The Relative Reduced Redlich-Kister and Herráez Equations for Correlating Viscosities of 1,4-Dioxane + Water Mixtures at Temperatures from 293.15 K to 323.15 K

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Abstract Viscosity deviations from ideal mixing for 1,4-dioxane + water mixtures over the entire range of composition at temperatures of (293.15, 303.15 and 313.15) K and atmospheric pressure were calculated from experimental viscosity data presented in a previous work. The temperature range was extended to 323.15 K with data from the literature. This system exhibits very large positive deviations due to strong heteromolecular interactions and also due to size differences of the unlike molecules. The viscosity data as well as their corresponding relative functions were used to test the applicability of two correlative equations: the reduced Redlich-Kister equation and the recently proposed Herráez equation. These relative functions are important to reduce the effect of temperature and, consequently, to reveal the effects of different types of interactions. Their correlation abilities at different temperatures, and using different numbers of parameters, are discussed for the case of limited experimental data. Generally, good agreement between experimental and calculated data was obtained with both equations provided more than three parameters were employed.

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1 Introduction

Among the physico-chemical properties of liquid mixtures, viscosity is a valuable tool for developing new theoretical models to understand the liquid state. On the other hand, excess thermodynamic functions and deviations of analogous non-thermodynamic functions of binary liquid mixtures are fundamental for understanding different types of intermolecular interactions in these mixtures.

This paper is a continuation of our earlier work that includes the study of the binary liquid mixture of 1,4-dioxane + water (D + W) [1–7]. In these previous papers, we investigated the excess molar volume V^E, shear viscosity deviation $\Delta\eta$, and excess Gibbs energy of activation of viscous flow ΔG^{*E} for the isobutyric acid + water (IBA + W) [8–11] and 1,4-dioxane + water (D + W) [1–7] systems over the entire range of mole fractions at several different temperatures. The 1,4-dioxane + water solvent mixture is most attractive, and this system has been well explored by many researchers [12–36] with different detailed experimental studies, in order to understand hydrogen bonding interactions and correlation lengths between unlike molecules involved in cluster formation.

Generally, the viscosity deviations have positive values for systems where charge-transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules. Many empirical and semi-empirical equations have been developed to describe the viscosity of binary liquid mixtures and their deviations from ideal mixing. Correlating the viscosity with these equations requires several adjustable parameters. In this work, viscosity deviations were fitted to the Redlich-Kister (R-K) and Herráez equations [37–39] and are interpreted in terms of molecular interactions and structural effects. The viscosity data for 1,4-dioxane + water mixtures was used to test the applicability of these two correlating equations. In addition to the viscosity deviation and the reduced R-K equation, we have also introduced their corresponding relative functions to reduce the effect of temperature and to reveal the effect of different types of interactions. Comparison between the two models at different temperatures and the effect of using different numbers of parameters will be discussed. Note that similar comparisons were made in previous papers [10, 40] for isobutyric acid + water mixtures both near to, and far away from, the critical temperatures. In these works [10, 40] we found that, at infinite dilution, values of the Herráez exponential function surprisingly converge to a single point (0.5) that is independent of temperature. Hence, in the present work, and according to a proposed expansion equivalent to the Debye-Hückel and Jones-Dole expressions [41–45], the recently proposed Herráez equation is improved by fixing the first constant of the corresponding exponential function to be equal to the value of 0.5.

2 Experimental Details

This is a summary of the experimental details of our earlier experiments whose results are being analyzed here. Densities of the pure components and their compositions were measured with a vibrating-tube densitometer (Anton Paar model DMA 5000), and were reproducible to 10^{-2} kg·m^{-3} with a 0.005 K temperature accuracy over a wide temperature range. The densitometer was calibrated with deionized and triple distilled water with a specific conductivity $< 10^{-4}$ S·m^{-1}. The measured densities are close to literature values [35, 36, 46–50]. The systems were prepared by mixing known masses of pure liquids in air tight vessels, with care being taken to minimize exposure to air (especially carbon dioxide). All measurements of mass were performed on an electronic balance accurate to 10^{-7} kg.

The viscosimeter was calibrated separately with fluids of known density and viscosity (high performance liquid chromatography grade), giving results that are close to the literature values [35, 36, 49, 51–55]. The reproducibility of viscosity measurements was 5×10^{-8} Pa·s. 1,4-Dioxane (Merck, ultra pure for analysis) was distilled under reduced pressure. The methods and techniques have been described in detail in our earlier papers [6–10].

3 Viscosity Results

At least 13 density and viscosity measurements were performed (with repetition) for the binary system, covering the entire mole fraction range. Dynamic viscosities η (Pa·s) of (D + W) mixtures at different compositions and temperatures were calculated from the density (ρ) and the kinematic viscosities (ν), both previously reported, from 293.15 to 313.15 K [6, 7], or taken from the literature at 323.15 K [12]. The viscosity deviation was calculated by Eq. 1:

$$\Delta\eta = \eta - (x_1\eta_1 + (1 - x_1)\eta_2) \tag{1}$$

where η, η_1 and η_2 are the viscosity of the mixture, pure dioxane (1) and of pure water (2), respectively, and x_1 is the mole fraction of dioxane. In Fig. 1, the viscosity deviation $\Delta\eta$ is plotted against the dioxane mole fraction x_1 at different temperatures.

For this system, the observed negative values of the excess volumes [1–4, 7, 23–25] are an indication of strong heteromolecular interactions in the liquid mixtures and, according to Fort et al. [56], this can be attributed to specific interactions between water and dioxane molecules as studied in some recent structural investigations [1, 2, 15–22], and to non-specific interactions (such as dipole-dipole and dipole-induced-dipole) that depend on temperature [56, 57]. On the other hand, 1,4-dioxane and water both have a proton acceptor group. Hence, there will be a significant degree of H-bonding leading to a strong intermolecular correlation. Moreover, the difference in size of the molecules can also play a role in this aspect [23–26]. Physico-chemical and thermodynamic properties of binary mixtures of dioxane with water have also been studied [2, 5–7, 12, 26–34].

