Use of Nonideality Parameters for the Analysis of the Thermodynamic Properties of Binary Mixtures

Marcos Caroli Rezende,* Vanderlei Gageiro Machado, Simone Morales, and Matías Vidal

ABSTRACT: Two parameters are introduced, a nonideality index (NII) and a nonideality area (NIA), for the analysis of the variations of thermodynamic properties of binary mixtures. Their calculation is based, for the NII, on experimental plots of the variation of a given property (density, refractive index, viscosity, etc.), and for the NIA, on experimental plots of its excess value (excess enthalpies, molar volumes, viscosities, refractive indices, isentropic compressibilities, etc.) with the mixture composition. Both nonideality parameters are therefore not based on any theoretical model or on its derived parameters, being applicable with any fitting equation. The NII or NIA values for a thermodynamic property of a series of related binary mixtures reveal interesting trends, which are not evident in most analyses of such systems. Besides their predictive value, these trends provide information on the relevance of solvent characteristics of the binary mixture, thus supporting new insights or interpretations of the experimental data.

1. INTRODUCTION

A large number of papers are found in the literature, where the thermodynamic properties of binary mixtures such as densities, refractive indices, viscosities, molar volumes, or heat capacities, are reported throughout their compositions and at different temperatures.1–10

Attempts are inevitably carried out to compare related systems. The identification of reliable trends helps researchers draw conclusions regarding the microscopic factors responsible for the observed behavior and for predictions of related systems. The definition of parameters to quantify and summarize such a wealth of experimental data is therefore as important as the accumulation of measurements for novel systems.

We have previously been concerned with the phenomenon of preferential solvation (PS) of solvatochromic probes in binary mixtures, deduced from measurements of the medium polarity with the variation of their composition.11–13

Models that rationalize PS in these systems have been available for more than two decades, and the derived equations have been employed by many groups to understand and interpret this phenomenon in a large variety of systems.14–18

The difficulties in translating such models and of demonstrating through simulations and theoretical calculations the existence and effects of putative solvating species led us to propose a preferential-solvation index (PSI) to compare and analyze this phenomenon in related systems. The index has found applications in the study of PS in solvent mixtures comprising conventional organic solvents11,12 and electrolyte solutions.13

The PSI ultimately measures the degree of departure from ideality of the solvation shell of a solvatochromic probe, compared with the bulk composition of a mixture. It therefore constitutes a particular example of a more general concept—that of nonideality in binary mixtures—which can be developed for the comparison and analysis of a large variety of properties of related binary mixtures. In the present paper, we develop this idea and describe a nonideality index (NII)
and the concept of nonideality area (NIA) for the study and comparison of any thermodynamic property that varies with the composition of a binary mixture. The potentialities of the nonideality approach, based on the NII or NIA parameters, for comparing thermodynamic properties of binary mixtures, comprising common solvents and ionic liquids (ILs) are presented below. Examples from the literature of properties such as densities, viscosities, refractive indices, excess enthalpies, molar volumes, and isentropic compressibilities were analyzed within this novel framework. The obtained values of NII or NIA were used to search for trends within a series of related systems, thus highlighting the effect of particular solvent properties on the experimental data.

2. RESULTS AND DISCUSSION

2.1. Calculation of the NII and NIA Parameter. The NII parameter can be easily calculated from plots that describe the variation of a given property \( P \) with the composition \( X_2 \) of component 2, in a binary mixture with component 1. Schematic examples of such plots are shown in Figure 1.

The NII is calculated as the ratio \( A_1/A_2 \) between the two areas shown in the plots. An arbitrary convention is adopted, defining the NII as positive if the nonideal curve (in red) is biased toward or governed by the values of component 2, as indicated by the arrows in plots (a) and (b). It is negative if nonideality is governed by component 1, as shown by the arrow in plots (c) and (d). Absolute values of NII normally vary between 0 (ideal behavior) and 1, but can also exceed unity in extremely nonideal behaviors, sometimes referred to as indicative of a “synergistic” effect [plot (e)]. Finally, it may also occur that the NII changes sign as the mixture composition changes, as shown in plot (f). In this case, two partial NII values are calculated, and the total index is given by the algebraic ratio \( (A_1 + A_1')/A_2 \).

The NII approach is a robust method for comparison of related systems, since NII values do not vary significantly with different fitting equations. It can be applied to any property that varies its absolute value with the composition of a binary mixture.

In many instances, variation of a thermodynamic property with the composition of a binary mixture is recorded in relative values, as excess differences from the ideally expected values. Thus, plots of viscosities,\(^1,7\) excess molar volumes,\(^4,6,8,19,20\) isentropic compressibilities,\(^4,19,20\) refractive indices,\(^19,21\) or enthalpies\(^5,20,22\) are encountered, where the experimental data are fitted with equations derived from different models, with variable success.
The nonideality approach does not require any assumption from a theoretical model, nor is it limited to any particular fitting equation derived from any model. In fact, its robustness derives from the fact that it can be used with any equation that provides good fittings to the experimental data. For all cases, similar areas and area ratios, and similar values for the corresponding NII and NIA parameters are obtained.

