}}(\sigma_m, \sigma_n)$.

The chemical potential of surface segments or, equivalently, the surface segment activity coefficients of a segment with charge density σ_m and probability $p(\sigma_m)$, is given by [1–8]

$$\ln \Gamma\left(\sigma_m\right) = \ln \Gamma_m = -\ln\left\{\sum_{n=0}^{k} p\left(\sigma_n\right)\Gamma_n \exp\left[\frac{-\varepsilon_{\mathrm{pair}}\left(\sigma_m,\sigma_n\right)}{kT}\right]\right\} \tag{15}$$

In order to establish the link between this COSMO terminology and the more widely used terminology of surface area fractions, we may express the probability $p(\sigma_m)$ as follows:

$$p\left(\sigma_m\right) = \theta_m = \frac{Q_m n_m}{n_q} = \frac{n_m Q_m}{n_1 Q_1 + \ldots + n_k Q_k}\,\frac{n_1 Q_1 + \ldots + n_k Q_k}{n_0 + n_1 Q_1 + \ldots + n_k Q_k} = \Theta_m \theta,\ m = 1,\ldots,k \tag{16}$$

Θ_m in eq. 16 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

$$\theta = \frac{n_1 Q_1 + \ldots + n_k Q_k}{n_0 + n_1 Q_1 + \ldots + n_k Q_k} = \frac{Qn}{Qn + n_0} = \frac{Qn}{n_q} \tag{17}$$

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

$$E = \sum_{i=0}^{k}\sum_{j\geq i}^{k} n_{ij}\varepsilon_{\mathrm{pair}}\left(\sigma_i,\sigma_j\right) = \sum_{i=0}^{k} n_{0i}\varepsilon_{\mathrm{pair}}(0,i) + \sum_{i=1}^{k}\sum_{j\geq i}^{k} n_{ij}\varepsilon_{\mathrm{pair}}\left(\sigma_i,\sigma_j\right) = E_0 + E_1 \tag{18}$$

The link between the segment-activity coefficients Γ_m and the non-randomness factors Γ_{mn} for the distribution of a segment m around a central segment n is established by the equation

$$\Gamma_{mm} = \Gamma_m \Gamma_n \exp\left[\frac{-\varepsilon_{\mathrm{pair}}\left(\sigma_m,\sigma_m\right)}{kT}\right] = \Gamma_m \Gamma_n \tau_{mn} \tag{19}$$

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

$$n_{mn} = znQ\Theta_m \theta_n \Gamma_{mn} = znQ\theta\Theta_m\Theta_n\Gamma_m\Gamma_n\tau_{mn} \tag{20}$$

and between segments m and m, by the equation

$$n_{mm} = \frac{1}{2}znQ\Theta_m\theta_m\Gamma_{mm} = \frac{1}{2}znQ\theta\Theta_m^2\Gamma_m^2\tau_{mm} \tag{21}$$

In a similar manner, the number of contacts 0 – 0 between empty sites in our system is given by

$$n_{00} = \frac{1}{2}zn_0\theta_0\Gamma_{00} = \frac{1}{2}zn_0\theta_0\Gamma_0^2 \tag{22}$$

where $\theta_0 + \theta = 1$.

Mass balance or conservation equations for the inter-segmental contacts take, then, the form

$$\sum_{n=0}^{k} n_{mn} = zn_m Q_m \text{ or } \theta_0 \Gamma_{m0} + \theta \sum_{n=1}^{k} \Theta_n \Gamma_{mn} = \Gamma_m \left\{ \theta_0 \Gamma_0 + \theta \sum_{n=1}^{k} \Theta_n \Gamma_n \tau_{mn} \right\} = 1 \tag{23}$$

which gives the working equation for calculating segment-activity coefficients

$$\Gamma_m = 1 / \left\{ \theta_0 \Gamma_0 + \theta \sum_{n=1}^{k} \Theta_n \Gamma_n \tau_{mn} \right\} \tag{24}$$

This is the alternative way of writing eq. 15 in terms of surface area fractions. In the case of a compact system without empty sites (as in the case of the plain COSMO models), eq. 24 becomes

$$\Gamma_m = 1 / \left\{ \sum_{n=1}^{k} \Theta_n \Gamma_n \tau_{mn} \right\} \text{ no empty sites} \tag{25}$$

As discussed previously [9,15], eqs. 15, 24, and 25 reflect the quasi-chemical character of the COSMO models. In the quasi-chemical framework, then, we may write the full form of the configurational partition function in its maximum term approximation as follows [9,10,15,16,21,22]:

$$\Xi = \Omega_{\mathrm{R}} \frac{\prod_{m} \left(n_{mn}^{0}! \right) \prod_{n \neq m} \left[\left(\frac{1}{2} n_{mn}^{0} \right)! \right]^2}{\prod_{m} \left(n_{mn}! \right) \prod_{n \neq m} \left[\left(\frac{1}{2} n_{mn} \right)! \right]^2} \exp \left(- \frac{\sum_{m} \sum_{n \geq m} n_{mn} \varepsilon_{\mathrm{pair}} \left(\sigma_m, \sigma_n \right)}{kT} \right) \tag{26}$$

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 [30] as in COSMOtherm and in NRHB. Superscript 0 refers to the perfectly random case. The corresponding quantities in the case of non-randomness are given by

$$n_{mn} = n_{mn}^{0} \Gamma_{mn} = n_{mn}^{0} \Gamma_m \Gamma_n \tau_{mn} \tag{27}$$

Before proceeding further, it is worth writing down some key equations expressing the equivalence between quantities in NRHB and in COSMO models.

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

$$zq_i = \sum_{m=1}^{k} \nu_{mi} z Q_m \tag{28}$$

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

$$n_m = \sum_{i=1}^{t} N_i \nu_{mi} \tag{29}$$

and

$$znQ = z \sum_{m=1}^{k} n_m Q_m = z \sum_{i=1}^{t} \sum_{m=1}^{k} N_i \nu_{mi} Q_m = zN \sum_{i=1}^{t} \sum_{m=1}^{k} x_i \nu_{mi} Q_m = zqN \tag{30}$$

Combining eqs. 16, 17, 29, and 30, we obtain

$$zn_m Q_m = zN\sum_{i=1}^{t} x_i \nu_{mi} Q_m = zqN\Theta_m = znQ\Theta_m \tag{31}$$

The equivalent of eq. 31 in COSMO terminology is obtained by recalling that

$$zq_i = \frac{A_i}{\alpha_{\text{eff}}} \tag{32}$$

and

$$A_i(\sigma_m) = A_i p_i(\sigma_m) \tag{33}$$

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, $p_i(\sigma_m)$ is the probability to find a segment of charge σ_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

$$p_i\left(\sigma_m\right) = \frac{A_i\left(\sigma_m\right)}{A_i} = \Theta_m^i = \frac{z\nu_{mi}Q_m}{zq_i} \tag{34}$$