Fig. 1 Viscosity deviation ($\Delta\eta$) in 10^{-3} Pa·s, for dioxane(1) + water(2) mixtures versus the mole fraction x_1 of dioxane at the temperatures: (●) 293.15 K; (○) 303.15 K; (▲) 313.15 K [6]; and (△) 323.15 K [12]

Fig. 2 Experimental relative
deviation of viscosity $\Delta\eta/\eta$ for
dioxane + water mixtures versus
the mole fraction x_1 of dioxane at
the temperatures: (●) 293.15 K;
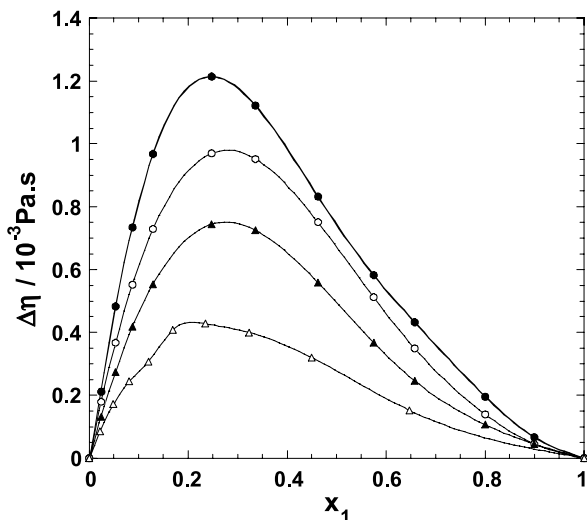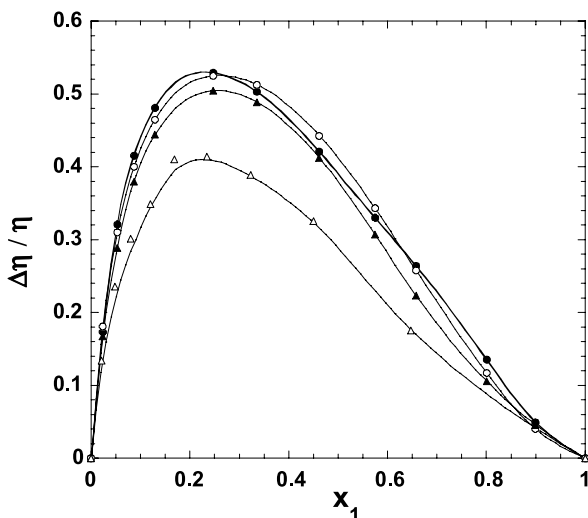(○) 303.15 K; (▲) 313.15 K [6];
and (△) 323.15 K [12]

The experimental viscosity deviations $\Delta\eta$ are positive over the whole range of composi-
tions as shown in Fig. 1. The values of $\Delta\eta$ are very large and exceed 50% at 293.15 K. For
the whole studied temperature range, the maximum in $\Delta\eta$ occurs at approximate dioxane
mole fractions between 0.23 and 0.30. The large positive $\Delta\eta$ values can be interpreted qual-
itatively by considering the strength of intermolecular hydrogen bounding, molecular size
and shape of the components. Also, the values indicate stabilization of the cluster structure
[1, 15–17, 58, 59]. In fact, below this range ($0.23 < x_1 < 0.30$) we must also consider the
appreciable modification of the liquid structure at dioxane mole fractions > 0.08 (30% by
weight) [1, 16, 23, 60, 61]. We note that inspection of the relative viscosity deviations $\Delta\eta/\eta$
in Fig. 2 shows that the effect of temperature on the ordinate of the maximum is minimized
or very reduced. We can improve upon the preceding conclusion: values of $\Delta\eta$ are very large
and exceed 50% for all temperatures in the studied range. Also, the mole fraction where the
$\Delta\eta/\eta$ maximum occurs doesn't change outsider of the range $0.23 < x_1 < 0.30$ and becomes
almost fixed at $x_1 \approx 0.23$.

4 Empirical Equations

The viscosity deviation values $\Delta\eta$ were correlated with the mole fraction using two proce-
dures. First, the Redlich-Kister [38] expression (Eqs. 4 and 6, described below) was fitted
with least-squares polynomials. Secondly, the recently proposed Herráez [37] correlation
equation that uses an exponent polynomial (Eqs. 12 and 13, described below), which is a
function of the mole fraction x_1 of 1,4-dioxane, was fitted at the four different temperatures.
Note that for all techniques, the goodness of fit is discussed as a function of the number of
the adjustable parameters for different temperatures.

4.1 Redlich-Kister Equation

For the 1,4-dioxane + water mixtures, the viscosity deviations were correlated by the
Redlich-Kister [38] equation (Eq. 2) and thus the function $\Delta\eta/(x_1(1 - x_1))$ was fitted to

a polynomial with $(2x_1 - 1)$ as a variable (Eqs. 2, 3 and 4),

$$\Delta \eta = x_1(1 - x_1) \sum_{p=0}^{p=n} A_{n,p,T}(2x_1 - 1)^p \tag{2}$$

where x_1 is the mole fraction of 1,4-dioxane, n is the polynomial order and the $A_{n,p,T}$ are adjustable parameters for each degree p of monomial $(2x_1 - 1)^p$ and fixed temperature T.

We note that in previous papers [1, 2, 6, 7], for the excess molar volume V^E, the dynamic viscosity deviation $\Delta \eta$, and the excess Gibbs energy of activation ΔG^{*E} of viscous flow, more parameters ($n + 1$ in Eq. 2) were needed in order to obtain concordance with experimental data, especially for $\Delta \eta$. Therefore, it is observed that the Redlich-Kister expression does not reproduce the main features of the experimental data even when a large number of adjusted parameters are used to describe V^E, $\Delta \eta$ and ΔG^{*E} for D + W mixtures [1, 2, 6, 7, 39].

In the same context, Desnoyers et al. [39] showed that an examination of the trends of the dependence of y^E on x_1 suggested that many of these systems are similar, and the differences in interactions are mostly significant in solutions rich in component 2. Actually, even though one of the excess partial molar quantities was intentionally taken as being identical for all the systems while the other one was varied, these systems are all basically different [39]. From the treatment of excess thermodynamic quantities for liquid mixtures proposed by Desnoyers et al. [39], we can conclude that the excess quantity (y^E) gives an overall view of the origin of the nonideality in the mixtures but still can be quite misleading, especially for systems that show strong interactions at high dilution. Desnoyers et al. [39] suggested that, in agreement with the original statements of Redlich and Kister [38], it is better to use the ratio $y^E/(x_1(1 - x_1))$ for this purpose. Also, the excess thermodynamic quantities have the advantage of illustrating the sign and magnitude of their nonideality, but the reduced Redlich and Kister function $y^E/(x_1(1 - x_1)$ gives a much better handle on the origin of the nonideality. We note that the reduced Redlich-Kister excess property $y^E/(x_1(1 - x_1)$ is more sensitive than the direct excess property y^E to interactions that occur at low concentrations [2, 39]. In general, if the fitting equation requires more than four parameters, one should either suspect the presence of specific interactions or systematic errors in the data [2, 39]. We note that Redlich and Kister treated the data with a power series, putting all the weight on data near 0.5 mole fraction [39]. As Desnoyers et al. have shown, this is not always the best approach for mixtures having specific interactions such as association at low concentration.

