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Activity coefficients at infinite dilution via a perturbation method of NRHB model

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HIGHLIGHTS

- Expressions for activity coefficients at infinite dilution of mixtures of low molecular weight fluids.
- Analytical expressions are obtained via perturbation of Non-Random Hydrogen Bonding EoS model.
- The approach accounts for specific intermolecular and intramolecular interactions.

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ABSTRACT

Activity coefficients of solutes at infinite dilution play a central role in molecular thermodynamics of phase equilibria, solvation, solubility and related properties. Numerous equation-of-state models highly appropriate for concentrated systems have been developed in the open literature. Quite often, however, their equations for the chemical potential or the activity coefficient are not analytical and recursive numerical methods are needed for their use. This is the case for the versatile and widely used Non-Randomness with Hydrogen-Bonding equation of state model and, in the present work, a straightforward perturbation method is used for the derivation of analytical expressions for the chemical potential or the activity coefficient of solute at infinite dilution. The derivations are validated and compared with the full numerical calculations as well as with relevant experimental data. It is shown that calculations with the approximate analytical equations are essentially identical with the full numerical ones. These derivations are of a general character and may be used in a variety of other analogous thermodynamic models.

1. Introduction

Infinite dilution activity coefficients (IDAC) (γ^{∞}) are of great importance in the development of molecular thermodynamic models and in a broad spectrum of practical applications of chemical and environmental engineering (Tiegs et al., 1986; Prausnitz et al., 1999; Danner and High, 1993; Kontogeorgis et al., 1993; Fredenslund et al., 1994; Afrashtehfar and Cave, 1986; Weidlich et al., 1987; Moller et al., 2014; Brouwer et al., 2021). The developments, as an example, of activity coefficient models and entropic expressions need infinite dilution activity coefficient data for solutes of different shapes and sizes at various temperatures in asymmetric systems. If both infinite dilution activity coefficients are known for a binary system, parameters in a two-parameter activity coefficient model can be determined. Similarly, for one-parameter activity-coefficient models, one IDAC datum is sufficient for the model-parameter determination. This, then, permits the predictions of phase equilibria over the entire composition range (Kikic et al., 1980; Elbro et al., 1990; High and Danner, 1990; Lee and Danner, 1997; Kouskoumvekaki et al., 2002; Kannan et al., 2005).

Infinite dilution activity coefficients provide a convenient way of testing the performance of the combinatorial, free volume, rotational and vibrational models in the range of maximum degree of non-ideality and may shed light into eventual conformational changes upon mixing (Panayiotou et al., 2016). These investigations are necessary, because, apart from internal changes, the separate effects of molecular interactions, size, shape and differences in free volume ratios in liquids are not yet adequately treated by the solution of classical groups methods (Fredenslund et al., 1975). Classical solvation models in the quantitative structure–property relationships - QSPR-type approach (Abraham, 1993; Abraham et al., 2004; Abraham et al., 2010), are also heavily based on activity coefficients and solvation energies at infinite dilution.

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The study and use of infinite dilution activity coefficients at low-pressure is also particularly important in equations of state developments and in mixing-rules validation and optimization. In the last couple of decades, they have been proved particularly valuable in the development and parameterization of quantum-mechanics based or COSMO-type models (Klamt, 2004; Lin and Sandler, 2002). In these COSMO-type models the limitations are, at present, on one hand its inability to account for high-temperature and high-pressure vapor–liquid equilibria, and on the other hand its inability to properly account for the thermodynamics of polymer systems. An attempt was made recently for free volume incorporation in the formalism that led to the derivation of a COSMO-type equation of state applicable to polymer solutions (Panayiotou et al., 2015). Sets of IDAC from various homologous series are then very useful for parameterizing these COSMO-type equation-of-state models.

On the experimental side, the partition gas–liquid chromatography (GLC) utilizes the changes of three important thermodynamic parameters (free energy, entropy and enthalpy) of chemical and physical processes involved in a system and, thus, it has potential applications to many and varied systems and materials. GLC and its classical variation of inverse-gas chromatography (IGC) is a traditional method to determine gas–liquid partition coefficients, activity coefficients of solutes at infinite dilution and thermodynamic parameters of solvation (Letcher et al., 2009; Xu et al., 2012; Marciniak and Wlazło, 2018; Acree et al., 2012). Ebulliometry and setups of high dilution phase-equilibria are also very useful in this respect (Coutinho and Macedo, 1994; Afzal et al., 2009). The great advantage with infinite dilution activity coefficient measurements is that they are generally simpler and potentially more accurate than other phase equilibrium measurements (Eckert et al., 1981).

In practical applications, one convenient method for predicting the effectiveness of various solvents in separating a liquid mixture by extractive distillation or solvent extraction, is to compare the selectivity and capacity of the components in the mixture at infinite dilution.

The selectivity, $S_{12,s}$ is formally defined as:

$$S_{12,s} = \frac{\gamma_{1s}^{\infty}}{\gamma_{2s}^{\infty}} \tag{1}$$

where γ_{is}^{∞} is the infinite dilution activity coefficient of solute i in solvent s. The selectivity gives an indication of the relative volatility of the two components that are to be separated, when dissolved in the solvent. The larger the selectivity value, the more effective will be the separation of the components.

The capacity, $k_i = 1/\gamma_{is}^{\infty}$ gives an indication of the solubility of component i in the solvent, s. If the capacity for a component is low (less than unity), then the amount of that component that can be dissolved in the solvent, will be small. If both of the components have low capacities, then the separation will be relatively inefficient. These practical measures are highly useful today as novel green solvents, such as ionic liquids and deep-eutectic solvents, are intensively explored for environmentally benign processes (Brouwer et al., 2021; Letcher et al., 2009; Xu et al., 2012; Marciniak and Wlazło, 2018; Acree et al., 2012).

In all the above applications, it is particularly useful to have analytical equations, the terms of which may be attributed a clear physical meaning in a straightforward manner. NRHB (Non-Randomness with Hydrogen-Bonding) model (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020) is a most convenient, versatile, relatively simple equation-of-state model for handling systems from the glassy state up to the supercritical and gas state (Mensitieri et al., 2020; Grenner et al., 2008; Baldanza et al., 2022; Dirauf et al., 2021; Paduszyński et al., 2011; Scherillo et al., 2012; De Nicola et al., 2017). NRHB, as explained in detail in our previous review article (Mensitieri et al., 2020) is in essence an equation-of-state framework, which combines two central approaches, the lattice-fluid with non-randomness (Panayiotou and Vera, 1982) and the lattice-fluid with hydrogen-bonding (Panayiotou and Sanchez, 1991). The rationale for infinite dilution activity coefficients exposed in the present work is directly applicable to these two constituent approaches, including also different version of NRHB model present in literature as the one developed by Yeoma et al. (Yeoma et al., 1999). It is, thus, expected to steer some broader interest.

NRHB handles non-randomness in molecular arrangements via Guggenheim's quasi-chemical approach (Guggenheim, 1952), in pretty much the same way COSMO-type models (Klamt, 2004; Lin and Sandler, 2002) do. Strong specific interactions of the hydrogen-bonding or Lewis acid-base type interactions are handled via Veytsman's statististics (Panayiotou and Sanchez, 1991; Veytsman, 1990), which turns NRHB well conformable to Solvation and QSPR-type models (Abraham, 1993; Abraham et al., 2004; Abraham et al., 2010). So far, however, explicit analytical equations for the activity coefficient at infinite dilution for NRHB are not available in the literature.

In this work, NRHB analytical expressions for IDAC are provided, which are obtained by applying a straightforward perturbation method. The resulting equations are relatively simple analytical ones, while the various terms of the IDAC equation do have a clear physical meaning. Thus, in the next section, the perturbation method is presented and applied, first, to the hydrogen-bonding terms of the activity –coefficient equation. Subsequently, the limiting equations for the non-randomness terms are derived and the full IDAC-equation is reported. Some representative examples of use of this equation are reported in the section on Application.