For the experimental data of all systems of Tables 1 and 2, we employed fitting eq 1 derived from the solvent-exchange model,14−17 where \( \Delta P \) is the variation of property \( P \), \( X_2 \) is the molar ratio of the second, added component to the binary mixture, and \( A, B, C, \) and \( D \) are fitting parameters.

\[
P - P_i = \Delta P = [A X_2^2 + B(1 - X_2)X_2]/[(1 - X_2)^2 + C X_2^2 + D(1 - X_2)X_2] \quad (1)
\]

Equation 1 has been derived from a model applicable to the preferential solvation of a probe in a binary solvent mixture. The model is clearly not applicable to variations of thermodynamic properties of binary mixtures. Therefore, eq 1 is little more than a mathematical tool. Nevertheless, it proved highly effective as a fitting equation, with squared correlation coefficients \( r^2 > 0.99 \) for most systems of Tables 1 and 2.

Plots of the experimental data with the fitting curves derived from eq 1 that were utilized for the calculation of the NII and NIA values of Tables 1 and 2 are reproduced in the Supporting Information, together with the corresponding fitting parameters \( A, B, C, \) and \( D \), and the resulting correlation coefficients.

2.3. Analysis of Thermodynamic Properties with Nonideality Indices (NII). Table 1 lists examples of the application of the NII to various properties that depend on the

### Table 1. Values of the Nonideal Index (NII) for Various Composition-Dependent Properties of Binary Mixtures

| entry | binary mixture | property | NII ref |
|-------|----------------|----------|---------|
| 1     | propan-2-ol/DMA | density   | 0.07    | 23 |
| 2     | butan-2-ol/DMA  | density   | −0.02   | 23 |
| 3     | pentan-2-ol/DMA | density   | −0.09   | 23 |
| 4     | hexan-2-ol/DMA  | density   | −0.14   | 23 |
| 5     | heptan-2-ol/DMA | density   | −0.19   | 23 |
| 6     | propan-2-ol/DMC | density   | 0       | 24 |
| 7     | butan-2-ol/DMC  | density   | −0.07   | 24 |
| 8     | pentan-2-ol/DMC | density   | −0.13   | 24 |
| 9     | hexan-2-ol/DMC  | density   | −0.18   | 24 |
| 10    | heptan-2-ol/DMC | density   | −0.22   | 24 |
| 11    | decan-1-ol/MeOH at 288.15 K | viscosity | 0.19 | 25 |
| 12    | decan-1-ol/ethyl alcohol at 288.15 K | viscosity | 0.16 | 25 |
| 13    | decan-1-ol/propan-2-ol at 288.15 K | viscosity | 0.08 | 25 |
| 14    | decan-1-ol/butan-2-ol at 288.15 K | viscosity | 0.09 | 25 |
| 15    | decan-1-ol/meoh at 298.15 K | viscosity | 0.15 | 25 |
| 16    | decan-1-ol/meoh at 308.15 K | viscosity | 0.10 | 25 |
| 17    | decan-1-ol/meoh at 318.15 K | viscosity | 0.05 | 25 |
| 18    | decan-1-ol/meoh at 328.15 K | viscosity | −0.09 | 25 |
| 19    | methanol/butylammonium fluoride | density   | 0.59 | 26 |
| 20    | ethanol/butylammonium fluoride | density   | 0.43 | 26 |
| 21    | propan-1-ol/butylammonium fluoride | density | 0.33 | 26 |
| 22    | butan-1-ol/butylammonium fluoride | density | 0.23 | 26 |
| 23    | pentan-1-ol/butylammonium fluoride | density | 0.19 | 26 |
| 24    | methanol/[Bmim] BF_4 | viscosity | 278.15 K | −0.67 | 27 |
| 25    | methanol/[Bmim] BF_4 | viscosity | 288.15 K | −0.63 | 27 |
| 26    | methanol/[Bmim] BF_4 | viscosity | 298.15 K | −0.58 | 27 |
| 27    | methanol/[Bmim] BF_4 | viscosity | 308.15 K | −0.54 | 27 |
| 28    | methanol/[Bmim] BF_4 | viscosity | 318.15 K | −0.50 | 27 |
| 29    | methanol/[Emim] BF_4 | viscosity | 278.15 K | −0.59 | 27 |
| 30    | methanol/[Emim] BF_4 | viscosity at 288.15 K | −0.55 | 27 |
| 31    | methanol/[Emim] BF_4 | viscosity at 298.15 K | −0.51 | 27 |
| 32    | methanol/[Emim] BF_4 | viscosity at 308.15 K | −0.48 | 27 |
| 33    | methanol/[Emim] BF_4 | viscosity at 318.15 K | −0.44 | 27 |
| 34    | MD/MCH | density at 298.15 K | −0.15 | 28 |
| 35    | MDD/MCH | density at 298.15 K | −0.20 | 28 |
| 36    | MTD/MCH | density at 298.15 K | −0.24 | 28 |
| 37    | MD/MCH | density at 293.15 K | 0.11 | 28 |
| 38    | MD/MCH | density at 303.15 K | 0.09 | 28 |
| 39    | MD/MCH | density at 313.15 K | 0.07 | 28 |
| 40    | MD/MCH | density at 323.15 K | 0.05 | 28 |
| 41    | 1-BuOH/Me acrylate | viscosity at 288.15 K | 0.54 | 29 |
| 42    | 1-BuOH/Me acrylate | viscosity at 298.15 K | 0.52 | 29 |
| 43    | 1-BuOH/Me acrylate | viscosity at 308.15 K | 0.48 | 29 |
| 44    | 1-BuOH/Me acrylate | viscosity at 318.15 K | 0.43 | 29 |
| 45    | 1-Hexanol/Me acrylate | viscosity at 298.15 K | 0.51 | 29 |
| 46    | 1-Octanol/Me acrylate | viscosity at 298.15 K | 0.46 | 29 |
| 47    | 1-decanol/Me acrylate | viscosity at 298.15 K | 0.41 | 29 |
| 48    | H_2O/THF | refractive index | 0.60 | 30 |
| 49    | H_2O/DMF | refractive index | 0.58 | 30 |
| 50    | H_2O/DMSO | refractive index | 0.49 | 30 |
| 51    | H_2O/ethylene glycol | refractive index | 0.42 | 30 |
| 52    | H_2O/MeCN | refractive index | 1.34 | 30 |