Therefore, elimination of the factor $[x_1(1 - x_1)]$ in the reduced Redlich-Kister excess function $Q_{\exp,T}$ (Eq. 3) removes this effect and gives a specific reduced function $Q_{\exp,T}$ characterizing the viscosity or other property and also gives evidence to the existence of important interactions:

$$Q_{\exp,T}(x_1) = \Delta \eta/(x_1(1 - x_1)) \tag{3}$$

Considering Eq. 2, we can write:

$$Q_{n,T}(x_1) = \sum_{p=0}^{p=n} A_{n,p,T}(2x_1 - 1)^p \tag{4}$$

For the system studied in this work, the experimental reduced viscosity deviation $Q_{\exp,T}(x_1)$, Eq. 3, is plotted in Fig. 3 *versus* the mole fraction x_1 of dioxane.

Fig. 3 Experimental reduced Redlich-Kister excess properties $Q_{\exp,T}(x_1)$ in units of 10^{-3} Pa·s, for the ratio $\Delta\eta/(x_1(1-x_1))$ of the dynamic viscosity deviation (Eq. 3) for dioxane + water mixtures versus the mole fraction x_1 of dioxane at the temperatures: (●) 293.15 K; (○) 303.15 K; (▲) 313.15 K [6]; and (△) 323.15 K [12]
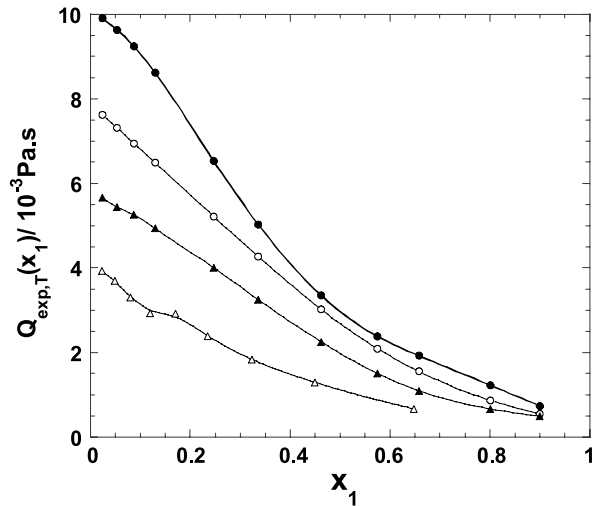
Changes in curvature (Fig. 3) were found for the reduced viscosity deviation $Q_{\exp,T}(x_1)$. We give explanations for these anomalies, as follows:

(a) In the very dilute region, the change of curvature can be associated with a thermodynamic hydration equilibrium. In fact, in the highly dilute region (Fig. 3), we must take into account solvation of dioxane molecules by water and cluster formation [1, 2, 15–28]. We point out that the beginning of a structural change of water is observed in this region [23]. Also, a significant degree of H-bonding occurs between water and dioxane molecules, leading to a strong intermolecular correlation, and difference in molecular size can also play an important role in this respect [23–26].

(b) Although 1,4-dioxane + water mixtures are nonelectrolyte solutions, we can adopt an expansion equivalent to the Debye-Hückel and Jones-Dole expressions [41–45] for very dilute nonelectrolyte solution where the first parameter a_1 (of Eq. 5) is related to solute-solute interaction while the second parameter a_2 is related to solute-solvent interaction. The experimental reduced Redlich-Kister excess viscosity (Eq. 3) $Q_{\exp,T}(x_1)$ must increase exponentially and diverges at infinite dilution of dioxane in water (as $x_1 \to 0$).

$$\eta = \eta_2(1 + a_1 x_1^{1/2} + a_2 x_1 + \cdots) \tag{5}$$

Considering Eqs. 1, 2 and 3, the reduced Redlich-Kister expression $Q_{\exp,T}(x_1)$, at fixed temperature, can be improved by using a limited asymptotic expansion in x_1 near zero:

$$Q_{\exp,T}(x_1) = \frac{\eta_2}{x_1^{1/2}(1-x_1)}\left[a_1 + \left(a_2 - \frac{\eta_1 - \eta_2}{\eta_2}\right)x_1^{1/2}\right] \tag{6}$$

where the function $Q_{\exp,T}(x_1)$ is defined over the open interval 0, 1[in mole fraction x_1].

From the presence of the $[x_1^{1/2}(1-x_1)]$ term in Eq. 6, we can explain the eventual divergence of $Q_T(x_1)$ at high dilution ($x_1 \approx 0$), Fig. 3, which shows that the parameter a_1 [41–44] is not negligible for some nonelectrolyte mixtures. However, we note that, in the possible case of no solute-solute interactions ($a_1 = 0$), Eq. 6 leads to a

new limiting asymptotic expansion. In this case, a rapid change at very low concentration is not observed. However, we must be mindful that a divergence of $Q_{\exp,T}(x_1)$ at very high dilution ($x_1 \to 0$) could be missed when the number of measurements is limited [39].

(c) The Redlich-Kister correlation does not consider all possible interactions that occur in the mixtures studied, especially the structure changes for water at $x_1 \approx 0.08$ and cluster formation [23–26]. We note that, at higher temperatures, there will be a competition between molecular interactions and thermal agitation. On the other hand, the absence of a divergence of the experimental reduced Redlich-Kister viscosity deviation (Fig. 3) at infinite dilution of water in dioxane ($x_1 \to 1$) gives evidence for a negligible a_1 parameter. In fact, for nonelectrolyte solutions, the absence of solute-solute interactions leads us to consider that the a_1 value is always zero. In the same context, the slight decrease of $Q_{\exp,T}(x_1)$ for very dilute water in dioxane ($x_1 \approx 1$) permits us to investigate the basic information on solute-solvent interactions (B_{21}) in the absence of the solute-solute interactions. Hence, on the basis of the extended conformal solution (ECS) theory [59, 60], the value $Q_{\exp,T}(x_1 = 1)$ is the regular viscosity term and is denoted by η_{21} [43, 44, 62, 63], and we can deduce the B_{21} coefficient for a nonelectrolyte binary solution as described by Nakagawa [43] from:

$$B_{21} = M_1[(\eta_2 - \eta_1) + \eta_{21}]/(1000\rho_1\eta_1) \tag{7}$$

where $\eta_{21} = Q_{\exp,T}(x_1 = 1)$, and the subscripts 1 and 2 denote dioxane and water, respectively. The B_{21} coefficient is divided into two parts: B_{id} based on the contribution of an ideal mixture (first term in Eq. 7), and the B_n coefficient based on the net interaction between the solute water and solvent dioxane [43].