2. Derivation of the NRHB IDAC equation

Before proceeding to the perturbation method, in the next subsection we recall briefly the NRHB equation for the activity coefficient along with some essentials of the NRHB approach. Details of derivations, calculations, and numerous applications may be found in a recent review article (Mensitieri et al., 2020) and in the relevant literature (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020; Grenner et al., 2008; Tsivintzelis et al., 2007; Tsivintzelis et al., 2008; Tsioptsias et al., 2010; Panayiotou, 2011).

2.1. The NRHB essentials

In the frame of the NRHB model, the activity coefficient of a solute (component 1) in a solvent (component 2) may be considered to consist of two terms, a hydrogen-bonding (HB) one and a non-hydrogen-bonding one, or

$$ln\gamma_1 = ln\gamma_{1,non-HB} + ln\gamma_{1,HB} \tag{2}$$

The non-HB term reflects the contribution of the weak van der Waals interactions from the omnipresent dispersive forces up to the moderately strong polar interactions. Since NRHB model meets the ideal-gas limit (Baldanza et al., 2022; Neau, 2002; von Konigslow et al., 2017; von Konigslow et al., 2018), it is convenient to adopt the solvation approach for an insightful break-down of the non-HB term. In NRHB, this term is considered to consist of three contributions or one compressibility (comp) or size/shape-asymmetry term, one cavitation (cav) term and one charging (chrg) or non-randomness term:

$$ln\gamma_{1,non-HB} = ln\gamma_{1,comp} + ln\gamma_{1,cav} + ln\gamma_{1,chrg} \tag{3}$$

The compressibility term reflects the difference of the compressibility factors Z_1 and Z of solute and solution, respectively, or the corresponding difference of molar volumes V_{m1} and V_m at the same temperature, T, and pressure, P, conditions, and reads:

$$ln\gamma_{1,comp} = ln\frac{Z_1}{Z} = ln\frac{r_1}{r} + ln\frac{\tilde{\rho}}{\tilde{\rho}_1} = ln\frac{V_{m1}}{V_m} \tag{4}$$

The cavitation term reflects the difference of the work needed to accommodate one solute molecule in itself (pure solute state) and in solution and reads:

$$ln\gamma_{cav} = r_1 ln\frac{\left(1-\tilde{\rho}_1\right)}{\left(1-\tilde{\rho}\right)} + \frac{z}{2} r_1(s_1-1) ln\frac{1-\tilde{\rho}_1+s_1\tilde{\rho}_1}{1-\tilde{\rho}+s\tilde{\rho}} \tag{5}$$

The subscript 1 in the last two equations must be clarified before we proceed. In NRHB, each molecule of species k-th is assumed to be divided in r_k segments of a universal volume v^* = 9.75 cm^3mol^{-1} each (Panayiotou and Vera, 1982). The total number of external contacts per molecule in a quasi-lattice arrangement is $q_k = s_k r_k$, where s_k is a shape characteristic of the molecule and is considered to be identical to the classical UNIQUAC/UNIFAC surface area-to-volume ratio (Fredenslund et al., 1975). Thus, each molecule is characterized by a hard-core or occupied volume $V_k^* = r_k v^* = M_k v_{sp,k}^*$, M_k being its molar mass and $v_{sp,k}^*$ its specific hard-core volume. The fraction of occupied volume, $\tilde{\rho} = V^*/V_m$, is the reduced density and, in a pure component it reads:

$$\tilde{\rho}_k = \frac{V_k^*}{V_{mk}} = \frac{M_k v_{sp,k}^*}{M_k v_{sp,k}} = \frac{1}{\tilde{v}_k} \tag{6}$$

The free-volume fraction is, then, equal to $1-\tilde{\rho}$. The quasi-lattice coordination number, z, in NRHB is usually assumed to be equal to 10.

The charging term in Eq. (3) reflects the difference in strength of the intermolecular or, rather, intersegmental interaction energy,

$$\varepsilon_{ij}^* = z\frac{\varepsilon_{ij}}{2} \tag{7}$$

in pure solute and in solution (which, in turn, influences the non-randomness factors, Γ, for the distribution of molecular segments in the system) and reads:

$$ln\gamma_{1,chrg} = \frac{z}{2} r_1 \left[s_1 ln\frac{\Gamma_{11}}{\Gamma_{11}^0} - ln\frac{\Gamma_{00}}{\Gamma_{00}^0} \right] \tag{8}$$

The subscript ij of Γ is directly related to the probability to find a segment of type i as a first-neighbor of a central segment of type j at given average concentration. Subscript 0 indicates empty site while superscript 0 indicates pure solute state.

We are left with the hydrogen-bonding (HB) term of Eq. (2). In the most general case of solutes and solvents capable of forming m × n kinds of donor – acceptor hydrogen bonds, α-β, the HB term reads:

$$ln\gamma_{1,HB} = \sum_\alpha^m d_\alpha^1 ln\left(\frac{v_d^{\alpha,0}}{v_d^\alpha}\frac{v_{\alpha 0}}{v_{\alpha 0}^0}\right) + \sum_\beta^n a_\beta^1 ln\left(\frac{v_a^{\beta,0}}{v_a^\beta}\frac{v_{\beta 0}}{v_{\beta 0}^0}\right) \tag{9}$$

and simplifies, further, in the classical case of molecules with one type of donor and/or acceptor sites, d_k and/or a_k, respectively, reading:

$$ln\gamma_{1,HB} = d_1 ln\left(\frac{v_d^0}{v_{\alpha 0}^0}\frac{v_{\alpha 0}}{v_d}\right) + a_1 ln\left(\frac{v_a^0}{v_{0\beta}^0}\frac{v_{0\beta}}{v_a}\right) \tag{10}$$

Superscript 0 indicates pure solute state while v indicates reduced quantities of hydrogen bond numbers, N_{ij}, or.

$$v_{ij} = \frac{N_{ij}}{rN} \tag{11}$$

Subscript $\alpha 0$ indicates the fraction of free (non-hydrogen-bonded) donor sites and subscript 0β indicates the fraction of free acceptor sites. Thus, the overall equation for the activity coefficient reads:

$$\begin{aligned} ln\gamma_1 = {} & ln\frac{V_{m1}}{V_m} + r_1 ln\frac{\left(1-\tilde{\rho}_1\right)}{\left(1-\tilde{\rho}\right)} + \frac{z}{2} r_1(s_1-1) ln\frac{1-\tilde{\rho}_1+s_1\tilde{\rho}_1}{1-\tilde{\rho}+s\tilde{\rho}} \\ & + \frac{z}{2} r_1 \left[s_1 ln\frac{\Gamma_{11}}{\Gamma_{11}^0} - ln\frac{\Gamma_{00}}{\Gamma_{00}^0} \right] + d^1 ln\left(\frac{v_d^0}{v_{\alpha 0}^0}\frac{v_{\alpha 0}}{v_d}\right) \\ & + a^1 ln\left(\frac{v_a^0}{v_{0\beta}^0}\frac{v_{0\beta}}{v_a}\right) \end{aligned} \tag{12}$$

The terms appearing in the second row of Eq. (12) constitute the overall charging or interactional-energy term of the activity coefficient.

At given external conditions of T, P, and composition, the use of Eq. (12) requires in practice the solution of the following set of non-linear equations:

$$\frac{\Gamma_{ij}^2}{\Gamma_{ii}\Gamma_{jj}} = exp\left(-\frac{\varepsilon_{ii}+\varepsilon_{jj}-2\varepsilon_{ij}}{RT}\right) \quad i,j = 0,1,2,\ldots \quad j > i \tag{13}$$

$$\sum_{j=0}^t \theta_j \Gamma_{ij} = 1 \quad i = 0,1,2,\ldots t \tag{14}$$

$$\frac{v_{\alpha\beta}}{v_{\alpha 0} v_{0\beta}} = \tilde{\rho}\, exp\left(-\frac{G_{\alpha\beta}}{RT}\right) \text{ for each } \alpha,\beta \text{ pair} \tag{15}$$

When molar volumes are not known, one has to obtain $\tilde{\rho}$ by solving the NRHB equation of state, not only for the solution but for the pure solute as well (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020; Grenner et al., 2008). The surface area fraction, θ_j, is given in terms of the numbers of moles, N_k, by the defining equation:

$$\theta_j = \frac{N_j q_j}{\sum_{k=0}^t N_k q_k} \tag{16}$$

In NRHB q_0 = 1 and $\varepsilon_{00} = \varepsilon_{0k}$ = 0. $G_{\alpha\beta}$ in Eq. (15) is the free-energy change upon formation of the hydrogen bond α-β.