\*At 298.15 K, DMA = dimethylacetamide, DMC = dimethyl carbonate. \*In g cm\(^{-3}\). \*In cp. \*At 298.15 K, BAB = n-butyllammonium butanoate. \*\([\text{Bmim}]\) BF_4 = 1-butyl-3-methylimidazolium fluoroborate, [Emim] BF_4 = 1-ethyl-3-methylimidazolium fluoroborate. \*\([\text{Mim}]\) BF_4 = 1-methyl-3-methylimidazolium fluoroborate. \*In mPa s. \*MD = methyl decanoate, MDD = methyl dodecanoate, MTD = methyl tetradecanoate, MCH = methyl cyclohexane. \*In N s m\(^{-2}\). \*Refractive index deviations at 298.15 K.
composition of binary mixtures. These properties include densities, viscosities, and refractive indices of mixtures comprising conventional solvents or ionic liquids, where either one component, or the mixture temperature was varied. Positive NII values denote nonideal deviations biased toward the second, or added component, which always appears as the right-hand term of the mixture in Table 1. Conversely, negative NII values correspond to deviations biased toward the first or left-hand component of the mixture in Table 1.

The examples of Table 1 illustrate the potentiality of the NII parameter for comparing related binary systems where one

Table 2. Values of the Nonideal Area (NIA) for Excess Thermodynamic Properties of Binary Mixtures from the Literature

| entry | binary mixture       | excess property | NIAa | ref |
|-------|----------------------|-----------------|------|-----|
| 1     | benzene/DMSO         | enthalpy        | 412  | 31  |
| 2     | toluene/DMSO         | enthalpy        | 578  | 31  |
| 3     | ethyl benzene/DMSO   | enthalpy        | 720  | 31  |
| 4     | 1-propylbenzene/DMSO | enthalpy        | 826  | 31  |
| 5     | 2-propylbenzene/DMSO | enthalpy        | 860  | 31  |
| 6     | 1-butylbenzene/DMSO  | enthalpy        | 918  | 31  |
| 7     | sec-butylbenzene/DMSO| enthalpy        | 837  | 31  |
| 8     | tert-butylbenzene/DMSO| enthalpy   | 874  | 31  |
| 9     | 1-chloropropane/DMSO | enthalpy       | 628  | 31  |
| 10    | 1-chlorobutane/DMSO  | enthalpy       | 720  | 31  |
| 11    | 1-chloropentane/DMSO | enthalpy       | 833  | 31  |
| 12    | 1-chlorohexane/DMSO  | enthalpy       | 928  | 31  |
| 13    | tetrachloromethane/DMSO | enthalpy | 161  | 31  |
| 14    | trichloromethane/DMSO| enthalpy       | −1806| 31  |
| 15    | 1,1,2,2-tetrachloroethane/DMSO | enthalpy | −2499| 31  |
| 16    | propan-1-ol/BAO      | molar volume b  | −0.51| 32  |
| 17    | butan-1-ol/BAO       | molar volume b  | −0.46| 32  |
| 18    | pentan-1-ol/BAO      | molar volume b  | −0.30| 32  |
| 19    | hexan-1-ol/BAO       | molar volume b  | −0.21| 32  |
| 20    | propan-1-ol/BAO      | isentropic compressibility b | −98 | 32  |
| 21    | butan-1-ol/BAO       | isentropic compressibility b | −73 | 32  |
| 22    | pentan-1-ol/BAO      | isentropic compressibility b | −53 | 32  |
| 23    | hexan-1-ol/BAO       | isentropic compressibility b | −39 | 32  |
| 24    | H2O/ethanol          | molar volume b  | −0.75| 33  |
| 25    | H2O/glycerol         | molar volume b  | −0.22| 33  |
| 26    | H2O/ethylene glycol  | molar volume b  | −0.22| 33  |
| 27    | H2O/diethyleneglycol | molar volume b  | −0.44| 33  |
| 28    | H2O/triethyleneglycol| molar volume b  | −0.51| 33  |
| 29    | H2O/PEG200          | molar volume b  | −0.60| 33  |
| 30    | H2O/PEG300          | molar volume b  | −0.72| 33  |
| 31    | H2O/PEG400          | molar volume b  | −0.79| 33  |
| 32    | H2O/PEG600          | molar volume b  | −0.88| 33  |