Inspecting the effect of temperature (Fig. 3) on the reduced Redlich-Kister function $Q_{\exp,T}(x_1)$ at the limits of infinite dilution of each component, we can conclude that the large separation of curves near $x_1 \approx 0$ and their closeness near $x_1 \approx 1$ suggests that the solute-solvent parameter a_2 (Eq. 5), which is equivalent to B parameter of the Jones-Dole equation [41–45], is much larger for dioxane in water (hydrophobic hydration) than for water in dioxane. Nevertheless, like the relative deviation $\Delta\eta/\eta$ (Fig. 2), we consider the relative reduced Redlich-Kister function, $Q_{\mathrm{rel},T}(x_1) = Q_{\exp,T}(x_1)/\eta$. The plot of $Q_{\mathrm{rel},T}(x_1)$ versus mole fraction x_1 (Fig. 4) shows that the curves merge and $Q_{\mathrm{rel},T}(x_1)$ seems to depend only very slightly on temperature. We conclude that the nearness and then the larger separation of curves in Fig. 3 at the two limits of infinite dilution do not depend only on the value of the solute-solvent parameter a_2 but are also affected by temperature. We remark that differences between their Arrhenius activation energy of viscosity E_{vis} can play an important role in this effect. Note that the relative reduced Redlich-Kister function $Q_{\mathrm{rel},T}(x_1)$ is also a good tool, like the reduced Redlich-Kister function $Q_{\exp,T}(x_1)$, for interpreting different types of interactions. We should observe that in Figs. 2 and 4, the curve corresponding to 323.15 K [12] has not merged with the other overall curves (for 293.15 to 313.15 K) [6], because of differences between experimental conditions used in the two studies. We add that the $Q_{\mathrm{rel},T}(x_1)$ curves for some excess properties of isobutyric acid + water mixtures [8–11] have an extremum at the same abscissa x_1 that is independent of temperature and is equal to the critical composition ($x_c = 0.1114$ for isobutyric acid).

Simple Arrhenius viscosity behavior is observed when the shear viscosity of the fluid system obeys the following equation:

$$\eta = A_S(x_1)e^{\frac{E_{\mathrm{vis}}(x_1)}{RT}} \tag{8}$$

Fig. 4 Experimental relative reduced Redlich-Kister excess properties $Q_{rel,T}(x_1)$, for the ratio $\Delta\eta/(x_1(1-x_1)\eta)$ of the dynamic viscosity deviation (Eq. 3) for dioxane + water mixtures versus the mole fraction x_1 of dioxane at the temperatures: (●) 293.15 K; (○) 303.15 K; (▲) 313.15 K [6]; and (△) 323.15 K [12]
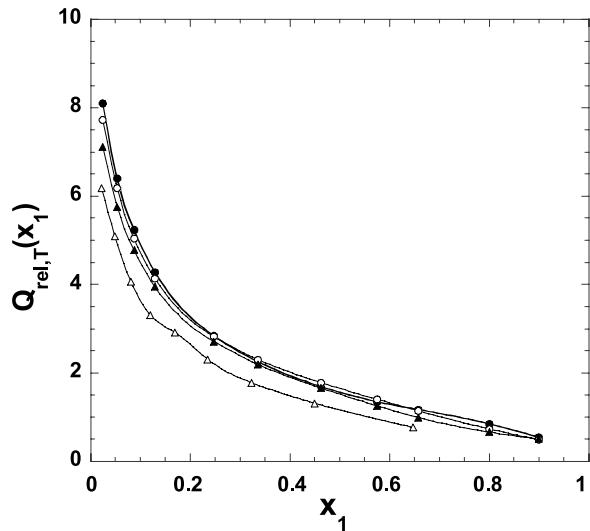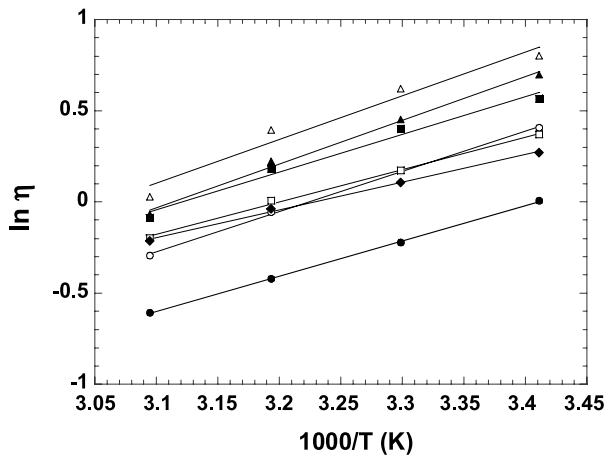

Fig. 5 Logarithm of shear viscosity $\ln(\eta)$ for the system of dioxane(1) + water(2) mixtures versus the reciprocal absolute temperature at some fixed mole fractions x_1 of dioxane: (●) $x_1 = 0.0$; (○) 0.0530; (▲) 0.1290; (△) 0.3360; (■) 0.5744; (□) 0.8005; and (◆) $x_1 = 1.0$

where R, E_{vis} and A_S are, respectively, the gas constant, the Arrhenius activation energy and the pre-exponential (entropic) factor of the Arrhenius equation for the mixture. Equation 8 can be rewritten in the logarithmic form:

$$\ln(\eta) = \ln(A_S) + \left(\frac{E_{vis}}{R}\right)\frac{1}{T} \qquad (9)$$

We can use Eq. 9 to determine the activation parameters E_{vis} and A_S ($E_{vis} = R(\frac{\partial\eta}{\partial(1/T)})_{x_1}$). However, the plot of the logarithm of shear viscosity $\ln(\eta)$ against the reciprocal of absolute temperature $(1/T)$ is practically linear (Fig. 5) and the Arrhenius parameters E_{vis} and A_S are thus independent of temperature over the studied temperature range (293.15 to 323.15 K). Using both graphical and least-squares fitting methods, the slope of the straight line is equal to E_{vis}/R and the intercept is equal to $\ln A_S$. Calculated values of E_{vis} are reported in Table 1 and are plotted against the mole fraction of dioxane in Fig. 6. In the