It is clear that the set of equations 13 – 15 can only be solved numerically and, thus, the equation for the activity coefficient cannot be obtained in closed analytical form. However, such an analytical form may be obtained in the case of a solute at infinite dilution in a solvent, as shown in the next sub-section.

2.2. Perturbation method applied to NRHB activity coefficient at infinite dilution

In the infinite dilution limit of solute 1 in solvent 2, Eq. (12) takes the form:

$$\begin{aligned} ln\gamma_{1/2}^\infty = {} & ln\frac{V_{m1}}{V_{m2}} + r_1 ln\frac{\left(1-\tilde{\rho}_1\right)}{\left(1-\tilde{\rho}_2\right)} + \frac{z}{2} r_1(s_1-1) ln\frac{1-\tilde{\rho}_1+s_1\tilde{\rho}_1}{1-\tilde{\rho}_2+s_2\tilde{\rho}_2} \\ & + \frac{z}{2} r_1 \left[s_1 ln\frac{\Gamma_{11}^\infty}{\Gamma_{11}^0} - ln\frac{\Gamma_{00}^\infty}{\Gamma_{00}^0} \right] + d^1 ln\left(\frac{v_d^0}{v_{\alpha 0}^0}\frac{v_{\alpha 0}}{v_d}\right) \\ & + a^1 ln\left(\frac{v_a^0}{v_{0\beta}^0}\frac{v_{0\beta}}{v_a}\right) \end{aligned} \tag{17}$$

Superscript ∞ indicates infinite dilution limit. Eq. (17) still inherits the problems of Eq. (12) and requires the use of numerical methods. The task now is to circumvent this problem and provide with analytical equations each of the Γ and v terms in Eq. (17). For this purpose, perturbation methods (Bender and Orszag, 1978; Holmes, 1995) can, in principle, be exploited to obtain an approximate closed-form solution of equations 13–15 in the limit of infinite dilution and, thus, explicit approximate expression of the activity coefficient. In fact, the approximate solution of the set of equations 13–15 could be used also for the determination of a set of good guess values in searching its numerical solution for the concentrated system.

Thus, in what follows, a perturbation approach for solving the above problem is presented. For the sake of readability, in the main manuscript are reported only the fundamental equations used for the derivations of the final operative expressions required by Eq. (17) in order to close the problem with the approximate analytical solutions. Full details on the whole procedure adopted are reported in the SI file. In this regard a perturbation of the set of solutions with respect to the case of the pure solvent component at the same pressure and temperature is considered so that the solute molar fraction x_1 represents the corresponding perturbation parameter. Regarding HB contribution, at most one kind of proton donor and one kind of proton acceptor have been allowed for each component. This is a good representative of the very common binary mixtures, in which HB interactions occur. In the infinite dilution limit the equation of state of the mixture is becoming identical to the equation of state of the pure solvent or, $\tilde{\rho} = \tilde{\rho}_2$ and, thus, the equation of state does not enter into the designed perturbation scheme. In addition, the subset of equations 13–14 for all Γ_{ij} may be decoupled from the set of Eq. (15) for hydrogen bonding $v_{\alpha\beta}$. We start with these HB quantities in the next subsection.

2.2.1. Perturbation method for the hydrogen bonding quantities in IDAC

In the case at hand, the set of equations 15 in the IDAC limit of $x_1 \to 0$, in their full form can be written as follows:

$$\begin{cases} \upsilon_{11}^2 - \left(-\upsilon_{12} - \upsilon_{21} + \frac{1}{\tilde{\rho}_2 \exp(-G_{11}/RT)}\right)\upsilon_{11} + \upsilon_{12}\upsilon_{21} = 0 \\ \upsilon_{12}^2 - \left(-\upsilon_{11} + \frac{a_2}{r_2} - \upsilon_{22} + \frac{1}{\tilde{\rho}_2 \exp(-G_{12}/RT)}\right)\upsilon_{12} - \upsilon_{11}\left(\frac{a_2}{r_2} - \upsilon_{22}\right) = 0 \\ \upsilon_{21}^2 - \left(\frac{d_2}{r_2} - \upsilon_{22} - \upsilon_{11} + \frac{1}{\tilde{\rho}_2 \exp(-G_{21}/RT)}\right)\upsilon_{21} - \upsilon_{11}\left(\frac{d_2}{r_2} - \upsilon_{22}\right) = 0 \\ \upsilon_{22}^2 - \left(\frac{d_2}{r_2} - \upsilon_{21} + \frac{a_2}{r_2} - \upsilon_{12} + \frac{1}{\tilde{\rho}_2 \exp(-G_{22}/RT)}\right)\upsilon_{22} \\ \qquad + \left(\frac{d_2}{r_2} - \upsilon_{21}\right)\left(\frac{a_2}{r_2} - \upsilon_{12}\right) = 0 \end{cases} \tag{18}$$

In these equations, subscript $\alpha\beta$ refers to HB interaction between a proton donor (PD) or Lewis acid of kind α and a proton acceptor (PA) or Lewis base of kind β. Moreover, $\tilde{\rho}_2$ is the reduced density the solvent while r_2 and is the number of segments of the solvent molecule.

The key assumption is that the solution of Eq. (18) can be represented as an expansion in terms of the small perturbation parameter x_1, i.e., under the condition that x_1 belong to the range $I_0 : 0 < x_1 \ll 1$:

$$\upsilon_{11} = c_{01} + c_{11}x_1 + c_{21}x_1^2 + O(x_1^3) \tag{19.1}$$

$$\upsilon_{12} = c_{02} + c_{12}x_1 + O(x_1^2) \tag{19.2}$$

$$\upsilon_{21} = c_{03} + c_{13}x_1 + O(x_1^2) \tag{19.3}$$

$$\upsilon_{22} = c_{04} + c_{14}x_1 + O(x_1^2) \tag{19.4}$$

The first step consists in substituting the expressions of the perturbed solution (19.1–19.4) in the set of Eq. (18), neglecting the corresponding $O(x_1^n)$ terms. Regarding υ_{11}, terms up to the quadratic ones have been retained in the present contribution, for reasons that will be clarified below.

In this way we have obtained a set of four polynomial expressions named hereafter as polynomial approximate system (PAS) of equations determined by nine c_{ij} coefficients. Finally, the last step of the perturbation method consists operatively in imposing that such truncated polynomial expressions PAS are identically equal to zero for each x_1 at least in a range $0 < x_1 \ll 1$. This is equivalently obtained by equating each polynomial coefficient to zero. In this way in the case at hand, a unique determination of nine coefficients c_{ij} is obtained as detailed in the SI file (section SI.1). Once these coefficients are retrieved, the expressions of the Eq. (19) are completely determined, and they are expected to provide an approximate solution of the set of Eq. (18) at least in a range I_1 ($0 < x_1 \ll 1$) contained in I_0. (See section SI.1 of SI file for full details on this point). This solution represents the perturbed solution of the system of equations 18 at least in I_1, and hereafter will be indicated as the approximate solution. Indeed, in principle a range of concentration of kind I_1 exists, such that the error of approximate solution can be done arbitrary low, but it is not known a priori and depends upon the choice of truncation procedure adopted and upon the numerical values of the model parameters (see again SI.1 section of SI file for a detailed discussion on this issue). The aim of the applications section 3.1–3.3 will consist in checking the maximum of relative error of the approximate solution as a function of x_1 for an exhaustive series of fictive systems as well as for two real-system case studies. In what follows, we report the recursive expressions of the nine c_{ij} coefficients (full details on their calculations are reported in the SI.1 section of the SI file). For simplicity, in the proposed expressions of the activity coefficient at infinite dilution, we have adopted first-order approximation in the set of Eqs. (19.1)–(19.3) (setting $c_{21} = 0$) and zero-order approximation in Eq. (19.4) (setting $c_{14} = 0$). In the SI.1 section of the SI file are reported the most general expression of the c_{ij} coefficients without imposing such simplifications. Actually, the reliability of these assumptions is satisfactorily validated below with case-studies.