“NIA units are the same of the excess property under study. Enthalpies (J mol⁻¹), molar volumes (cm³ mol⁻¹), and isentropic compressibilities (T Pa⁻¹) at 298.15 K. BAO = n-butylammonium oleate. PEG = poly(ethylene glycol).

Figure 2. Variations of thermodynamic properties with the composition of binary mixtures: (a) densities of methanol/n-butylammonium butanoate at 298.15 K; (b) viscosities of methanol/[Bmim]BF₄ (IL) at 298.15 K. Plots are original and employed eq 1 for the fitting curves, with fitting parameters A = 0.09, B = 0.93, C = 0.67, D = 6.7 (N = 21, r² = 1) [plot (a)] and A = 10.06, B = 5.51, C = 0.10, D = 0.48 (N = 15, r² = 1) [plot (b)]. Adapted from refs 26, 27.
variable (thermodynamic property, binary components, or temperature) is varied. The behavior of a binary mixture is determined by the properties of each component. In the following analyses, we will make use of four empirical solvent parameters introduced by Catalán, the solvent acidity $SA$, or hydrogen-bond-donating (HBD) strength of the solvent, its basicity $SB$, or its hydrogen-bond-accepting (HBA) strength, its dipolarity $SdP$, and its polarizability $SP$.34 These tabulated four parameters have been frequently employed as the basis of multiparametric regression analyses, to interpret solvent effects for a large variety of chemical processes.34,35

Entries 1–10 of Table 1 describe density variations at 298.15 K for binary mixtures of alkan-2-ols with dimethylacetamide (DMA)23 and with dimethylcarbonate (DMC).24 Experimental data were fitted with Redlich–Kister polynomials.36 We employed eq 1 for fitting the experimental data with very good results (see the Supporting Information).

Both series exhibit a similar trend with the increasing size of the alkan-2-ol, shifting from a nearly ideal behavior for mixtures with propan-2-ol ($NII \approx 0$) to increasingly negative $NII$ values with larger alkan-2-ols. By convention, these negative signs indicate deviations from ideality toward the first component (DMA or DMC), as the situation depicted in Figure 1c. For both series, the $NII$ variation points to an increasingly nonideal behavior for mixtures of DMA or DMC with larger alkan-2-ols. However, the alcohol property that governs this behavior differs for the two non-HBD solvents, as can be seen in Figure 3. For the ROH/DMA mixtures, the alcohol dipolarity is responsible for the observed nonideal behavior, which increases with the decreased $SdP$ values of the alcohol (Figure 3a). For the ROH/DMC mixtures, the nonideal behavior increases with the alcoholic polarizability $SP$ (Figure 3b).

In an effort to interpret the observed deviations, two models were employed by the author to interpret the variations of density and viscosities of DMA/2-alkanol mixtures.23 In the case of the DMC/2-alkanol mixtures, two other elaborate models were applied, besides five semiempirical equations derived from different methods.24 The obtained fitting parameters, however, were not used for any interpretation of the existing interactions. Following a common practice, comparison of the employed models was ultimately carried out by comparing the fittings provided by their derived equations to the experimental data.

The $NII$ approach, without invoking any models or assumptions, provides interesting predictive information for the two series. Regardless of the possible interpretations of the obtained trends, they stress the participation of other interactions in the mixtures besides hydrogen bonds, as interpreted by the author.23,24 None of these interactions were detected, after application of a large variety of models to the systems.

A different picture emerges when the co-solvent added to an alkanol is an HBD species, as the IL $n$-butylammonium butanoate (BAB), for which values of $NII$ for densities of ROH/BAB mixtures are listed in entries 19–23.26 It is
reasonable to expect for these mixtures rather strong interactions between the acidic BuNH₃⁺ cation and the basic alcohol, and this is indeed observed when the NII values are plotted against the basicity SB parameter of the alkan-1-ols (Figure 4a).

The authors did not apply any particular model to interpret the possible interactions in the mixtures. After employing a Redlich–Kister-type equation to fit the experimental data, inspection of the obtained graphs led to the general conclusion that “the thermodynamic results suggest that the structural effects and dispersion type interactions must outweigh other possible effects present in the mixtures studied.” The additional piece of information gathered from the NII approach is clearly more specific.

A similar reasoning is applicable to mixtures of alkan-1-ols with another HBD co-solvent, decan-1-ol,25 for which NII values for viscosities at 288.15 K are listed in Table 1, entries 11–14 (Figure 4b). Hydrogen-bond interactions between the acidic decan-1-ol and the added basic alkan-1-ols govern variations in viscosity of the mixtures, as can be seen from the linear plot of Figure 4b.