In group-contribution terminology, the equation for the chemical potential of component i becomes

$$\begin{aligned}\frac{\mu_i}{RT} &= \ln\tilde{\rho}\frac{\varphi_i}{\omega_i r_i} - r_i l + r_i\left(\tilde{v}-1\right)\ln\left(1-\tilde{\rho}\right) - \frac{z}{2}r_i\left[\tilde{v}-1+\frac{q_i}{r_i}\right]\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right] \\ &+ zr_i\left(\tilde{v}-1\right)\ln\Gamma_0 + r_i\frac{P\tilde{v}v^*}{kT} + zq_i\sum_{m=1}^{k}\Theta_m^i \ln\Gamma_m\end{aligned} \tag{35}$$

The last term in eq. 35 may be written in COSMO terminology as

$$zq_i\sum_{m=1}^{k}\Theta_m^i \ln\Gamma_m = \frac{A_i}{\alpha_{\text{eff}}}\sum_{m=1}^{k} p_i\left(\sigma_m\right)\ln\Gamma_m \tag{36}$$

In this combined terminology, the Gibbs energy of cavitation of pure component i is given by

$$\frac{\Delta G_{i/i}^{*\text{CAV}}}{RT} = -r_i\ln\left(1-\tilde{\rho}\right) + \frac{z}{2}\left(r_i - q_i\right)\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right] \tag{37}$$

while the charging component of the Gibbs energy of self-solvation is given by

$$\frac{\Delta G_{i/i}^{*\text{CHR}}}{RT} = -zr_i\ln\Gamma_0 + zq_i\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_m \tag{38}$$

The hydrogen-bonding factor: From NRHB to NRCosmo

An alternative way of expressing the partition function in NRHB is as follows:

$$\Xi = \Xi_p \Xi_{\text{HB}} \tag{39}$$

The first factor encompasses all contributions from all types of intermolecular forces except for the hydrogen-bonding ones. The second factor is a correction factor and accounts for the contributions of the hydrogen-bonding interactions. As already mentioned, this second factor was formulated in NRHB on the basis of the Veytsman statistics [23,24]. The key advantage of this formulation was the capacity to handle complex 3-dimensional hydrogen-bonding networks in a simple and straightforward manner at any external conditions of the fluid system.

In the COSMO approach, the hydrogen-bonding interactions are also separated from all other interactions. The key advantage in this case is the availability of hydrogen-bonding interactions for practically any system of interest (if the relevant *cosmo* files are not available in the existing databases, they can be obtained in a rather straightforward manner from widely available packages for quantum-mechanics calculations).

If we wish to extract information for the hydrogen-bonding interactions from the COSMO approach, we may write eq. 39 in the following manner:

$$\Xi = \Xi_p \Xi_{\text{HB-COSMO}} \tag{40}$$

There are various ways of formulating $\Xi_{\text{HB-COSMO}}$. In this work, we will present one simple way, just as an example. The starting point is eq. 26, which can be rewritten as

$$Q_{\text{HB-COSMO}} = \frac{\prod_m \left(n^0_{mn}!\right) \prod_{n \neq m} \left[\left(\frac{1}{2} n^0_{mn}\right)!\right]^2}{\prod_m \left(n_{mn}!\right) \prod_{n \neq m} \left[\left(\frac{1}{2} n_{mn}\right)!\right]^2} \exp\left(- \frac{\sum_m \sum_{n \geq m} n_{mn} \varepsilon_{\text{HB}}\left(\sigma_m, \sigma_n\right)}{kT} \right) \tag{41}$$

The contact numbers, $n_{mn} = n^0_{mn}\Gamma_{mn} = n^0_{mn}\Gamma_m\Gamma_n\tau_{mn}$, in this equation obey the quasi-chemical conditions [9,10,15,16]

$$\frac{4n_{mm}n_{nn}}{n^2_{mn}} = \frac{\Gamma_{mm}\Gamma_{nn}}{\Gamma^2_{mn}} = \exp\left(\frac{\Delta\varepsilon_{mn}}{RT}\right) m = 1,\ldots,t \text{ and } n = m+1,\ldots,t \tag{42}$$

where the interchange energy $\Delta\varepsilon_{mn}$ is given by

$$\Delta\varepsilon_{mn} = \varepsilon_{\text{pair}}(\sigma_m,\sigma_m) + \varepsilon_{\text{pair}}(\sigma_n,\sigma_n) - 2\varepsilon_{\text{pair}}(\sigma_m,\sigma_n) \tag{43}$$

In analogy to NRHB, a simple way of coupling the two approaches is to write eq. 40 as

$$\ln \Xi = \ln \Xi_p + g(\rho) \ln Q_{\text{HB-COSMO}} \tag{44}$$

where $g(\rho)$ is an appropriate function of the density satisfying two boundary conditions:

1) At zero densities (gaseous state): $g(\rho) = 0$
2) In the absence of empty sites (compact state) $g(\rho) = 1$

The second condition is a direct consequence of the fact that in the original COSMO formulation [1–8], there were no empty sites and there was no density-dependent factor multiplying the partition function Ξ, or, $g(\rho) = 1$. A simple function satisfying both boundary conditions is

$$g(\rho) = \theta \tag{45}$$

which will be adopted in this work. By applying the quasi-chemical conditions, eqs. 42 in the last term of eq. 44, and by making, in addition, use of eqs. 19 and 41, eq. 44 becomes

$$\ln \Xi = \ln \Xi_p - g\left(\rho\right) zN \sum_{i=1}^{t} x_i q_i \sum_{m=1}^{k} \Theta^i_m \ln \Gamma_{m-\text{HB}} \tag{46}$$

where $\Gamma_{m\text{-HB}}$ is the activity coefficient of segment m, as calculated by the COSMO model excluding all but the hydrogen bonding interactions. Equation 46 is the key equation of the NRCosmo model. By setting $g(\rho)$ equal to θ, the partition function of eq. 46 leads to the following equation for the chemical potential:

$$\begin{aligned}\frac{\mu_i}{RT} &= \ln\tilde{\rho}\frac{\varphi_i}{\omega_i r_i} - r_i l + r_i\left(\tilde{v}-1\right)\ln\left(1-\tilde{\rho}\right) - \frac{z}{2}r_i\left[\tilde{v}-1+\frac{q_i}{r_i}\right]\ln\left[1-\tilde{\rho}+\frac{q}{r}\tilde{\rho}\right] \\ &+ \frac{zq_i}{2}\left(\ln\Gamma_{ii} - \frac{\varepsilon_{i,p}}{kT}\right) + zr_i\left(\tilde{v}-1\right)\ln\Gamma_0 + r_i\frac{P\tilde{v}v^*}{kT} + zq_i\theta\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_{m-\text{HB}} \\ &+ zr_i\left(\frac{q_i}{r_i}-\frac{q}{r}\right)\theta\theta_0\sum_{i=1}^{t}\Theta_i\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_{m-\text{HB}}\end{aligned} \tag{47}$$

where $z\varepsilon_{i,p}/2 = \varepsilon_i{}^*$ is the average interaction energy per segment of molecule i encompassing all types of intermolecular interactions except for the hydrogen-bonding ones. It is the classical scaling constant for the energy of the NRHB model. The last term in eq. 47 makes a practically insignificant contribution and may be neglected. A comparison of eq. 47 with the corresponding equation of the plain NRHB model (eq. 8 above) leads to the following expression for the hydrogen-bonding contribution to the chemical potential of component i in the mixture

$$\frac{\mu_{i,\text{HB}}}{RT} = zq_i\theta\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_{m-\text{HB}} \tag{48}$$

In a similar manner, eq. 46 leads to the following expression for the equation of state

$$\frac{pv^*}{kT} + \ln\left(1-\tilde{\rho}\right) - \frac{z}{2}\ln\left[1+\frac{q}{r}\tilde{\rho}-\tilde{\rho}\right] - \tilde{\rho}l + z\ln\Gamma_0 + z\theta^2\sum_{i=1}^{t}\Theta_i\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_{m-\text{HB}} = 0 \tag{49}$$

The last term in eq. 49 corresponds to the term $\tilde{\rho}v_H$ of the plain NRHB model (cf. eq. 12 above). In this term, Θ_i is the surface fraction of component i in the compact (no empty sites) mixture.

The equation for the cavitation component of the solvation Gibbs energy, in this case, is identical to eq. 37, while the charging component is given by

$$\frac{\Delta G_{i/i}^{*\text{CHR}}}{RT} = \frac{zq_i}{2}\left(\ln\Gamma_{ii} - \frac{\varepsilon_{i,p}}{kT}\right) - zr_i\ln\Gamma_0 + z\left(q_i + r_i\right)\theta\sum_{m=1}^{k}\Theta_m^i\ln\Gamma_m \tag{50}$$

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

$$\begin{aligned}\frac{\Delta G_{1/2}^{*S} - \Delta G_{1/1}^{*S}}{RT} &= \frac{\mu_1\left(T,p,x_1\to 0\right) - \mu_1^{IG}\left(T,p,x_1\to 0\right)}{RT} - \frac{\mu_1^0\left(T,p\right) - \mu_1^{0,IG}\left(T,p\right)}{RT} \\ &+ \ln Z\left(x_1\to 0\right) - \ln Z\left(x_1 = 1\right) = \ln\gamma_{1/2}^{\infty} + r_1\frac{l}{r} - l_1 + \ln\frac{r_2}{r_1} + \ln\frac{\tilde{\rho}_1}{\tilde{\rho}_2}\end{aligned} \tag{51}$$

where Z is the compressibility factor. By making the appropriate substitutions, we obtain

$$\begin{aligned}\ln\gamma_{1/2}^{\infty} &= \ln\frac{r_1\tilde{\rho}_2}{r_2\tilde{\rho}_1} - r_1\ln\frac{\left(1-\tilde{\rho}_2\right)}{\left(1-\tilde{\rho}_1\right)} - \frac{z}{2}\left[q_1 - r_1\right]\ln\frac{\left[1-\tilde{\rho}_2 + {}^{q_2}\!/_{r_2}\,\tilde{\rho}_2\right]}{\left[1-\tilde{\rho}_1 + {}^{q_1}\!/_{r_1}\,\tilde{\rho}_1\right]} \\ &+ \frac{zq_1}{2}\ln\frac{\Gamma_{rr,2}}{\Gamma_{rr,1}} - \frac{zr_1}{2}\ln\frac{\Gamma_{00,2}}{\Gamma_{00,1}} - 2q_1\theta_2\Gamma_{rr,2}\frac{\varepsilon_{12}^{*} - \varepsilon_2^{*}}{RT} + \frac{q_1}{\tilde{T}_1} - \frac{q_1}{\tilde{T}_2} \\ &+ \left\{zq_1\theta\sum_{m=1}^{k}\Theta_m^1 \ln\Gamma_{m-\mathrm{HB}}\right\}_{x_1=0} - \left\{zq_1\theta\sum_{m=1}^{k}\Theta_m^1 \ln\Gamma_{m-\mathrm{HB}}\right\}_{x_1=1}\end{aligned} \tag{52}$$

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

$$\Omega_{1/2}^{\infty} = \gamma_{1/2}^{\infty}\left(\frac{r_2\rho_2^{*}}{r_1\rho_1^{*}}\right) \tag{53}$$

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

$$\ln\frac{k_{\mathrm{H},1}}{p_1^0\left(T\right)} = \ln\gamma_1^{\infty}\left(T,p\right) \tag{54}$$

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 [33], or

$$y_1 = \frac{1}{\gamma_{1/2}^{\infty}}\left(\frac{f_1^{0S}}{f_1^{0L}}\right) \tag{55}$$

The term in parenthesis 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

$$\ln\left(\frac{f_1^{0S}}{f_1^{0L}}\right) = \frac{\Delta H_1^m}{RT}\left(\frac{T}{T_1^m} - 1\right) \tag{56}$$

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

APPLICATIONS

All calculations will be done by using either the *Cosmotherm-C12* and *Cosmo base* package of Cosmologic GmbH [25] or the Virginia Tech database of sigma profiles [26], while TURBOMOLE [28] will be used for obtaining *cosmo* files. There are many possible combinations of NRHB and COSMO approaches, but here we will confine ourselves to one approach, named hereafter as *NRCosmo*, where the calculations will be done with eqs. 47 and 49. Before proceeding further, however, it is essential to comment at this point on the nature of the intermolecular interactions that we will consider in this work.

As already mentioned, in systems of non-electrolytes, the interactions considered in NRHB are of two types: the strong specific (hydrogen-bonding) interactions and all other interactions collectively called "physical" interactions. In the COSMO approach and apart from the hydrogen-bonding interactions, the remaining interactions can be broken down into four types [1–8]. The "misfit" interactions are the first type. The misfit and the hydrogen-bonding interactions can be accounted for when the COSMO sigma profiles of the fluids are available. The other three types of interactions are discussed in the frame of the solvation picture, but in the COSMO approach they are not considered to contribute to the non-random distribution of the interacting segments. Of these, the second type is the van der Waals or dispersion interactions. In the COSMO approach, these interactions are nonspecific and are considered proportional to the exposed surface of the atoms in the system. The third type of interaction 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.