$$\begin{cases} c_{01} = 0 \\ c_{02} = 0 \\ c_{03} = 0 \\ c_{04} = \dfrac{\frac{d_2}{r_2} + \frac{a_2}{r_2} + \frac{1}{\tilde{\rho}_2 \exp(-G_{22}/RT)} - \sqrt{\left(\frac{d_2}{r_2} + \frac{a_2}{r_2} + \frac{1}{\tilde{\rho}_2 \exp(-G_{22}/RT)}\right)^2 - 4\frac{d_2 a_2}{r_2^2}}}{2} \end{cases} \tag{20}$$

$$\begin{cases} c_{11} = 0 \\ c_{12} = d_1\left(\frac{1}{r_2} + \frac{1}{-r_2 - a_2\tilde{\rho}_2 \exp(-G_{12}/RT) + r_2\tilde{\rho}_2 \exp(-G_{12}/RT)c_{04}}\right) \\ c_{13} = a_1\left(\frac{1}{r_2} + \frac{1}{-r_2 - d_2\tilde{\rho}_2 \exp(-G_{21}/RT) + r_2\tilde{\rho}_2 \exp(-G_{21}/RT)c_{04}}\right) \end{cases} \tag{21}$$

where, c_{04} is given by the set (20).

As anticipated, since $c_{01} = c_{11} = 0$, in order to express a composition dependence for the approximate solution of υ_{11}, a truncation order higher than 1 in Eq. (19.1) is necessary (see the detailed discussion reported in the section SI.1 of the SI file on this issue).

Summarizing, the expressions from Eq. (19)–(21) provide an approximate solution for a binary system in which each component displays one kind of proton acceptor and one kind of proton donor. This is quite a general case for low molecular weight com-

pound binary mixtures. In fact, this approximate solution is also able to describe any sub-case for binary systems, namely.

A) A system displaying one kind of proton acceptor and one kind of proton donor on the same component (only one self-associating component);
B) A system displaying one kind of proton acceptor on one component and one kind of proton donor on the other component (only one cross-association);
C) A system displaying one kind of proton acceptor and one kind of proton donor on one component and one different kind of proton donor on the other component (one self-association and one cross-association);
D) A system displaying one kind of proton acceptor and one kind of proton donor on one component and one different kind of proton acceptor on the other component (one self-association and one cross-association).

In principle each sub-case can be operatively addressed starting from the more general case explicitly investigated in this contribution through a limit procedure. In fact, in view of the shape of the system 18, it is evident that the solution of each sub-case can be obtained by imposing in the system 18 that all the υ_{ij}, not involved in the considered sub-case, are zero. Operatively, this is equivalent to solve the system 18 in the limit that all the corresponding Gibbs energy of formation (G_{ij}) approach $+\infty$ (Veytsman, 1990). To the aim of the present contribution, we have also verified that the described limiting procedure on the Gibbs energy still holds in the case of the proposed approximate solution, given by Eq. (19)–(21). In fact, it can be shown that the expressions of the set of υ_{ij} not null, calculated through this limit procedure on the Gibbs energy, converge consistently to the approximate solution, that one would obtain performing the perturbation method directly on the subset of equations which defines the sub-case under consideration provided that one adopts the same order of approximation in the corresponding Eq. (19). (See again the SI.1 section of the SI file for mathematical details on this point).

2.2.2. Perturbation method for the lattice-fluid non-randomness factors in IDAC

The set of minimization conditions regarding the non-randomness factors of lattice-fluid contacts in a binary system can be written as (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020):

$$\begin{cases} \frac{\Gamma_{01}^2}{\Gamma_{00}\Gamma_{11}} = \exp\left(-\frac{\varepsilon_{11}}{RT}\right) \\ \frac{\Gamma_{02}^2}{\Gamma_{00}\Gamma_{22}} = \exp\left(-\frac{\varepsilon_{22}}{RT}\right) \\ \frac{\Gamma_{12}^2}{\Gamma_{11}\Gamma_{22}} = \exp\left(-\frac{\varepsilon_{11}+\varepsilon_{22}-2(1-k_{12})\sqrt{\varepsilon_{11}\varepsilon_{22}}}{RT}\right) \end{cases} \tag{22.1}$$

The set 22.1 is coupled with the contact-number balance equations (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020):

$$\begin{cases} \Theta_0\Gamma_{00} + \Theta_1\Gamma_{01} + \Theta_2\Gamma_{02} = 1 \\ \Theta_0\Gamma_{01} + \Theta_1\Gamma_{11} + \Theta_2\Gamma_{12} = 1 \\ \Theta_0\Gamma_{02} + \Theta_1\Gamma_{12} + \Theta_2\Gamma_{22} = 1 \end{cases} \tag{22.2}$$

This is further simplified by factorizing each Γ_{ij} into molecular Γ_i as follows (Lin and Sandler, 2002; Panayiotou et al., 2015):

$$\Gamma_{ij} = \Gamma_i\Gamma_j\tau_{ij} \text{ for each } i,j = 0,\ 1,\ 2 \tag{23}$$

where:

$$\tau_{ij} = \exp\left(\frac{(1-k_{ij})\sqrt{\varepsilon_{ii}\varepsilon_{jj}}}{RT}\right) \text{for each } i,j = 0,\ 1,\ 2 \tag{24.1}$$

In Eq. (24.1), $k_{ii} = 0$ and in the NRHB approach $\varepsilon_{00} = 0$, so that Eq. (24.1) implies the following conditions:

$$\tau_{0i} = 1 \text{ for each } i = 0,\ 1,\ 2 \tag{24.2}$$

$$\tau_{ii} = \exp\left(\frac{\varepsilon_{ii}}{RT}\right) \text{for each } i = 1,2 \tag{24.3}$$

According to equations 24, it is straightforward to verify that the set 23 satisfies set 22.1 and one only needs to focus on the set 22.2. To this aim, one can substitute the sets 23–24 into Eq. (22.2) and obtain a new system of three equations in the remaining three unknowns Γ_0, Γ_1 and Γ_2:

$$\begin{cases} \Gamma_0(\Theta_0\Gamma_0 + \Theta_1\Gamma_1 + \Theta_2\Gamma_2) = 1 \\ \Gamma_1(\Theta_0\Gamma_0 + \Theta_1\Gamma_1\tau_{11} + \Theta_2\Gamma_2\tau_{12}) = 1 \\ \Gamma_2(\Theta_0\Gamma_0 + \Theta_1\Gamma_1\tau_{12} + \Theta_2\Gamma_2\tau_{22}) = 1 \end{cases} \tag{25}$$

The solution of the set (25) can be obtained by applying the same perturbative method as the one described above for hydrogen-bonding and the following approximate expressions can be assumed for the set (Γ_0, Γ_1, Γ_2):

$$\Gamma_0 = \Gamma_0^p + g_0x_1 \tag{26.1}$$

$$\Gamma_1 = \Gamma_1^p + g_1x_1 \tag{26.2}$$

$$\Gamma_2 = \Gamma_2^p + g_2x_1 \tag{26.3}$$

Superscript p indicates pure solvent - component 2 at the same P and T.