Table 1 Arrhenius activation energy E_{vis} and Arrhenius entropic factor A_S for {dioxane(1) + water(2)} mixtures as a function of the mole fraction of dioxane x_1 over the temperature range (293.15 to 323.15) K

x_1	E_{vis}/ kJ·mol^{-1}	$A_S/10^{-3}$ Pa·s
0	16.1	1.36
0.0240	17.0	1.17
0.0530	18.4	0.79
0.0870	19.2	0.66
0.1290	19.9	0.57
0.2470	20.4	0.55
0.3360	19.9	0.65
0.4621	18.4	1.09
0.5744	17.1	1.61
0.6578	16.9	1.63
0.8005	14.7	3.46
0.8993	13.1	6.16
1.0000	12.6	7.38

Fig. 6 Arrhenius activation energy E_{vis} of viscosity (Eqs. 8 and 9) for dioxane + water mixtures versus the mole fraction x_1 of dioxane in the temperature range (293.15 to 323.15 K)
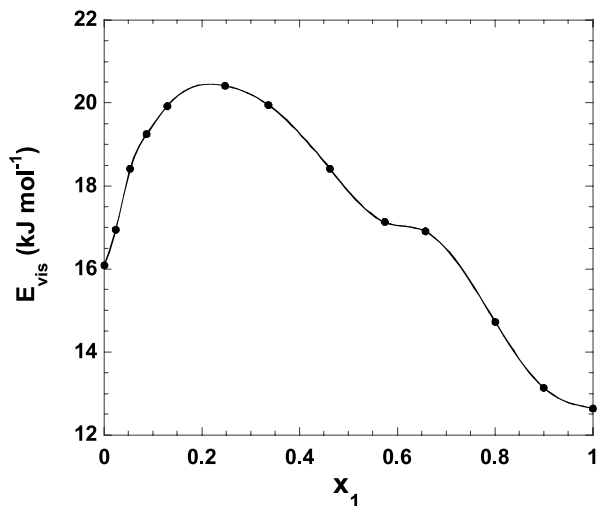
water-rich region and before reaching the composition $x_1 = 0.23$, the E_{vis} values increase with increasing mole fraction of dioxane, showing an effect on E_{vis} resulting from strong interactions between the water and dioxane molecules in the vicinity of $x_1 = 0.23$. After that, $E_{vis}(x_1)$ decreases to the $E_{vis,1}$ value of pure dioxane. This fact suggests that structural order is not destroyed much by the activation process, inasmuch as bonds are not broken between the associated molecules to form smaller units. We conclude that there are two association-type structures limited by a composition around $x_1 \approx 0.23$ (corresponding approximately to one dioxane molecule per three or four water molecules). These distinct behaviors are clearly shown when the correlation between disorder and order is plotted in Fig. 7 (enthalpy factor against the corresponding entropy one). In addition, previous studies [60, 61] on the self-diffusion of ^{153}Gd(III) in water + dioxane mixtures + Gd(NO$_3$)$_3$ (with low dielectric constants) show distinct composition regions having generally different behaviors. These domains are approximately separated by the following mole fractions: 0.2 and 0.5, i.e., cor-

Fig. 7 Correlation between the Arrhenius activation energy E_{vis} of viscosity and the logarithm of the entropic factor of Arrhenius $\ln A_S$ for dioxane + water mixtures in the temperature range (293.15 to 323.15 K)
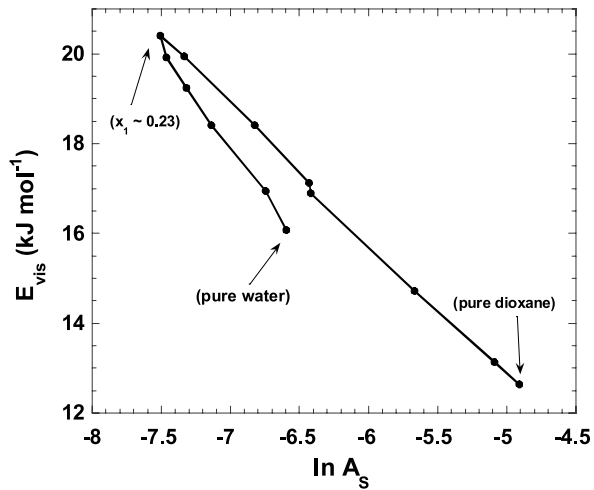
responding to ($C_4H_8O_2 \cdot 4H_2O$) and ($C_4H_8O_2 \cdot H_2O$). We note that the particular mole fraction value $x_1 = 0.23$ is not an absolute feature of dioxane + water mixture and it is affected by the studied temperature range, especially for the viscosity deviation $\Delta\eta$ that depends on the factor of $[x_1(1 - x_1)]$. Consequently, it can eventually approach a true specific composition characterizing a phenomenon such as cluster formation or structure change.

In order to evaluate the validity of the studied models, we have used 13 compositions covering the whole composition range at the four temperatures. The calculated results for different polynomial fitting orders, for each temperature, were assessed by adopting the χ^2 goodness of fit test used to optimize the fit (also called chi-square minimization). It is defined as the follows:

$$\chi^2 = \frac{1}{N-k} \sum_{i=1}^{i=N} \left(\frac{\eta_{i,\text{exp}} - \eta_{i,\text{cal}}(a_0, \ldots, a_p, \ldots, a_k)}{\sigma} \right)^2 \tag{10}$$

where N is the number of data points, k is the number of parameters a_p of the fitting equation with degree n, and σ is the standard deviation of the fits to η_i as defined in Eq. 11. Note that the fitted parameters a_p in Eq. 10 are denoted as $A_{n,p,T}$ in the Redlich-Kister equation and as $B_{n,p,T}$ in the Herráez function (Eq. 13, below), where p is the corresponding polynomial's order:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=N} (\eta_{i,\text{exp}} - \eta_{i,\text{cal}})^2}{N-k}} \tag{11}$$

The reduced Redlich-Kister polynomials $Q_{n,T}(x_1)$ were fitted with a least-squares optimization procedure to a series of monomials $(2x_1 - 1)^p$. The optimized fitted parameters $A_{n,p,T}$ (Eq. 4) for correlating the viscosity deviation $\Delta\eta$, and their corresponding chi-square minimization χ^2 values, are listed in Table 2. The data analysis was performed using the fitting programs *Kaleidagraph* 4.1 and *OriginPro* 7.5.