The NII values for viscosity variations of the same series at different temperatures also revealed a trend commonly found when variations of a thermodynamic property of a mixture are measured at increasing temperatures: a nonideal behavior is usually found at lower temperatures, changing to an ideal situation (NII ≈ 0) as temperature increases. This is verified for viscosities of decan-1-ol/methanol mixtures, at increasing temperatures (entries 11 and 15–18): the corresponding NII values decrease, and even change sign, in the order 0.19 (288.15 K) > 0.15 (298.15 K) > 0.10 (308.15 K) > 0.05 (318.15 K) > −0.09 (328.15 K). Such a trend, illustrated graphically in Figure 5, is also found for variations of viscosity of another mixture composed of methanol and an IL ([Bmim][BF₄]) or [Emin][BF₄] (entries 24–28).27 In all cases, the absolute values of the NII converge to an ideal situation (NII ≈ 0) as the temperature increases (Figure 5).

Densities and viscosities of binary mixtures of methyl esters of fatty acids with methylcyclohexane have been measured at different temperatures.28 The authors employed no theoretical models in their analysis, besides Redlich–Kister third-order polynomial equations for their fittings. The use of eq 1 provided equally good fittings for the experimental data, as shown in the Supporting Information.

NII values for some of the corresponding variations are given in entries 34–40 of Table 1. The nonideal behavior of the viscosity variations decreased with temperature, from an NII value of 0.11 at 293.15 K to 0.05 at 323.15 K. This points to a decreased interaction between the two components as temperature rises, a conclusion also reached by the authors, who suggested an “elongation of intermolecular distance with the temperature rising.” This interaction is mainly due to the polarizabilities of the two components, as shown by the variation of the NII values of the mixture densities at 298.15 K. In fact, absolute NII values increase in the order decanoate (−0.15) < dodecanoate (−0.20) < tetradecanoate (−0.24), showing that mixtures of the latter with methylcyclohexane exhibit the largest nonideal behavior, and the strongest intermolecular interactions. Although SP values for the three esters are not available, values for other families of analogous compounds, such as n-alkanols, show that SP values increase with the size of the normal alkyl chain.24 Methylcyclohexane, with an SP value of 0.675, interacts mainly by induced polarization with the methyl esters, being thus rather sensitive to their polarizability. Thus, the NII approach offers a clue to the nature of the interactions between the fatty acid esters and methylcyclohexane, in contrast with the authors’ vague conclusion that “strong specific interactions between unlike molecules take place.”28

The viscosities of binary mixtures of 1-alkanols with methyl acrylate were measured at various temperatures.29 Some of the corresponding NII values are given in Table 1, entries 41–47, for different temperatures and/or alcohols. The observed decrease in the absolute NII values with the increasing temperature for 1-BuOH/Me acrylate mixtures has been observed for the viscosity of other mixtures (entries 37–40, 24–28, 29–33) and reflects the decreased interactions between the two components, as the temperature rises. In all cases, the increased temperature leads to an increasingly ideal situation (NII = 0).

At a constant temperature (298.15 K), the NII values of the 1-alkanol mixtures decrease in the order 1-BuOH (0.52) > 1-hexanol (0.51) > 1-octanol (0.46) > 1-decanol (0.41) (entries 42 and 45–47). A multiple regression analysis of these values in terms of the alcohol properties yielded a very good dependence (r² = 0.99) of the NII values on the alcohol polarizability (SP) and dipolarity (SdP), according to eq 2.

\[
\text{NII} = 5.54 \text{SP} + 1.38 \text{SdP} - 4.12
\]  

(2)

Replacement of either polarizability or dipolarity by the alcohol acidity (SA) led to much poorer correlations (r² = 0.81), showing that hydrogen-bond donation by these hydroxyllic co-solvents plays a secondary role in the viscosity of the mixtures. This is far from evident without the NII approach. The authors correctly observed that the interactions decreased (decreased NII values) with the chain length of the alcohol, but attributed this to the fact that “H-bonding formed between 1-alkanol molecules and MA molecules weakens as the chain length increases”,29 a conclusion that is not validated by the nonideal analysis.

Different thermodynamic properties of aqueous solutions of organic solvents were determined at 298.15 K.30 The computed values were fitted with a Redlich–Kister polynomial equation. As is often the case, attempts to interpret the
obtained graphics were limited to a qualitative ordering of the mixtures, according to their graphic appearance. Entries 48–52 of Table 1 list examples of deviations of refractive indices (Δn) for some aqueous mixtures. The corresponding NII values were determined by fitting the experimental data with eq 1. As can be seen in the Supporting Information, fittings were always very good, with $r^2 > 0.99$.

In search of the factors responsible for the observed deviations, correlations were sought between the calculated NII values and properties of the corresponding organic solvents. A reasonable correlation ($r^2 = 0.79$) was obtained between the NII values and Catalán’s basicity parameter SB of the five organic solvents for which such values were available.