Substituting the set 26 into the set 25 and retaining the terms up to x_1, one obtains a linear polynomial system in x_1, so that according to the perturbation method, each coefficient of x_1 must be set equal to zero. This leads to a system of six equations in the six unknown coefficients Γ_0^p, Γ_1^p, Γ_2^p, g_0, g_1 and g_2. It is possible to decouple a subset of three equations from the general system in the only unknown Γ_0^p, Γ_1^p and Γ_2^p, which provides the following corresponding unique solution:

$$\Gamma_0^p = \frac{\left(2\Theta_0^p - 1 + \sqrt{1-4(\tau_{22}-1)(\Theta_0^p-1)\Theta_0^p}\right)\sqrt{\frac{1}{2\Theta_0^p-1-2\tau_{22}\sqrt{1-4(\tau_{22}-1)(1-\Theta_0^p)\Theta_0^p}}}}{\sqrt{2}\Theta_0^p} \tag{27.1}$$

$$\Gamma_1^p = \frac{1}{\left(\Theta_0^p\Gamma_{0p} + (1-\Theta_0^p)\Gamma_{2p}\tau_{12}\right)} \tag{27.2}$$

$$\Gamma_2^p = \sqrt{\frac{2}{2\Theta_0^p - 1 - 2\tau_{22}\sqrt{1-4(\tau_{22}-1)(1-\Theta_0^p)\Theta_0^p}}} \tag{27.3}$$

where:

$$\Theta_0^p = \frac{r_2(\tilde{\nu}_2 - 1)}{r_2\left(\tilde{\nu}_2 - 1\right) + q_2} \tag{28}$$

By substituting the solution set 29 in the remaining equations, one can determine a unique solution also for the unknown g_0, g_1 and g_2, so that the whole set of coefficients of the set 26 is univocally determined. These expressions are reported in the SI.2 section of the SI file. As a consequence of the discussed decoupling of the general system in the six unknown coefficients of equations 26, we observe that equations 27 represent the subset which defines the zero-order coefficients independently from any possible order adopted in proposing the polynomial shapes of Γ_0, Γ_1 and Γ_2 in equations 26. Consequently, the three zero-order coefficients are

always given by equations 27, also in the case of the zero-order assumption (setting $g_0 = g_1 = g_2 = 0$) in equation 26. In particular, this simplification has been applied in the proposed expressions of the activity coefficient at infinite dilution. Actually, the reliability of such assumption will be also satisfactorily validated below in the case- study section. Thus, the rather cumbersome equations for c_{14} and for g_0, g_1 and g_2 do not enter into the calculations. This is further emphasized in the next sub-section.

2.3. Activity coefficient at infinite dilution

As mentioned already and, on the basis of the previous two subsections, the explicit expression of the activity coefficient at infinite dilution in a binary mixture is given by Eq. (17), which is retyped here for convenience.

$$ln\gamma_{1/2}^{\infty} = ln\frac{V_{m1}}{V_{m2}} + r_1 ln\frac{\left(1-\tilde{\rho}_1\right)}{\left(1-\tilde{\rho}_2\right)} + \frac{z}{2}r_1(s_1-1)ln\frac{1-\tilde{\rho}_1+s_1\tilde{\rho}_1}{1-\tilde{\rho}_2+s_2\tilde{\rho}_2} + \frac{z}{2}r_1\left[s_1 ln\frac{\Gamma_{11}^{\infty}}{\Gamma_{11}^{0}} - ln\frac{\Gamma_{00}^{\infty}}{\Gamma_{00}^{0}}\right] + d^1 ln\left(\frac{v_d^0}{v_{\alpha 0}^0}\frac{v_{\alpha 0}^{\infty}}{v_d^{\infty}}\right) + a^1 ln\left(\frac{v_a^0}{v_{0\beta}^0}\frac{v_{0\beta}^{\infty}}{v_a^{\infty}}\right) \tag{17}$$

The non-randomness factors with the infinity superscript are now calculated from the molecular Γ_i as follows (cf. Eqs. (23), (24) and (27)):

$$\Gamma_{11}^{\infty} = \Gamma_1^p\Gamma_1^p exp\left(\frac{\varepsilon_{11}}{RT}\right) = \Gamma_1^{\infty}\Gamma_1^{\infty} exp\left(\frac{\varepsilon_{11}}{RT}\right) \tag{29}$$

$$\Gamma_{12}^{\infty} = \Gamma_1^p\Gamma_2^p exp\left(\frac{\varepsilon_{12}}{RT}\right) = \Gamma_1^{\infty}\Gamma_2^{\infty} exp\left(\frac{(1-k_{12})\sqrt{\varepsilon_{11}\varepsilon_{22}}}{RT}\right) \tag{30}$$

and.

$$\Gamma_{00}^{\infty} = \Gamma_0^p\Gamma_0^p = \Gamma_0^{\infty}\Gamma_0^{\infty} \tag{31}$$

where:

$$\Gamma_0^{\infty} = \frac{\left(2\Theta_0^{\infty} + \sqrt{1+4(\tau_{22}-1)\Theta_0^{\infty}\Theta_2^{\infty}} - 1\right)\sqrt{\frac{1}{2\Theta_0^{\infty}+2\tau_{22}\Theta_2^{\infty}+\sqrt{1+4(\tau_{22}-1)\Theta_0^{\infty}\Theta_2^{\infty}}-1}}}{\sqrt{2}\Theta_0^{\infty}} \tag{32}$$

$$\Gamma_1^{\infty} = \frac{1}{\left(\Theta_0^{\infty}\Gamma_0^{\infty} + \Theta_2^{\infty}\Gamma_2^{\infty}\tau_{12}\right)} \tag{33}$$

$$\Gamma_2^{\infty} = \sqrt{\frac{2}{2\Theta_0^{\infty} + 2\tau_{22}\Theta_2^{\infty} + \sqrt{1+4(\tau_{22}-1)\Theta_0^{\infty}\Theta_2^{\infty}} - 1}} \tag{34}$$

and.

$$\Theta_0^{\infty} = \frac{r_2(\tilde{v}_2 - 1)}{r_2\left(\tilde{v}_2 - 1\right) + q_2} \tag{35}$$

$$\Theta_2^{\infty} = 1 - \Theta_0^{\infty} \tag{36}$$

The superscript zero in Eq. (17) refers to quantities in the pure solute state (same T, P) and are given by the NRHB equations (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020):

$$\Gamma_{10}^0 = \frac{2}{1+\sqrt{1+4(\tau_{11}-1)\theta_0^0\theta_1^0}} \tag{37}$$

$$\theta_0^0\Gamma_{00}^0 + \theta_1^0\Gamma_{10}^0 = 1$$

$$\theta_1^0\Gamma_{11}^0 + \theta_0^0\Gamma_{10}^0 = 1 \tag{38}$$

where:

$$\theta_0^0 = \frac{\tilde{v}_1 - 1}{\tilde{v}_1 - 1 + s_1}$$

$$\theta_1^0 = 1 - \theta_0^0 \tag{39}$$

Regarding hydrogen-bonding quantities, the following analytical equations apply, now, in the limit of infinite dilution (cf. Eqs. (19)–(21)):

$$\begin{cases} v_{11}^{\infty} = 0 \\ v_{22}^{\infty} = \dfrac{\frac{a_2+d_2}{r_2} + \frac{1}{\tilde{\rho}_2 exp(-G_{22}/RT)} - \sqrt{\left(\frac{a_2+d_2}{r_2} + \frac{1}{\tilde{\rho}_2 exp(-G_{22}/RT)}\right)^2 - \frac{4a_2d_2}{r_2^2}}}{2} \\ v_{11}^{0} = \dfrac{\frac{a_1+d_1}{r_1} + \frac{1}{\tilde{\rho}_1 exp(-G_{11}/RT)} - \sqrt{\left(\frac{a_1+d_1}{r_1} + \frac{1}{\tilde{\rho}_1 exp(-G_{11}/RT)}\right)^2 - \frac{4a_1d_1}{r_1^2}}}{2} \\ v_{12}^{\infty} = x_1c_{12} = x_1d_1\left(\frac{1}{r_2} + \frac{1}{-r_2+a_2\tilde{\rho}_2 exp(-G_{12}/RT)+r_2\tilde{\rho}_2 exp(-G_{12}/RT)v_{22}^{\infty}}\right) \\ v_{21}^{\infty} = x_1c_{13} = x_1a_1\left(\frac{1}{r_2} + \frac{1}{-r_2+d_2\tilde{\rho}_2 exp(-G_{21}/RT)+r_2\tilde{\rho}_2 exp(-G_{21}/RT)v_{22}^{\infty}}\right) \end{cases} \tag{40}$$

Thus in Eq. (17) the following identities hold:

$$\left(\frac{v_d^{1,0}}{v_d^{1,\infty}}\frac{v_{10}^{\infty}}{v_{10}^0}\right) = \frac{\frac{d_1}{r_2} - c_{12}}{\frac{d_1}{r_1} - v_{11}^0} = \frac{r_1}{r_2}\frac{d_1 - r_2c_{12}}{d_1 - r_1v_{11}^0} \tag{41}$$

$$\left(\frac{v_a^{1,0}}{v_a^{1,\infty}}\frac{v_{01}^{\infty}}{v_{01}^0}\right) = \frac{\frac{a_1}{r_2} - c_{13}}{\frac{a_1}{r_1} - v_{11}^0} = \frac{r_1}{r_2}\frac{a_1 - r_2c_{13}}{a_1 - r_1v_{11}^0} \tag{42}$$

These are the working analytical equations in the infinite dilution limit.