In the approach adopted in this work, we consider that the physical interactions contribute to the actual free-volume distribution and account for it through the plain NRHB procedure [21,22]. The physical interactions for each component in the system are assumed to vary linearly with the temperature, or

$$\varepsilon_h = \varepsilon^*_h + \varepsilon^*_s\,(T - 298.15\ K) \tag{57}$$

The hydrogen-bonding interactions are considered to contribute to the non-random distribution of interacting molecular segments and account for it through the COSMO approach. This is entirely analogous to the corresponding structure of NRHB, where the hydrogen-bonding interactions are treated separately from all other interactions.

In this approach, each pure fluid is characterized by the two NRHB scaling constants, the specific hard-core volume, v^*_{sp}, and the average per-segment interaction energy, ε^*. Table 1 presents the scaling constants for some representative common fluids. A weak variation with temperature is allowed for both constants, as shown in Table 1. No other parameters are needed as long as the COSMO sigma profiles [1–8] of the fluid are available. The NRHB constants were obtained as before [21,22] from vapor pressure, heat of vaporization, and density data of the DIPPR compilation [34], Perry's handbook [35], and Zoller's compilation [36].

Table 1 Characteristic constants of pure fluids (NRCosmo).

Fluid	ε_h^*/J·mol^{-1}	ε_s^*/J·K^{-1}·mol^{-1}	$v^*_{sp} = \rho^{*-1}$/cm^3·g^{-1}	v_{sp1}/cm^3·g^{-1}·K^{-1}
Methane	2047	–0.8710	2.2560	–0.0003
Ethane	2965	–0.6369	1.6195	–0.0003
Propane	3420	0.1617	1.4330	–0.0003
n-Butane	3693	0.9716	1.3490	–0.0003
n-Pentane	3843	1.0577	1.2930	–0.0003
n-Hexane	3959	1.4147	1.2766	–0.0003
n-Heptane	4071	1.3553	1.2520	–0.0003
n-Octane	4134	1.5842	1.2287	–0.0003
n-Nonane	4122	1.6535	1.1972	–0.0003
n-Decane	4242	1.6900	1.1991	–0.0003
n-Undecane	4272	1.8159	1.1913	–0.0003
n-Dodecane	4281	1.9678	1.1863	–0.0003
n-Hexadecane	4419	1.6596	1.1242	–0.0003

(*continues on next page*)

Table 1 (*Continued*).

Fluid	ε_h*/J·mol^{-1}	ε_s*/J·K^{-1}·mol^{-1}	$v^*_{sp} = \rho^{*-1}$/cm^3·g^{-1}	v_{sp1}/cm^3·g^{-1}·K^{-1}
Cyclohexane	4559	0.7663	1.1500	0.0001
Benzene	5098	0.1899	1.0808	–0.0000
Toluene	5059	0.1507	1.0714	0.0001
Methanol	3478	–1.9495	1.2676	–0.0001
Ethanol	4220	–2.2019	1.2180	–0.0001
1-Propanol	4321	–0.9417	1.1889	–0.0001
1-Butanol	4428	–0.3947	1.1640	–0.0001
1-Pentanol	4446	0.2570	1.1468	–0.0001
1-Hexanol	4497	0.4639	1.1394	–0.0001
1-Octanol	4545	0.9546	1.1250	–0.0001
1-Decanol	4594	0.9550	1.1002	–0.0001
Phenol	7237	2.7430	0.9630	–0.0001
2-Methoxy ethanol	4507	0.3715	1.0163	–0.0001
2-Ethoxy ethanol	4383	0.5146	1.0337	–0.0001
Ammonia	4048	–2.9690	0.8589	–0.0001
Acetic acid	5644	–0.7503	0.9510	–0.0000
Propionic acid	5220	–1.8283	0.9676	–0.0000
n-Butyric acid	5307	–1.3141	1.0015	–0.0000
Water	1234	–11.697	1.0090	–0.0000
Carbon dioxide	3509	–2.6270	0.7907	–0.0000
Acetone	4858	–0.4754	1.1597	–0.0000
Butyl acetate	4488	0.5572	1.008	–0.0000
Vinyl acetate	4637	–0.2817	0.9410	–0.0000
Tetrahydrofuran	4702	0.3031	1.0037	–0.0001
Chloroform	4968	0.0249	0.6124	–0.0000
Paracetamol	6449	2.5944	1.1065	0.0001
Poly(vinyl acetate)—PVAc	5970	2.5919	0.8092	0.0001

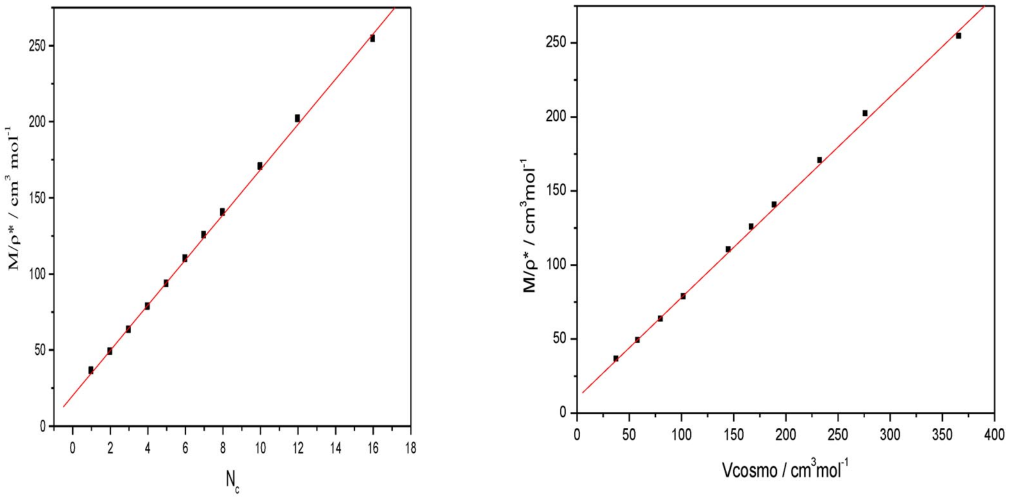
The scaling constants of the NRCosmo model vary in a regular manner within homologous series. Thus, Fig. 1 shows the variation of hard-core volume of normal alkanes vs. the number of carbon atoms of the hydrocarbon chain and vs. the corresponding COSMO volume [1–8]. In both cases, a straight line is obtained.