The estimated NII values could be expressed as

$$\text{NII}(\text{calc}) = 1.95 - 2.36 \text{ SB} \tag{3}$$

Figure 6 shows the obtained correlation between the NII values calculated according to eq 3 and the experimental NII values.

\[ \begin{array}{c|c|c}
\hline
\text{NII (calc)} & \text{NII (exp)} \\
\hline
\text{MeCN} & 1.50 \\
\text{EG} & 1.25 \\
\text{THF} & 1.00 \\
\text{DMF} & 0.75 \\
\text{DMSO} & 0.50 \\
\hline
\end{array} \]

Figure 6. Correlation between the experimental and calculated NII values for the refractive indices of aqueous organic solvents (entries 48–52 of Table 1). Values of NII (calc) were obtained from eq 3 for tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethylene glycol (EG), and acetonitrile.

The dependence of NII values on the basicity of the organic co-solvent, much more significant than on its acidity ($r^2 = 0.13$), dipolarity ($r^2 = 0.30$) or polarizability ($r^2 = 0.66$), suggests that hydrogen-bond interactions between the acidic water with the HBA co-solvent should play a major role in the observed refractive index deviations. Although limited to a small number of data points, this piece of information, provided by the NII approach, offers a contribution to an otherwise purely descriptive study of refractive indices of aqueous mixtures.

2.4. Analysis of Excess Properties with Nonideality Areas (NIA). Table 2 lists examples of the application of the NIA parameter to various excess properties that depend on the composition of binary mixtures. These properties include excess enthalpies, molar volumes, and isentropic compressibilities of mixtures comprising conventional organic solvents or ionic liquids, where either one component, or the mixture temperature was varied. Positive NIA values denote positive deviations and negative NIA values correspond to negative excess deviations.

Figure 7 depicts the good fittings obtained by applying eq 1 to literature data. Analogous plots with the same fitting equation were used for the calculation of the NIA values of Table 2 and are reproduced in the Supporting Information together with the fitting parameters.

The excess enthalpies of mixing were measured for arene/DMSO and polyhaloalkanes/DMSO mixtures at 298.15 K. The corresponding NIA values were determined from plots such as those of Figure 7, and are listed in Table 2, entries 1–15.

DMSO is a highly polarizable (SP = 0.830), dipolar solvent (SdP = 1.00), as indicated by its values of solvent polarizability (SP) and dipolarity (SdP), according to Catalán’s multiparametric approach.\textsuperscript{34} Arenes like benzene (SP = 0.793 and SdP = 0.270) and toluene (SP = 0.782 and SdP = 0.284) show a similar polarizability but are much less dipolar than DMSO.

Therefore, the main interaction between these two classes of solvent should be between induced dipoles, and the observed excess enthalpies should mainly reflect variations of the arene polarizabilities. Unfortunately, SP values are not available for most substituted benzenes of Table 2. Nevertheless, an alternative solvent polarity parameter $A$, based on purely physical constants can be employed, which “relates to the overall polarizability” of individual solvent molecules within the solvent volume.\textsuperscript{37} Polarity parameter $A$ is defined as the product of the molar volume $M/\rho$ by the Onsager or Lorentz–Lorenz function $f(n)$, according to eq 4, where $M$ is the solvent molecular weight, $\rho$ is its density, and $n$ is its refractive index.

$$A = (M/\rho)f(n) = (M/\rho)[(3(n^2−1)/4\pi(n^2 + 2)] \tag{4}$$

Figure 8 shows a plot of NIA values vs $A$, for all benzene derivatives of systems 1–8 of Table 2. It is seen that NIA varies linearly with the polarizability parameter $A$, in an indication
that the arene polarizability determines the enthalpy of mixing of DMSO with the series of benzene derivatives. A different situation is found with the polyhaloalkanes/DMSO series (entries 9−15 of Table 2), in which there are four solvents (1-chlorobutane, tetrachloromethane, trichloromethane, and 1,1,2,2-tetrachloroethane) for which SP and SdP values are available.34 A plot of NIA vs SP for these four mixtures (Figure 9a) yields a modest correlation coefficient ($r^2 = 0.71$), which is improved ($r^2 = 0.92$) when a second contribution from the polyhaloalkane dipolarity is included in the regression equation (Figure 9b).

The dependence of NIA on the polyhaloalkane polarizability and dipolarity ($r^2 = 0.92$), reflected in eq 5, highlights the origin of the interactions between DMSO and the haloalkanes, responsible for the observed variations of excess enthalpies of mixing.

$$\text{NIA} = 14,429 - 1,825 \text{ SdP} - 1,8650 \text{ SP} \quad (5)$$

The haloalkane polarizability is still the major contributor, almost 10-fold more important than its dipolarity, to the enthalpy of mixing with DMSO. Both factors tend to increase the interactions of the polyhaloalkane with DMSO, changing the enthalpy of mixing from an endothermic process, with haloalkanes of relatively small polarizability/dipolarity, to a strongly exothermic process, with largely polarizable, dipolar polyhaloalkanes (trichloromethane and 1,1,2,2-tetrachloroethane). Tetrachloromethane represents an intermediate situation with a nearly ideal enthalpy of mixing (NIA = 160.9 J·mol$^{-1}$), being a transition from an endo- to an exothermic process. Although highly polarizable (SP = 0.768), it has no dipolar character (SdP = 0).