3. Applications

Having the approximate analytical equation for IDAC or for the chemical potential, we may now apply them to real systems. However, before this, it is essential to compare their calculations with the corresponding full numerical calculations with the original equation 12 at solute mole fractions near zero. This is done in the next sub-section.

3.1. Comparison of approximate explicit method with the solution of the exact problem

In order to validate the approximate explicit IDAC expression from the above perturbation method, we will compare results with the numerical and, essentially, "exact" ones by Eq. (12). However, at infinite dilution, the numerical approach requires non-conventional techniques and/or an estimate of the guess values rather very close to the analytical solution. In fact, this is one of the main reasons for the necessity of developing the approximate solution in the present investigation. As a matter of fact, in solving equations 12–15 in the dilute concentration range, we have used the approximate (perturbed) solutions as guess values.

For this purpose, we have generated a set of binary fictive systems, displaying one kind of proton donor and one kind of proton acceptor for each component and with a broad variety of physically reasonable equation-of-state and hydrogen-bonding parameters. For hydrogen-bonding $G_{\alpha\beta}^0$ of each pure component, very low val-

ues of 3000 J/mol as well as very high values of 30000 J/mol were adopted (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020; Grenner et al., 2008). Permutation of these extreme values generates four combinations of binary systems. The two cross-association Gibbs energies have been set equal to the arithmetic mean value of the corresponding self-association energies of pure components. Analogously, we have selected two possible values of lattice fluid interaction energies, ε_i^*, for each component: a very low one of 2000 J/mol and a very high one of 5000 J/mol, so that, the total number of possible fictive systems becomes 16. The corresponding cross lattice fluid interactions have been dictated by NRHB mixing rules, $\varepsilon_{12}^* = (1 - k_{12})\sqrt{\varepsilon_{11}^* \varepsilon_{22}^*}$, and, to this regard, we have selected three k_{12} values (-0.1, 0, 0.1), which allows to describe a wide range of cross lattice fluid interaction energies (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020; Grenner et al., 2008). This, then, increases the number of system combinations to 48. Each system has been investigated at room temperature (300 K) and at two different values of pressure (0.1 MPa and 1 MPa), thus, in correspondence of the energy ranges considered, both liquid and vapour phase conditions have been explored. As for the remaining NRHB parameters of each component and for the molecular weights, we have selected the parameters of methanol and water for the solute and the solvent, respectively. This is a classical system of self-associated and cross-associated components - a general system described with the perturbation method. In conclusion, the total number of combinations considered in this validation procedure results in 96 fictive systems.

In the following calculations, we have divided the range $5x10^{-6} - 5x10^{-5}$ of solute molar fraction, x_1, in five equally spaced points and we have reported activities $\alpha_1^\infty = x_1\gamma_1^\infty$ as a function of x_1 for both full numerical and approximate solutions. In all systems, both methods display the expected linear behaviour. In particular, since γ_1^∞ spans a wide range of values, it is appropriate to consider a relative error, which can be defined as:

$$err_{rel} = \left| \frac{\gamma_{1,app}^\infty - \gamma_{1,num}^\infty}{\gamma_{1,num}^\infty} \right| \tag{43}$$

On the basis of the generated grid of 96 fictive systems, the corresponding set of relative error falls within the range $6.9x10^{-5} - 5.5x10^{-3}$. For visual inspection, Fig. 1 shows α_1^∞ vs x_1 for the system which has displayed the highest values of the relative error.

As shown in Fig. 1, the expected linear trend is very well observed for both the numerical and the approximate solution.

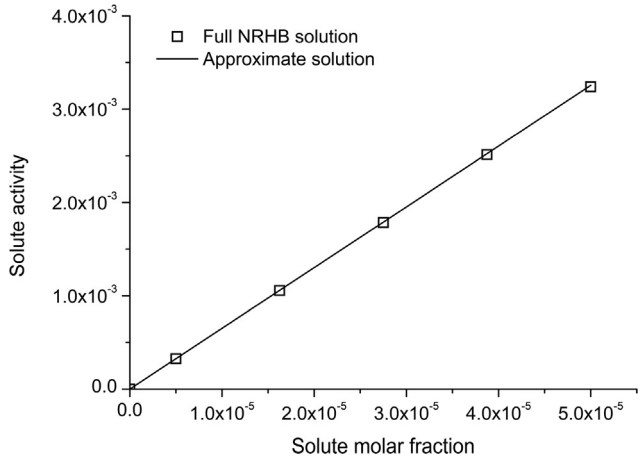

Fig. 1. Solute activity α_1^∞ vs x_1. Comparison of the full NRHB numerical solution (circles) with the approximate solution (solid line).

Since, the two calculations (symbol points and lines) are essentially fully overlapping, the corresponding linear fittings provide values of activity coefficients essentially identical, for x_1 close to zero. Having validated the above perturbation method, we may now proceed to representative applications in real systems.

3.2. Case study 1: Methanol (1) – Water (2) system

In NRHB model, water molecules are commonly described assuming the presence of one kind of proton donor (two hydrogen bonding proton donor sites per molecule) and one kind of proton acceptor (two proton acceptor sites per molecule) (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020; Grenner et al., 2008). In the case of methanol, each molecule is assumed to display-one kind of proton donor (one proton donor site per molecule) and one kind of proton acceptor (one proton acceptor site per molecule). Consequently, in the water-methanol system two kinds of self-association and two kinds of cross-association occur. In the case study, methanol is the solute (subscripts 1).

Equation-of-state and HB interaction parameters are reported in Table 1, while cross hydrogen bonding interaction parameters are obtained according to the equation (Tsivintzelis et al., 2007):

$$E_{\alpha\beta}^0 = \frac{E_{\alpha\alpha}^0 + E_{\beta\beta}^0}{2} \tag{44.a}$$

$$S_{\alpha\beta}^0 = \left(\frac{S_{\alpha\alpha}^{0\ 1/3} + S_{\beta\beta}^{0\ 1/3}}{2} \right)^3 \tag{44.b}$$

The validation procedure, proposed in this section, consists in retrieving the adjustable interaction parameter, k_{ij}, from methanol activity coefficient at infinite dilution collected at several temperature (Dulitskaya, 1945). Usually, k_{ij} exhibits a temperature dependence, which can be expressed through the following empirical linear relationship (Baldanza et al., 2022; Tammaro et al., 2021):

$$k_{ij} = k_{ij,0} + a_T \cdot T \tag{45}$$

According to equations 44–45, $k_{ij,0}$ and a_T represent the two adjustable parameters of the proposed fitting procedure.

In Fig. 2, the experimental IDAC data (Dulitskaya, 1945) and the two optimized correlations with the approximate / perturbative method and the full numerical solution of NRHB model are reported. Both models show a good and essentially identical performance, further verified by the values of the two pairs of adjustable parameters reported in Table 2. This confirms that both models converge to the same chemical potential for methanol at infinite dilution.