4.2 The Proposed Herráez Equation

In a recent work [37], Herráez et al. proposed a new empirical correlation equation for the dynamic viscosity (Eq. 12), which introduces a correcting polynomial (Eq. 13) as an

Table 2 Variation of least-squares constants $A_{n,p,T}$ of the fits to the reduced Redlich-Kister excess viscosity (Eq. 4), $Q_{n,T}(x_1)$, with temperature and the corresponding $R(\%)$ and χ^2 values for each model of degree n (n vary from 2 to 5) at (293.15, 303.15 and 313.15) K [6] and at 323.15 K [12]

T (K)	$A_{n.0}$	$A_{n.1}$	$A_{n.2}$	$A_{n.3}$	$A_{n.4}$	$A_{n.5}$	$R(\%)$	$\chi^2 \times 10^4$
$Q_{2,T}(x_1) = A_{2,0} + A_{2,1}(2x_1 - 1) + A_{2,2}(2x_1 - 1)^2$								
293.15	3.2159	−5.0535	2.4875	0	99.863	5.10		
303.15	2.7575	−3.9494	1.3514		99.961	1.00		
313.15	2.0767	−2.9652	1.0299		99.852	2.20		
323.15	1.0958	−1.7930	1.1058		99.828	1.10		
$Q_{3,T}(x_1) = A_{3,0} + A_{3,1}(2x_1 - 1) + A_{3,2}(2x_1 - 1)^2 + A_{3,3}(2x_1 - 1)^3$								
293.15	3.1710	−5.4478	2.6786	0.72529	0	99.865	5.60	
303.15	2.7190	−4.2869	1.5150	0.62093		99.993	0.200	
313.15	2.0185	−3.4755	1.2772	0.93878		99.985	0.200	
323.15	1.0788	−1.8161	1.3376	0.31967		99.834	1.30	
$Q_{4,T}(x_1) = A_{4,0} + A_{4,1}(2x_1 - 1) + A_{4,2}(2x_1 - 1)^2 + A_{4,3}(2x_1 - 1)^3 + A_{4,4}(2x_1 - 1)^4$								
293.15	2.9571	−4.8695	5.0318	−0.51506	−3.2351	0	99.976	1.10
303.15	2.6954	−4.2230	1.7751	0.48382	−0.35760		99.999	0.0340
313.15	1.9820	−3.3767	1.6790	0.72699	−0.55238		99.999	0.0256
323.15	1.11704	−1.5568	0.94953	−2.2525	−2.1789		99.846	1.40
$Q_{5,T}(x_1) = A_{5,0} + A_{5,1}(2x_1 - 1) + A_{5,2}(2x_1 - 1)^2 + A_{5,3}(2x_1 - 1)^3 + A_{5,4}(2x_1 - 1)^4 + A_{5,5}(2x_1 - 1)^5$								
293.15	2.9831	−4.6002	4.5720	−2.0471	−2.4812	1.7196	99.993	0.400
303.15	2.6895	−4.2843	1.8799	0.83276	−0.52930	−0.39165	100.00	0.0036
313.15	1.9749	−3.4510	1.8058	1.1495	−0.76030	−0.47426	99.999	0.00786
323.15	1.3180	0.68767	2.4289	−24.236	−50.196	−27.404	99.908	1.00

exponential function of the mole fraction of one component of a binary mixture.

$$\eta(x_1) = \eta_2 + (\eta_1 - \eta_2)x_1^{P_{n,T}(x_1)} \tag{12}$$

In Eq. 12, $P_{n,T}(x_1)$ is a power polynomial with order n having $(n+1)$ adjustable parameters $B_{n,p,T}$:

$$P_{n,T}(x_1) = \sum_{p=0}^{p=n} B_{n,p,T} x_1^p \tag{13}$$

We note that the viscosity deviations calculated with this equation yield satisfactory results for many studied mixtures having a monotonic variation of the viscosity with mole fraction, but yields an inferior performance when the deviations exhibit an extremum [37]. We examined this equation for water + dioxane mixtures over the whole range of mole fraction and at different fixed temperatures. This mixture shows a pronounced maximum for the viscosity that can exceed twice the values for the pure components. The data analysis was performed using the fitting program *Kaleidagraph* 4.1. The resulting $B_{n,p,T}$ values are given in Table 3. Hence, the Herráez $P_{n,T}(x_1)$ polynomials of Eq. 13 can be analyzed both experimentally and graphically (Fig. 8) using Eq. 14:

$$P_{\exp,T}(x_1) = \frac{\ln\left(\frac{\eta_{\exp,T}(x_1) - \eta_2}{\eta_1 - \eta_2}\right)}{\ln x_1} \tag{14}$$

Table 3 Variation of the $B_{n,p,T}$ constants for the Herráez exponent polynomial (Eq. 13) $P_{n,T}(x_1)$ with temperature and the corresponding $R(\%)$ and χ^2 values for each model of degree n (n varies from 2 to 5); at (293.15, 303.15 and 313.15) K [6] and at 323.15 K [12]

T (K)	$B_{n,0}$	$B_{n,1}$	$B_{n,2}$	$B_{n,3}$	$B_{n,4}$	$B_{n,5}$	$R(\%)$	χ^2
$P_{2,T}(x_1) = B_{2,0} + B_{2,1}x_1 + B_{2,2}x_1^2$								
293.15	0.13912	−6.0810	5.3587	0			99.549	0.00177
303.15	0.22035	−5.6734	4.9559				99.867	0.00034
313.15	0.28927	−5.4063	5.3584				99.920	0.00012
323.15	0.32937	−4.4599	5.1602				99.750	0.00017
$P_{3,T}(x_1) = B_{3,0} + B_{3,1}x_1 + B_{3,2}x_1^2 + B_{3,3}x_1^3$								
293.15	0.19817	−7.2062	10.316	−5.5949	0		99.832	0.00072
303.15	0.22229	−5.7086	5.1049	−0.16283			99.867	0.00038
313.15	0.29950	−5.5867	6.1081	−0.80493			99.927	0.00012
323.15	0.36496	−5.1519	8.2940	−3.6818			99.848	0.00011
$P_{4,T}(x_1) = B_{4,0} + B_{4,1}x_1 + B_{4,2}x_1^2 + B_{4,3}x_1^3 + B_{4,4}x_1^4$								
293.15	0.24938	−8.4921	18.952	−25.831	14.835	0	99.946	0.00026
303.15	0.26865	−6.8691	12.771	−17.836	12.798		99.960	0.00012
313.15	0.31671	−6.0053	8.813	−6.9134	4.3312		99.940	0.00011
323.15	0.38907	−5.8245	13.328	−16.905	10.872		99.869	0.00012
$P_{5,T}(x_1) = B_{5,0} + B_{5,1}x_1 + B_{5,2}x_1^2 + B_{5,3}x_1^3 + B_{5,4}x_1^4 + B_{5,5}x_1^5$								
293.15	0.26692	−9.0616	24.314	−45.815	45.905	−16.760	99.952	0.00026
303.15	0.30265	−7.9675	22.967	−55.280	70.294	−30.704	99.986	0.00005
313.15	0.36439	−7.5171	22.621	−56.860	79.885	−39.733	99.991	0.00002
323.15	0.35734	−4.5687	−1.0015	48.207	−113.57	82.843	99.886	0.00012