Figure 2 shows that, in the case of normal alkanes, there is a linear relation between the interaction energy ε^*_h and the corresponding hard-core density. In addition, the mean molar intermolecular energy, $r\varepsilon_h$*, varies linearly with the corresponding COSMO surface area, as shown in Fig. 3. Almost linear is also the variation of the mean intermolecular energy, $r\varepsilon_s$*, with the corresponding COSMO surface area as shown in Fig. 4.

A similar picture is observed for the homologous series of 1-alkanols. Figure 5 shows the variation of hard-core volume of normal 1-alkanols vs. the number of carbon atoms of the hydrocarbon chain and vs. the corresponding COSMO volume. Again, a straight line is obtained in both cases.

Figure 6 shows the linear relation between the mean molar intermolecular energy, $r\varepsilon_h$*, of 1-alkanols and the corresponding COSMO surface area.

Regarding the correlation of orthobaric densities, heats of vaporization, and vapor pressures of pure fluids, the performance of the NRCosmo model is practically identical to that of the plain NRHB model. The significant advantage of NRCosmo over NRHB is the availability of hydrogen-bonding parameters for any fluids as long as the corresponding *cosmo* files or the sigma profiles are available. In contrast, in NRHB one must estimate the hydrogen-bonding parameters, and this is not always easy. Thus, for simplicity, NRHB uses one single set of hydrogen-bonding constants for all 1-alkanols. With



(a) (b)

Fig. 1 Hard-core volume of normal alkanes as calculated by the NRCosmo model. (a) Hard-core volume vs. the corresponding number of carbon atoms of *n*-alkanes. The line corresponds to the equation: $M/\rho^* = 20.0618 + 14.8581N_c$ (R = 0.9996). (b) Hard-core volume vs. the corresponding COSMO volume. The line corresponds to the equation: $M/\rho^* = 10.1748 + 0.6783 Vcosmo$ (R = 0.9994).

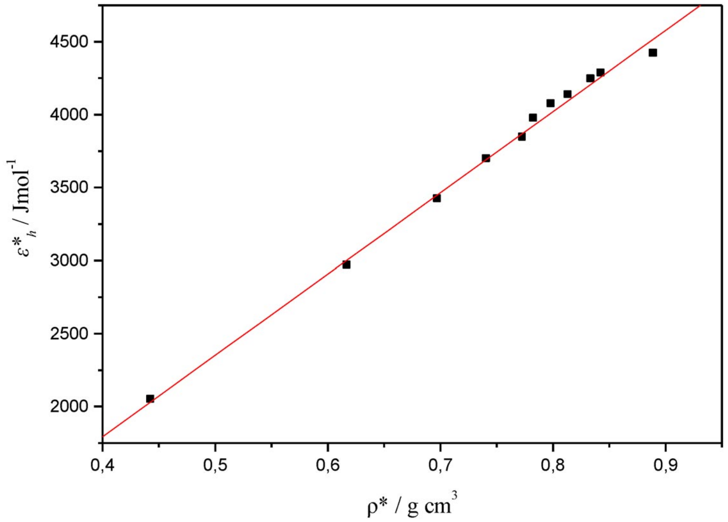


Fig. 2 Interaction energy ε^*_h of normal alkanes as calculated by the EOS model vs. the corresponding hard-core density of carbon atoms of *n*-alkanes. The line corresponds to the equation: $\varepsilon^*_h = -431.62 + 5565.73\rho^*$ (R = 0.998).

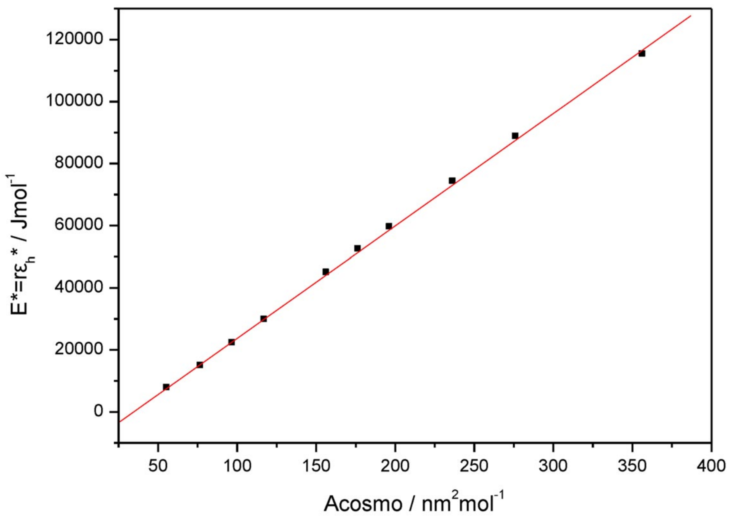


Fig. 3 Mean intermolecular energy, $r\varepsilon_h$*, as calculated by the present EOS model vs. the corresponding COSMO surface area for *n*-alkanes. The line corresponds to the equation: $E^* = -12552.19 + 362.41Acosmo$ (R = 0.9997).

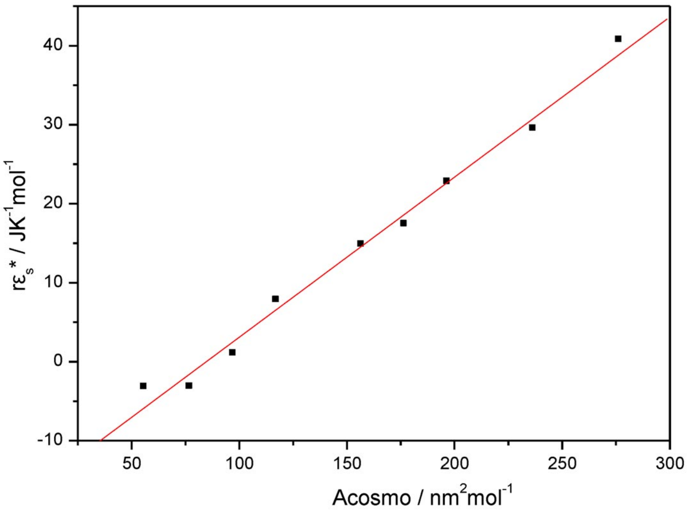
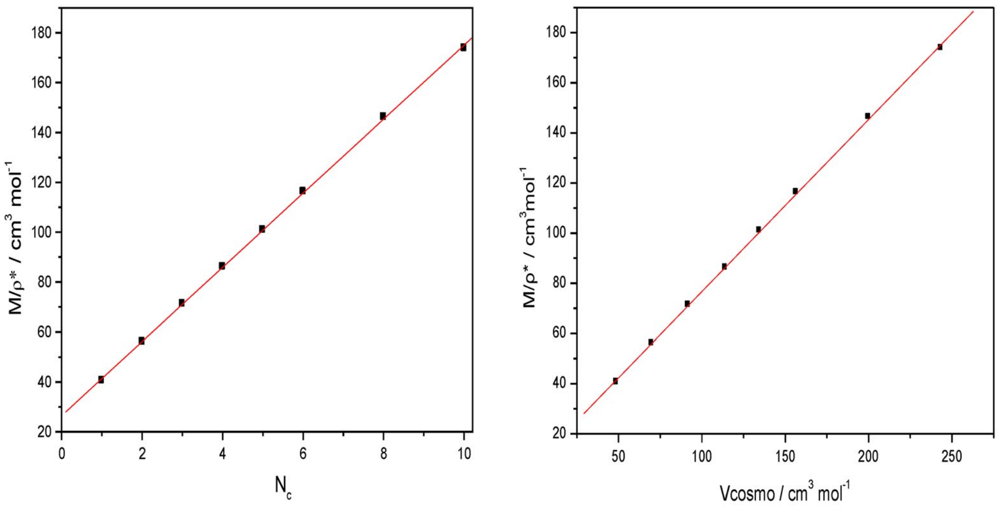