Once $k_{ij,0}$ and a_T have been determined, one may further test and validate the proposed perturbative procedure by predicting (through the NRHB model) the vapor–liquid equilibrium (VLE) behavior over the full concentration range by using the IDAC-based adjustable parameters of Table 2. Isothermal VLE data at 323 K, 328 K and 333 K for this system are reported in Fig. 3, along with the two NRHB predictions obtained by using the two pairs of parameters from Table 2. For the sake of comparison, the independent simultaneous NRHB fitting of the three isothermal VLE data (in temperatures different from those of IDAC data) is also reported in Fig. 3, assuming again $k_{ij,0}$ and a_T as adjustable parameters: $k_{ij,0} = 8.55 \cdot 10^{-5}$; $a_T = -8.27 \cdot 10^{-2} K^{-1}$.

As expected, the two types of NRHB predictions provide essentially the same satisfactory results. An improvement is obtained by performing the simultaneous NRHB fitting at each temperature. Indeed, equation 45 is expected to hold in a moderate temperature range. In our case, the parameters of $k_{ij,0}$ and a_T, were calculated in

Table 1
NRHB parameters of pure components (Tsivintzelis et al., 2007).

	ε_h(J mol^{-1})	ε_s (J mol^{-1}K^{-1})	$v_{sp,0}$ (cm^3 g^{-1})	S	E_{ii}^0(J mol^{-1})	S_{ii}^0(J mol^{-1}K^{-1})
Methanol	4202.3	1.52690	1.15899	0.941	−25100	−26.5
Water	5336.5	−6.50570	0.97034	0.861	−16000	−14.7

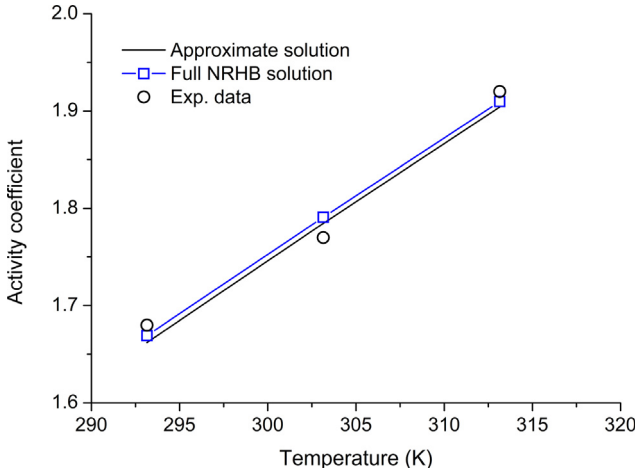

Fig. 2. Fitting of methanol activity coefficient at infinite dilution in water as a function of temperature. Experimental data (open circles) are compared with the full numerical NRHB calculations (line and symbols) and the approximate ones (solid line).

Table 2
Pairs of parameters of Eq. (45).

	$k_{ij,0} \cdot 10^4$	$a_T \cdot 10$(K^{-1})
Approximate NRHB model	5.09	−2.12
Full NRHB model	5.13	−2.14

the range of temperature of the activity coefficient data, which is different from the range of VLE data considered.

3.3. Case study 2: Chloroform (1) – Acetone (2)

In NRHB model, acetone is commonly described assuming the presence of one kind of proton acceptor site per molecule. In the case of chloroform, one kind of proton donor site per molecule is assumed. Consequently, in acetone-chloroform system one kind of cross-association occurs. This makes this system of interest for testing the general expression of the perturbation method in one of the subcases discussed in section 2 (case B).

Equation-of-state parameters are reported in Table 3. The cross-hydrogen bonding interaction parameters, $E_{12}^0 = -10621$ J mol^{-1} and $S_{12}^0 = -13.75$ J mol^{-1} K^{-1}, are taken also from ref. (Tsivintzelis et al., 2007). To the best of our knowledge, activity coefficient at infinite dilution data for this binary system is available in literature only at one temperature (323 K) and refers to the case of acetone as solvent (Tassios, 1971). As a consequence, it is not possible to retrieve a reliable value of the k_{ij} parameter from a fitting procedure. Therefore, our validation approach in this case consists in retrieving the k_{ij} parameter by fitting VLE data at 308 K (data from (Apelblat et al., 1980)) and, afterwards, in predicting the experimental activity coefficient at infinite dilution in acetone at 323 K with Eq. (17).

In Fig. 4, chloroform-acetone VLE data are compared with the optimized NRHB prediction by using k_{ij} as adjustable parameter (k_{ij} = 0.0014). It is evident that the model is able to properly

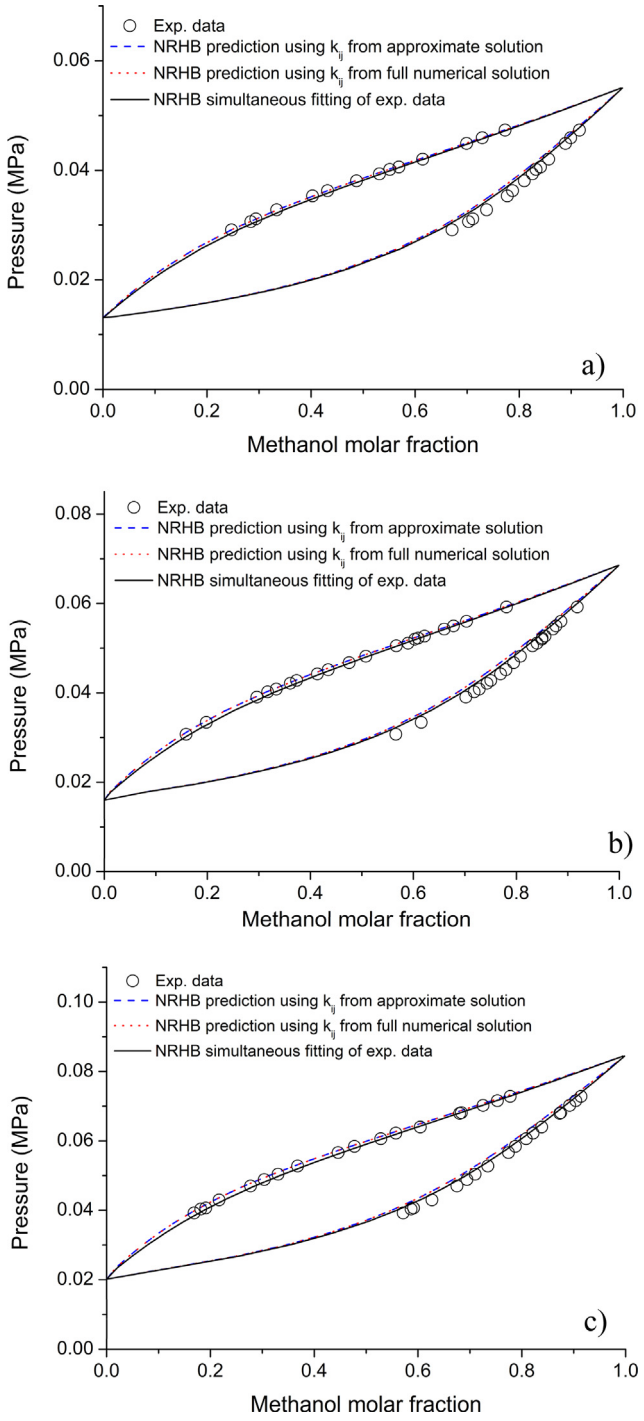

Fig. 3. Isothermal water-methanol vapor–liquid equilibrium data at (a) 323 K, (b) 328 K and (c) 333 K. Comparison between NRHB predictions using $k_{ij,0}$ and a_T from Table 2 and NRHB simultaneous fitting at the three temperatures.

describe the azeotropic binary mixture behavior of the system. In this calculation, k_{ij} cannot be determined as function of the temperature.

Table 3
NRHB parameters of pure components (Tsivintzelis et al., 2007).