The molar volumes and isentropic compressibilities of alkan-1-ol/n-butylammonium oleate mixtures were determined at 298.15 K for four different alcohols (entries 16−23 of Table 2). The corresponding NIA values indicate that nonideality decreases with the increased size of the alcohol. As observed for other binary mixtures of alcohols + ammonium salts (see entries 19−23 of Table 1), the hydrogen-bond interaction between the basic alcohols and the acidic alkylammonium cation governs the thermodynamic properties of the mixtures. The linear plots of NIA vs the alcohol basicity expressed by the SB parameter34 (Figure 10) echo a parallel behavior for an analogous ROH/ammonium salt system (Figure 4a).

In a study of the thermodynamic properties of aqueous solutions of poly(ethylene glycols) (PEGs), their excess molar volumes were determined at different temperatures.33 The data points were fitted with a Myers−Scott-type equation.36 We obtained very good fittings ($r^2 > 0.99$) employing eq 1, which yielded the nonideal areas listed in Table 2, entries 24−32.

How did the water−PEG interactions vary with the chain length of the polymeric co-solvent, and what kind of interactions played a major role in these mixtures? After thorough measurements, the authors answered these questions in a qualitative way, by showing that the excess molar volumes of the aqueous mixtures were all negative, and increased in absolute values in the order ethylene glycol (EG) < diethylene glycol (DEG) < triethylene glycol (TEG) < PEG200 < PEG400 < PEG600. The nature of the water−PEG interactions was rather vaguely "ascribed to the predominance of structural effects and at high capacity that the unlike molecules present in the mixtures have to form intermolecular interactions by hydrogen bond."33

The nonideality approach provides a quantitative framework to answer these questions.

PEG chemical formulae can be represented as HO−(−CH$_2$CH$_2$O−)$_n$H. Estimates of the average number $n$(−CH$_2$CH$_2$O−) of ethyleneoxy units in PEGs are therefore equal to (MM − 18)/44, where MM is the average molecular mass of the polymer. Values of $n$(−CH$_2$CH$_2$O−) are equal to 4.1 (PEG200), 6.4 (PEG300), 8.7 (PEG400), and 13.2 (PEG600).
mixtures, as a function of the average number of monomeric units, suggests that these di-alkane like EG, but with strong interactions with the framework, rather more detailed than a purely qualitative approach.

It is always problematic to fit structural conclusions from thermodynamic data. In a study of preferential solvation of phenobarbital in aqueous ethylene glycol ether solutions, the authors admitted that “it is always problematic to draw structural conclusions from thermodynamic data.”49 In a study of preferential solvation of phenobarbital in aqueous mixtures, after an elaborate application of the inverse Kirkwood−Buff integrals, authors arrived at the conclusion that “the specific solute−solvent interactions are not well understood despite the thermodynamic treatment developed.”40

Such a failure to obtain more detailed information on microscopic interactions in these mixtures has led to the ultimate use of the available models and their derived equations, many of them of an empirical, or semiempirical character, as little more than fitting tools.23,24,29 The quality of the obtained fitting ultimately decides on the validity of the model. After comparing equations from seven different models to the viscosity of binary mixtures of methyl acrylate and 1-

Nonideality and water−PEG interactions increase with the number of ethereal (CH2CH2O−) units in the polymer, showing that the major interaction between the two solvents is due to hydrogen bonds between the acidic water and the increasingly basic polyether. As the number of monomeric units increases, so does the number of basic oxygen centers in the polymer. Their effect however is dampened by internal chain folding of the increasingly larger polymer, which limits the access of water molecules.

The rather large (−0.75) NIA value for aqueous ethanol, a small molecule like EG, but with strong interactions with water, suggests that these differ from those of water−PEG mixtures.

Thus, the nonideality approach suggests valuable clues to the interactions in these systems, supported by a quantitative framework, rather more detailed than a purely qualitative rationalization.

2.5. Appraisal of the Nonideality Approach. The use of a nonideality index to quantify unequal or nonideal distributions in a system is not new. It dates back to the beginning of the 20th century, with the suggestion of a coefficient derived from experimental graphics—the Gini coefficient—to measure the unequal distribution of income in a population. Since then, the Gini coefficient has been widely employed to compare different societies or their evolution in time. It does not offer interpretations, nor does it propose or reject any model, it simply points out facts.

To our knowledge, this is the first time that a nonideality index is used in chemistry, to compare the nonideal behavior of related systems. Its use as a preferential-solvation index (PSI) has been described by us recently,11−13 in the study of the unequal distributions of solvating molecules around a probe in binary mixtures. The analogy between the PSI and the Gini coefficient has also been stressed by us in one of these articles.23

What is the contribution of the NII or NIA to the study of composition-dependent properties of a binary mixture? As hopefully shown in the above examples, its application is fairly general, and rather simple. Unlike all models developed to explain particular properties, it is not associated with any derived equations. Possible interpretations to observed trends can be offered, but they are not unique nor do they exclude alternative explanations. Nevertheless, as shown in the above examples, many of the clues provided by the NI approach, based on microscopic interactions between mixture components, are not obvious and are frequently overlooked after application of different models.