Fig. 8 The experimental Herráez exponent polynomials (Eq. 14) $P_{\exp,T}(x_1)$ for dioxane + water mixtures *versus* the mole fraction x_1 of IBA at the temperatures: (●) 293.15 K; (○) 303.15 K; (▲) 313.15 K [6]; and (△) 323.15 K [12]
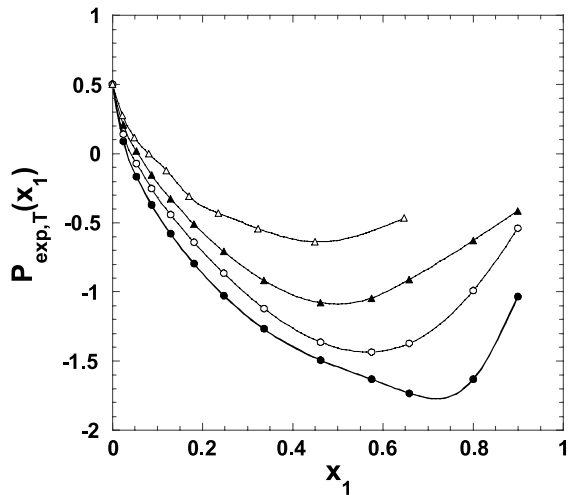
where η_1 and η_2 are the dynamic viscosities of the pure components dioxane and water, respectively, and $\eta_{\exp,T}(x_1)$ is the dynamic viscosity of dioxane + water mixtures at mole fraction x_1 and fixed temperature T.

The variation of $P_{n,T}(x_1)$ against the mole fraction x_1 of dioxane shows a monotonic decrease without any anomaly, and reaches a minimum in the very dioxane-rich region. However, at infinite dilution ($x_1 \rightarrow 0$), the $P_{\exp,T}(x_1)$ values surprisingly converge to a single point ($P_{\exp,T}(0) = 0.5$) that is independent of temperature (Fig. 8), giving a fixed value for the $B_{n,0,T}$ constant (Eq. 13). We can also ascertain this observation when we inspect the $B_{n,0,T}$ values in Table 3. In fact, the fitted $B_{n,0,T}$ constant starts from a small positive value but increases to the limit value (0.5) when both the polynomial degree n and temperature T increase (Table 3). Note that this same remark was made in previous works [10, 40] involving the dynamic viscosity and electrical conductivity of isobutyric acid + water mixtures.

Considering Eqs. 12 to 14 and the limiting expansion of Eq. 5, we can write the Herráez polynomial $P_{n,T}(x_1)$ as a limiting expansion for low concentrations of dioxane in water:

$$P_{\exp,T}(x_1) = 1/2 + \frac{\ln[\frac{\eta_2}{\eta_1-\eta_2}a_1] + \frac{a_2}{a_1}x_1^{1/2}}{\ln x_1} \qquad (15)$$

We can easily justify the limiting value of $P_{n,T}(x_1)$ at infinite dilution in water, $\lim_{x_1 \rightarrow 0^+} P_{n,T}(x_1) = 1/2$, and we conclude that the first monomial of $P_{n,T}(x_1)$ has a fixed value independent of temperature equal to 0.5 for the dynamic viscosity η (i.e., $B_{n,0,T} = 0.5$) for this type of mixture. We note that this universal exponent B_0 can take another value such as 1.0 if the parameter for solute-solute interactions a_1 is null or has a very low values.

4.3 Discussion

We note that the positive constant $A_{n,0,T}$ increases when the temperature or polynomial degree of $Q_{n,T}(x_1)$ increases. At the same time, the variations of the parameters $R(\%)$ and χ^2 cited in Table 2 show that the goodness of fit to data is improved. Hence, the variation of the reduced viscosity deviation $Q_{n,T}(x_1) = \Delta\eta/\{x_1(1-x_1)\}$ with mole fraction was used in every case to test the quality of the data; this function is extremely sensitive to experimental errors, particularly at low concentrations. Additionally, its values at infinite dilution are equivalent to partial excess physical quantities at infinite dilution ($x_1 \rightarrow 0$) [59], which can be also calculated from their fitted parameters using:

$$Q_{n,T}(x_1 = 0) = A_{n,0,T} - A_{n,1,T} + \cdots + (-1)^p A_{n,p,T} + \cdots + A_{n,n,T}$$
$$= -(\eta_1 - \eta_2) + (\partial\eta_{\exp,T}/\partial x_1)_{T,x_1=0} \qquad (16)$$

and

$$Q_{n,T}(x_1 = 1) = A_{n,0,T} + A_{n,1,T} + \cdots + A_{n,p,T} + \cdots + A_{n,n,T}$$
$$= (\eta_1 - \eta_2) - (\partial\eta_{\exp,T}/\partial x_1)_{T,x_1=1} \qquad (17)$$

Equations 16 and 17 yield the limiting values of $Q_{n,T}(x_1 = 0)$ or $Q_{n,T}(x_1 = 1)$, respectively. Inspection of the results of Table 2 proves, within a good approximation, the validity of Eqs. 16 and 17 particularly for fitting polynomials of fourth or higher degree.