	ε_h(J mol^{-1})	ε_s(J mol^{-1}K^{-1})	$v_{sp,0}$(cm^3 g^{-1})	s
Chloroform	5072.0	−0.7373	0.59291	0.84
Acetone	4909.0	−1.1500	1.143	0.908

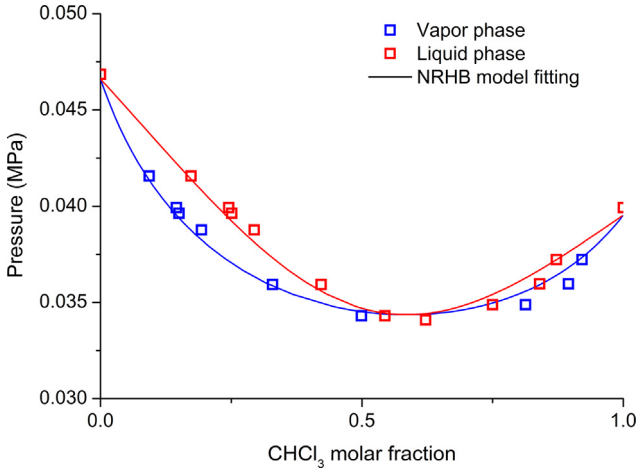

Fig. 4. Fitting of isothermal chloroform-acetone vapor–liquid equilibrium data at 308 K.

The predicted activity coefficient at infinite dilution by using the full numerical and the approximate method are extremely close, in this case, (coincident up to the third digit) and equal to $4.927{\cdot}10^{-1}$. Despite the assumption of temperature-independent k_{ij}, the predicted values are close to the experimental datum (Tassios, 1971), which is $4.95{\cdot}10^{-1}$ (relative error 0.5 %). This is rather expected since the temperature of the VLE data (308 K) is close to the one (323 K) of the datum of the experimental activity coefficient at infinite dilution. This agreement of experimental and calculated IDAC further confirms the validity of the approximate perturbation approach.

3.4. Prediction / correlation of IDAC in n-hexadecane

Having validated the approximate perturbation method used in this work, we may now use Eq. (17) to predict IDAC from the pure-component parameters. In Table 4 are reported such predictions for IDAC of alkanes, cyclohexane, benzene and toluene in *n*-hexadecane at ambient conditions. Solvation energy, $\Delta G_{1/2}$, data, or $L_1 = -\Delta G_{1/2}/RT$, in solvent *n*-hexadecane are available for numerous compounds (Endo et al., 2015). The activity coefficients at infinite dilution may, then, be obtained from the classical equation (Acree and Jiang, 2017):

$$\gamma_{1/2}^{\infty} = \frac{RT}{K_{1/2}P_1^0 V_{m2}} = \frac{RT}{10^{L_1}P_1^0 V_{m2}} \tag{46}$$

where, the vapor pressure, P_1^0, of solute and the solvent molar volume, V_{m2}, may be obtained from the DIPPR compilation (Daubert, 1985) or other relevant compilations.

As seen in Table 4, the performance of the approximate model is rather satisfactory. Of course, besides prediction (k_{12} = 0), the experimental data may be used for determining k_{12} which could, then, be used for predicting phase equilibria over the full composition range, as done in the previous sub-section. To this regard, in Table 4, each k_{12} of correlation has been obtained as the only unknown in equation 17 once a single experimental IDAC datum is inserted in it. Moreover, in the table, it is also reported the column of the predictions of the pure solute molar volume compared to the experimental ones (Daubert, 1985). The lattice fluids and HB interactions parameters of all the systems have been retrieved from ref. 45.

It should be pointed out that these calculations are based on parameters from one single literature source (Tsivintzelis et al., 2007). As well known, the equation-of-state parameters of this

Table 4
Comparison of experimental and predicted activity coefficients of hydrocarbons and alkanols at infinite dilution in *n*-hexadecane at 298.15 K.

Solute	Molar Volume (cm^{3}mol^{-1})		Activity Coefficient at infinite dilution		
	Experim. (Dulitskaya, 1945)	NRHB Calcul.	Experim. (Eq. (46))	Predicted (k_{ij} = 0)	k_{ij} IDAC Correlation
Propane	89.56	89.81	0.788	0.776	0.001
n-Butane	101.39	100.76	0.839	0.769	0.0044
n-Pentane	116.05	115.63	0.848	0.796	0.0026
n-Hexane	131.36	131.43	0.892	0.829	0.0026
n-Heptane	147.02	147.56	0.937	0.862	0.0026
n-Octane	162.56	164.29	0.936	0.892	0.0013
n-Nonane	178.89	180.89	0.937	0.918	0.0005
n-Decane	195.83	198.14	0.954	0.942	0.0003
n-Undecane	212.24	215.05	0.973	0.961	0.0003
Cyclohexane	108.86	113.76	0.708	0.712	−0.0002
Cyclohexane*	108.86	110.29	0.708	0.704	0.0002
Benzene	89.48	89.91	1.09	0.768	0.0163
Toluene	106.65	105.65	1.033	0.866	0.007
Methanol	40.58	42.20	54.0	37.77	0.0332
Ethanol	58.62	59.22	34.0	34.97	−0.002
1-Propanol	75.17	75.92	27.3	32.71	−0.0099
1-Butanol	92.19	93.27	23.6	30.86	−0.012
1-Pentanol	108.5	110.51	20.1	29.24	−0.0142
1-Hexanol	125.2	126.43	21.3	27.91	−0.0089
1-Heptanol	141.5	144.95	22.1	26.47	−0.0052
1-Octanol	157.7	161.80	18.5	25.25	−0.0081
1-Nonanol	175	175.79	19.3	24.42	−0.0056
1-Decanol	192.8	194.28	15.8	23.25	−0.0083

* Calculations with the alternative set of equation-of-state parameters: ε_h = 4537.6 J/mol, ε_s = 1.6004 J/mol K^{-1}, v_{sp}^* = 1.1667 cm^3 g^{-1}.

type of models may vary, depending on the range of experimental data used for their determination. In the case of hydrogen-bonded systems, these parameters are very much influenced by the assumed HB interaction energies (Panayiotou et al., 2016). The adopted set of parameters has, then, an influence on the predicted IDAC. As an example, in Table 4 are shown calculations with two sets of equation-of-state parameters for cyclohexane, which correlate equally well pure-component data on vapor pressures, densities and heats of vaporization (Daubert, 1985). No further attempt was made here to select from alternative sets of pure-component NRHB parameters for the IDAC predictions. The main purpose of the present work was to derive approximate analytical NRHB expressions for IDAC, not to test the performance of NRHB itself, which has been already extensively tested in the open literature (Panayiotou et al., 2004; Panayiotou et al., 2007; Mensitieri et al., 2020; Grenner et al., 2008).

For the sake of clarity, a graphical representation of the results of Table 4 is also reported in section SI.3 of the SI file.

4. Conclusions

The formalism of the equation-of-state NRHB model has been further developed by deriving approximate but highly robust and reliable analytical equations for the activity coefficients or the chemical potentials in infinitely dilute systems. The approximate equations were derived by a straightforward perturbation approach and were successfully validated by a series of tests and comparisons with the full numerical solutions and with experimental data on activity coefficients at infinite dilution or vapor–liquid equilibria. These new derivations are useful not only in NRHB applications but also in a variety of models which are using either the quasi-chemical approach (Guggenheim, 1952) for non-randomness or the Veytsman statistics (Panayiotou and Sanchez, 1991; Veytsman, 1990) for hydrogen bonding. Ways of their direct use have been shown in the present work and include predictions of activity coefficients at infinite dilution, and direct determination of (adjustable k_{12}) binary interaction parameters and subsequent prediction of phase equilibria over the full composition range. Many other applications may be envisioned and include solvation phenomena, solubility predictions, solvent screening, determination of hydrogen bonding interaction energies and many others.

CRediT authorship contribution statement

A. Baldanza: Conceptualization, Methodology, Software, Writing – original draft. **G. Scherillo:** Conceptualization, Methodology, Writing – original draft. **G. Mensitieri:** Supervision, Writing – review & editing. **C. Panayiotou:** Supervision, Writing – original draft.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2022.118043.

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