Fig. 4 Mean intermolecular energy, $r\varepsilon_s$*, as calculated by the present EOS model vs. the corresponding COSMO surface area for 1-alkanes, from methane to *n*-dodecane. The line corresponds to the equation: $r\varepsilon_s^* = -17.1711 + 0.2027Acosmo$ (R = 0.995).

NRCosmo this simplification is not necessary. Figure 7 shows the free-energy change upon formation of the OH•••OH hydrogen bond in 1-alkanols, which varies from ca. –20 000 up to ca. –15 000 J•mol^{-1}. The single value adopted by NRHB (–17 200 J•mol^{-1}) is in-between the values calculated by NRCosmo.

The above-mentioned equivalence between NRHB and NRCosmo in the calculation of the thermodynamic properties of fluids extends to other thermophysical properties, such as the surface tension. Figure 8 compares the calculations of NRHB and NRCosmo for the surface tension of 1-propanol. As shown, the two calculations are practically identical.



(a) (b)

Fig. 5 Hard-core volume of normal 1-alkanols as calculated by the NRCosmo model. (a) Hard-core volume vs. the corresponding number of carbon atoms of 1-alkanols. The line corresponds to the equation: $M/\rho^* = 26.47865 + 14.8577N_c$ (R = 0.9999). (b) Hard-core volume vs. the corresponding COSMO volume. The line corresponds to the equation: $M/\rho^* = 7.9979 + 0.6867Vcosmo$ (R = 0.9999).

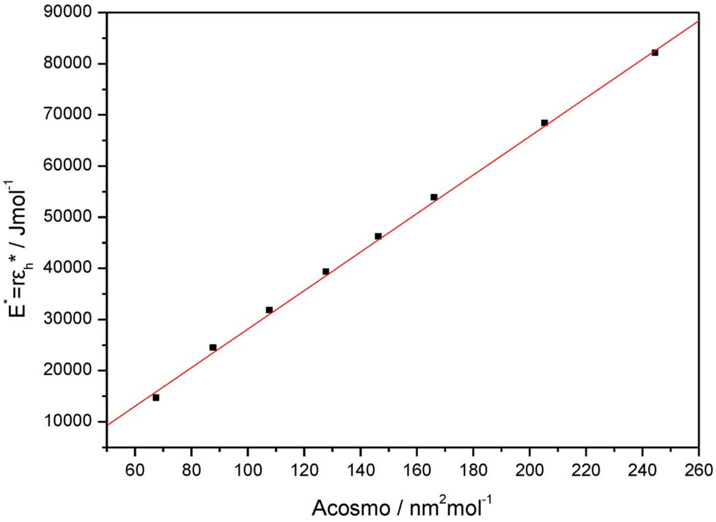


Fig. 6 Mean intermolecular energy, $r\varepsilon_h^*$, as calculated by the NRCosmo model vs. the corresponding COSMO surface area for 1-alkanols. The line corresponds to the equation: $E^* = -9584.81 + 376.95Acosmo$ (R = 0.9994).

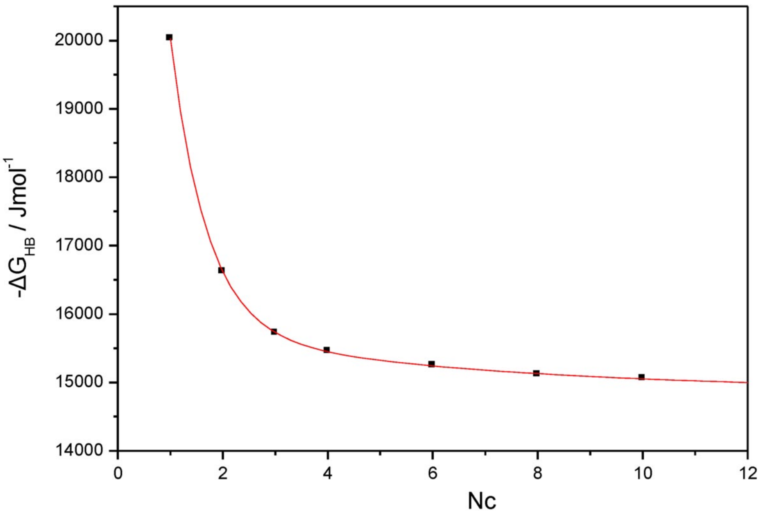


Fig. 7 Free-energy change upon hydrogen-bond formation in 1-alkanols as calculated by the COSMO approach at 298.15 K. The corresponding value for NRHB is –17 200 J•mol^{-1} for all alkanols. The line through the data is to aid the eye.

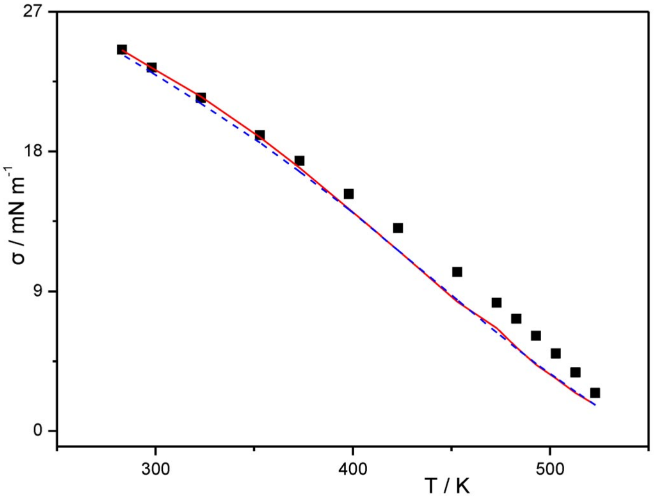


Fig. 8 Experimental [34] (symbols) and calculated (lines) surface tension of 1-propanol. Solid line was calculated by the NRCosmo approach while dashed line with the plain NRHB model [21,22].