The difficulty of obtaining clear-cut evidence of microscopic interactions from available models and their fitting parameters has been acknowledged in the literature. After studying the thermodynamic properties of aqueous ethylene glycol ether solutions, the authors admitted that “it is always problematic to draw structural conclusions from thermodynamic data.”49

Figure 11 is a plot of the NIA values of all aqueous PEG mixtures, as a function of the average number of monomeric units n(−CH2CH2O−).

Figure 10. Excess properties of alcohol/1-butylammonium oleate binary mixtures at 298.15 K. (a) Linear dependence (r2 = 0.97) of NIA values for the excess molar volumes on the alcohol basicity, expressed by the SB parameter.34 (b) Linear dependence of NIA values (r2 = 0.96) for the excess isentropic compressibilities on the alcohol basicity SB.

Figure 11. Variation of NIA values for the excess molar volumes at 298.15 K of aqueous mixtures of poly(ethyleneglycols) (PEGs) with the average number of monomeric units n(−CH2CH2O−).
alkanols, the final conclusion was that “the predicting ability of these correlating relations increases as the number of adjustable parameters in the relation increases.”29 This has hardly anything to do with the quality of the employed model. We have previously warned against the uncritical view that validates a model and its postulates by the good fittings obtained from the derived equations. 11,12 In line with this warning, we have deliberately employed in this work eq 1 to fit experimental data. It is derived from a solvent-exchange model for preferential solvation in binary mixtures, 14–17 with assumptions that clearly do not apply to composition-dependent thermodynamic properties of these mixtures. Therefore, fitting parameters A, B, C, and D in eq 1 are mathematical tools that do not “mean” anything. Nevertheless, curve fittings to the experimental data were always excellent, as can be seen in the Supporting Information. Thus, eq 1 compares well with the Hwang equation, 41 Myers–Scott equation, 42 or the widely employed Redlich–Kister equation, 43,44 originally derived from a thermodynamic model, 45 and ultimately used as a fitting tool. Like any of these fitting equations, it can be successfully used for the calculation of nonideality values of binary mixtures, which are therefore practically independent of the adopted method of fitting.

3. CONCLUSIONS

A novel approach to the study and interpretation of the variations of thermodynamic properties of binary mixtures was described, with the definition of two related parameters, a nonideality index (NII) and a nonideality area (NIA). Both parameters measure the degree of nonideality of experimental plots of the studied property against the mixture composition. The former index is applied to absolute variations of a given property, whereas the second is used in plots of the excess property.

The two parameters are not derived from any theory. They simply reflect and quantify experimental curves. As a consequence, they do not depend on any particular model or fitting equation to be calculated, being rather robust, as they only require good fittings to the experimental data. In particular, an equation derived from a solvent-exchange model for preferential solvation in binary mixtures 14–17 was employed for fitting literature data in the present paper. In spite of being derived from a model that is not applicable to the studied systems, almost all of the obtained fittings were excellent ($r^2 > 0.99$), converting this equation into a valuable mathematical tool, comparable to other widely used fitting equations, as, for example, the Redlich–Kister polynomial. 1,6,7,9,21,26,23,24,34

The determination of NII or NIA values for a thermodynamic property of a series of related binary mixtures reveals interesting trends, which are not evident in most analyses of such systems. Besides their predictive value, these trends provide information on the importance of particular solvent characteristics of the binary mixture, thus supporting new insights or interpretations of the experimental data.

4. COMPUTATIONAL METHODS

All fittings and graphical analyses were performed with the aid of the OriginPro 8.0 package. References from the literature provided the numerical data employed to draw all plots, after fitting them with eq 1. All obtained curves, together with the corresponding fitting parameters, are shown in the Supporting Information. The integration of the areas under the fitting curves provided the values of $A_1$, while $A_2$ values were calculated from the areas of the triangles, as illustrated in Figure 1. NII values were obtained as the $A_1/A_2$ ratio. A similar procedure was used to provide the NIA values, which were calculated by integrating the areas under the experimental curves. The detailed procedures used for calculation of the NII and NIA values are described in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01790.

Plots of all systems used in the calculations of NII and NIA values of Tables 1 and 2 and detailed procedures for the calculation of the NII and NIA values (PDF)

AUTHOR INFORMATION

Corresponding Author
Marcos Caroli Rezende – Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago 9170020, Chile; orcid.org/0000-0003-2040-9009; Email: marcos.caroli@usach.cl

Authors
Vanderlei Gageiro Machado – Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis 88040-900, Santa Catarina, Brazil; orcid.org/0000-0002-6995-6591
Simone Morales – Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago 9170020, Chile
Matias Vidal – Facultad de Química y Biología, Universidad de Santiago de Chile, Santiago 9170020, Chile

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01790

Notes
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