NRCosmo may be used for calculations in mixtures with the same ease as with the plain NRHB model. Once again, NRCosmo does not need any knowledge of cross-association hydrogen-bonding interactions that may operate when mixing different fluids. Figure 9 compares the predictions of the NRCosmo with experimental vapor–liquid equilibrium data for the CO_2–ethanol mixture at two temperatures. Of particular interest are the applications to polymer systems. In this case, one has to create the *mcos* files for the polymer [7] starting from the *cosmo* files of fragments or smaller molecular entities of the repeating units. Figure 10 compares the predictions of the NRCosmo model with the experimental vapor–liquid equilibrium data for the system methanol–poly(vinyl acetate). An analogous comparison is made in Fig. 11 for the system ethanol–poly(vinyl acetate). The same figure shows the

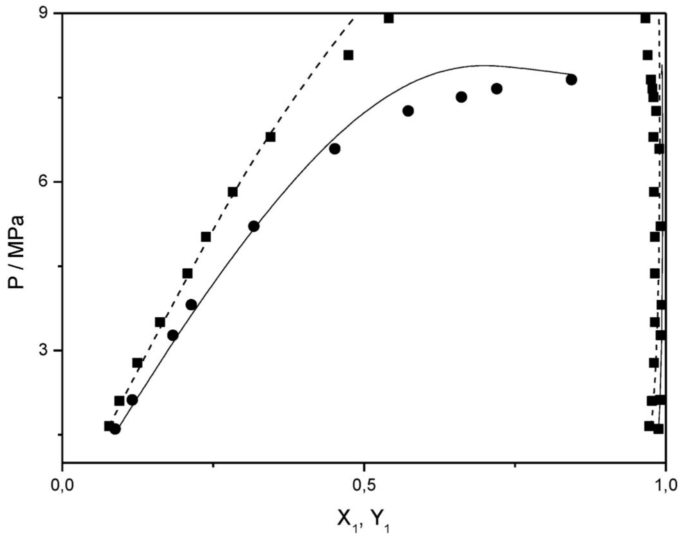


Fig. 9 Experimental [37] and calculated vapor–liquid equilibria for the system CO_2–ethanol at 313.15 K (circles + solid lines) and at 328.15 K (squares + dashed lines). The lines are predictions (ξ_{12} = 1.0) of the NRCosmo model.

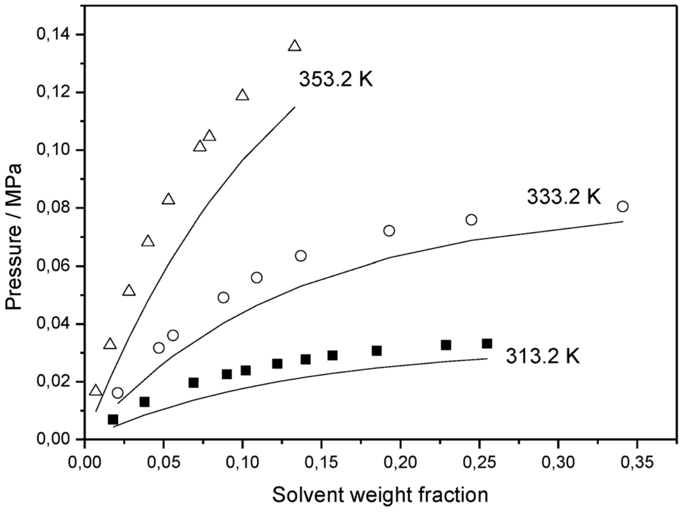


Fig. 10 Methanol–PVAc predictions of NRCosmo model (solid lines) and comparison with experimental data [38] (symbols).

corresponding calculations with the plain NRHB model. The picture that emerges from these last figures for the performance of NRCosmo is rather satisfactory and, essentially, equivalent to that of the NRHB model.

One may appreciate the advantages of NRCosmo by applying it to systems with many types of hydrogen bonds. Typical examples are the systems with paracetamol, whose molecule is shown in Scheme 1. In a mixture of paracetamol with ethanol, one has to account for nine different types of hydrogen bonds (considering the hydroxyl groups of paracetamol and ethanol different) or five different types (considering the two hydroxyls identical). In either case, the task of determining the corresponding hydrogen-bonding parameters is rather tedious for NRHB, while for NRCosmo these inter-

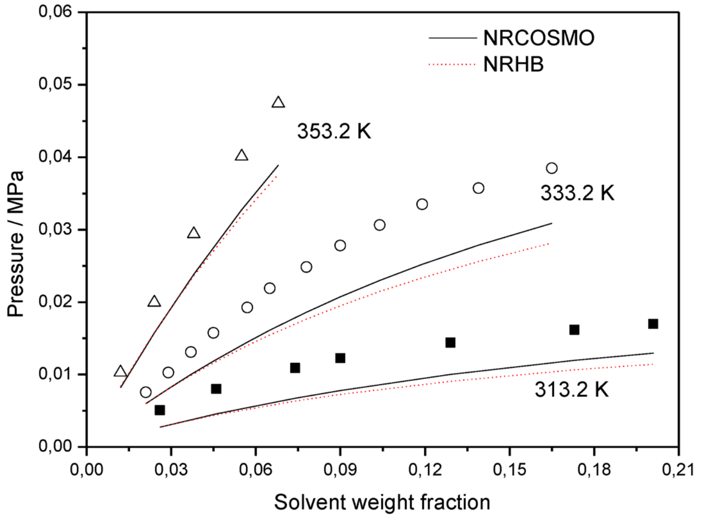
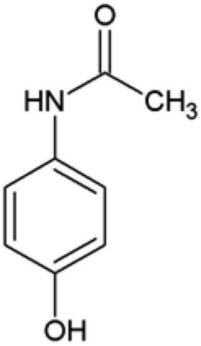


Fig. 11 Ethanol–PVAc predictions by plain NRHB (dashed lines) and by NRCosmo (solid lines). Comparison with experimental data [38] (symbols).



Scheme 1 Chemical form of paracetamol.

actions are already available when the *cosmo* files and sigma profiles for both molecules are available. Figure 12 compares the predictions of NRCosmo with the calculations of plain NRHB and with the experimental solid–liquid equilibrium data or solubility of paracetamol in ethanol. A similar comparison is made in Fig. 13 for the solubility of paracetamol in methanol. In view of the complexity of these systems, the predictions of the NRCosmo model are quite satisfactory.

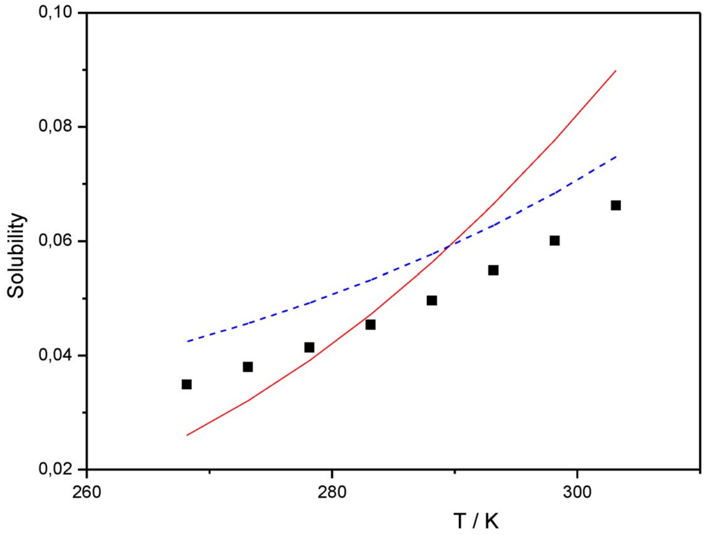


Fig. 12 Prediction of solubility of paracetamol in ethanol (SLE) as a function of temperature (solid line) with NRCosmo and calculations of plain NRHB with $k_{ij} = 1$ (dashed line). Symbols are experimental data [39].

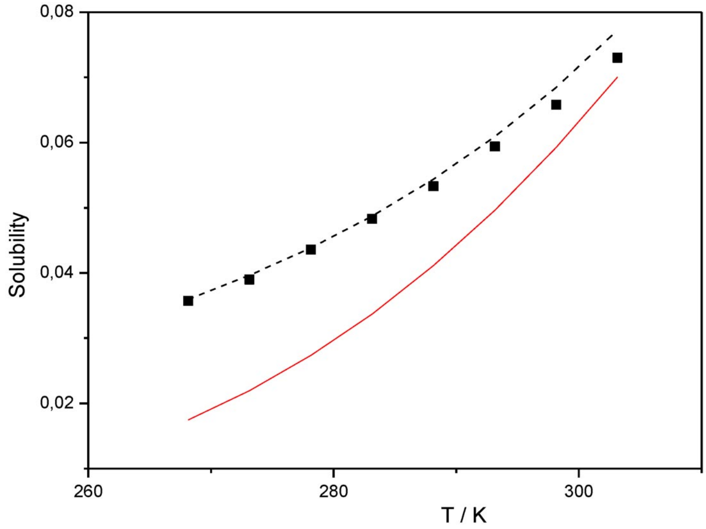


Fig. 13 Prediction of solubility of paracetamol in methanol (SLE) as a function of temperature (solid line) with NRCosmo and calculations of plain NRHB with $k_{ij} = 1$ (dashed line). Symbols are experimental data [39].

DISCUSSION AND CONCLUSIONS

The approach that we adopted in this work amounts to replacing the hydrogen-bonding factor in the configurational partition function of the NRHB model by the corresponding factor from the COSMO models [1–8]. In order to do this, one has to recognize that the configurational partition function of the COSMO models can be written down as a plain quasi-chemical group-contribution (or rather segment-contribution) model. Once this is recognized, the next step is the selection of the hydrogen-bonding interactions out of all intersegmental interactions. For this selection, we have adopted here the same criteria as those in the COSMO models (threshold sigma values and value of the hydrogen-bonding constant c_{hb}).

Having the exact form of the COSMO hydrogen-bonding factor of the partition function, the next step is the introduction of density or free volume in the system. One rather straightforward way of doing this is to allow for a number of empty sites to be present in the system and then follow the standard thermodynamic procedure as was done, as an example, in the PV model [19,20]. This approach was adopted earlier [15] and led to a consistent COSMO equation-of-state model where the density dependence of all interactions was emerging from the free-energy minimization (derivation of the equation of state). However, since this minimization was performed simultaneously with the free-energy minimization with respect to all cross non-randomness factors, Γ_{ij}, this approach is computationally intensive and relatively slow.

The alternative approach adopted in the present work is very much faster than the earlier one [15] and without any significant reduction in its overall performance. The density dependence of the COSMO term is done in a manner analogous to that for the NRHB model. The rationale amounts to adopting eq. 44 and the two boundary conditions for $g(\rho)$. This is certainly an approximation but, as in NRHB, the performance of the resulting model indicates that the approximation is not, at least, conceptually wrong. In essence, with the adopted approximation, the resulting NRCosmo model is as good as the NRHB model. However, NRCosmo has a great advantage over NRHB: It does not need any additional information regarding hydrogen bonds, no matter how involved they may be. All needed information, derived from quantum-mechanics calculations, is incorporated in the associated *cosmo* files or *sigma profiles* of the pure components of the system.

The new equation-of-state model can practically do all that NRHB does. It is applicable to molecules of any size, to the liquid, to the vapor as well as to the supercritical state, to homogeneous as well as to heterogeneous systems. The model can satisfactorily predict solid–liquid equilibria in rather complex systems like the ethanol-paracetamol one.

In its present form, the NRCosmo model requires two scaling constants per fluid, an interaction (free) energy, and a hard-core density. In homologous series, these constants vary in a regular manner obeying simple linear relations with the corresponding COSMO surface area or COSMO volume. A systematic study of these relations for a large number of fluids might uncover simple universal relations between the NRCosmo scaling constants and some basic properties available with the sigma profiles and the *cosmo* files of the fluids. This could turn NRCosmo into an entirely predictive equation-of state model even for pure fluids.

Thus, the present work has shown that, following the classical quasi-chemical approach [9,10,16,19] of group contributions of interacting surfaces, one may turn the COSMOtherm or the COSMO-SAC models into an equation-of-state model. With the same approach, one may derive the relation between the non-randomness factors and the chemical potentials or the activity coefficients of interacting surfaces. By further adopting a simple approximation for the density dependence of the hydrogen-bonding interactions, one may derive a versatile equation-of-state model—the NRCosmo. This new model can, practically, do what NRHB does but much easier and without the requirement to know the interaction constants for the various types of hydrogen bonds in the system. This broad range of applications makes this model a particularly useful one in the rational design of numerous processes of fluids, including the new paths for the production of high-technology materials such as drug nanocarriers, transparent aerogels, or the macroporous scaffolds for tissue engineering.

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