Considering the derivation function of viscosity η against molar fraction x_1 at fixed temperature, in the Herráez model (Eq. 12) it is given by:

$$(\partial\eta_{\exp,T}/\partial x_1)_T = (\eta - \eta_2)[\{\partial P_{n,T}(x_1)/\partial x_1\}\ln(x_1) + P_{n,T}(x_1)/x_1] \qquad (18)$$

We can easily find a relationship between the Herráez exponent polynomial $P_{n,T}(x_1 = 1)$ and the reduced Redlich-Kister deviation of viscosity $Q_{n,T}(x_1 = 1)$ at the limit of $x_1 = 1$(pure dioxane):

$$Q_{n,T}(x_1 = 1) = (\eta_1 - \eta_2)\{1 - P_{n,T}(x_1 = 1)\} \qquad (19)$$

As shown by Eq. 18, at infinite dilution (dioxane in water or water in dioxane) the limiting Herráez exponent polynomial values are related to the limits of the viscosity derivation function as:

$$P_{n,T}(x_1 = 0) = B_{n,0,T} = x_1(\partial \eta_{\exp,T}/\partial x_1)_{T,x_1=0}/(\eta_1 - \eta_2) \qquad (20)$$

and

$$P_{n,T}(x_1 = 1) = B_{n,0,T} + B_{n,1,T} + \cdots + B_{n,p,T} + \cdots + B_{n,n,T}$$
$$= (\partial \eta_{\exp,T}/\partial x_1)_{T,x_1=1}/(\eta_1 - \eta_2) \qquad (21)$$

We note that the $(\eta_1 - \eta_2)$ term corresponds to the difference from the ideal viscosity term in Eq. 3 and we conclude that the $B_{n,p,T}$ parameters have more mathematical than physical significance.

The values of χ^2 and $R(\%)$ (Eqs. 10 and 11, Table 3) were calculated for Eqs. 4 and 13 in order to compare the results with those from Eqs. 1, 2 and 12. For many experimental data in the literature, Herráez et al. [37] showed that when the function $\eta = f(x_1)$ exhibits strictly monotonic variation, then the data can be well represented by correlation equations having only one, two or three parameters [37, 38, 64–69]. Adopting Eqs. 2 and 13 with a maximum of three parameters is a common practice, because it is unusual to use more than three parameters in common correlation equations. Nevertheless, when the function $\eta_{\exp,T} = f(x_1)$ presents a pronounced extremum, these proposed equations yield inferior performance and the correlation fails, especially for binary mixtures that show critical behavior and especially near the phase transition temperature [3, 37]. In these mixtures we must evaluate Eqs. 5 and 13 with four or more parameters. Tables 2 and 3 present the coefficients of the fits of the correlation ($A_{n,p,T}$ in Eq. 4) and ($B_{n,p,T}$ in Eq. 13), as well as and their corresponding common values of χ^2 and $R(\%)$.

We see here that for 1,4-dioxane + water mixtures, the Redlich-Kister equation (Eq. 4) with three or more parameters gives better results than the proposed Herráez (Eq. 13) equation involving the same number of parameters. This trend can reverse as the number of experimental data values used for parameter evaluations is increased.

As shown in Tables 2 and 3, the chi-square minimization value χ^2 decreases when the degree n (Eqs. 4 and 13) and the temperature increase, but it increases at low temperature showing a strong correlation between the water and dioxane molecules.

We can consider that the Herráez polynomial $P_{\exp,T}(x_1)$ as a mathematical function that is a dimensionless number, and it represents a variable effective exponent that depends on the mole fraction of the mixture. Note that this function converges at infinite dilution of component (1) in component (2) to a common value 0.5 that is independent of temperature for the investigated system.

On the other hand, the reduced Redlich-Kister function $Q_{\exp,T}(x_1)$, (Eq. 3, Fig. 3) can be considered to be a physical function that can show different phenomena or behaviors, such as the beginning of cluster formation or structural changes.

We remark that preliminary fitting and calculation show that getting concordance with experimental data doesn't require more parameters (Figs. 9 and 10). Although many experimenters reach conclusions about improvement of fitting results based only on the goodness

Fig. 9 Comparison of experimental viscosity data: (●) at 303.15 K [6] with that calculated from Redlich-Kister models (Eqs. 1, 2 and 3) for different fixed degrees n of $Q_{n,T}(x_1)$ polynomials (n varies from 2 to 5)
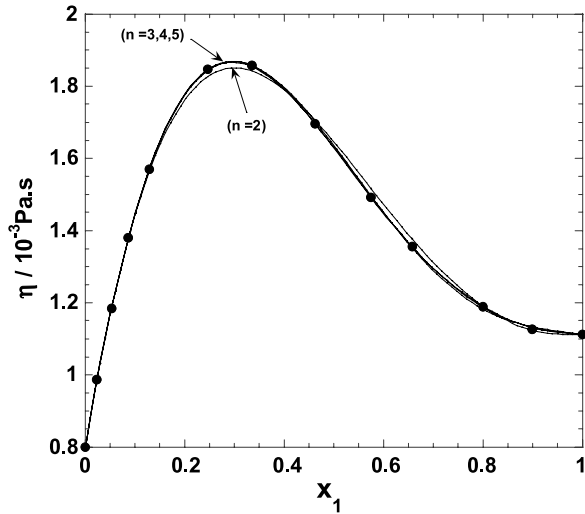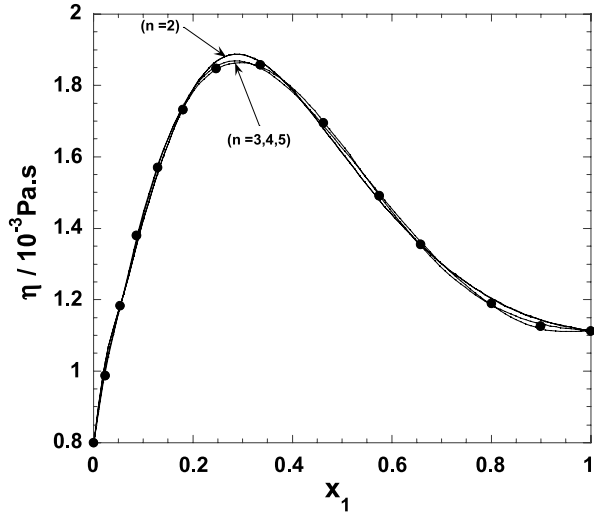

Fig. 10 Comparison of experimental viscosity data: (●) at 303.15 K [6] with that calculated from Herráez models (Eqs. 12 and 13) for different fixed degrees n of exponent polynomials $P_{n,T}(x_1)$ (n varies from 2 to 5)

of the statistical parameters, we ascertain that this feature is appreciably influenced by the number of experimental data. In fact, experimenters are frequently satisfied with calculating standard deviation without examining the agreement of calculated data with the experimental results in each zone of their investigated region, particularly for the values of the corresponding standard deviations.

5 Conclusion

In the case of viscosity data that present an extremum as a function of mole fraction, the two investigated equations show satisfactory performance using three or more parameters for their corresponding polynomials, especially at high temperatures and when there is only a small number of experimental data. The Redlich-Kister polynomial constants afford a more

physical explanation of binary mixture properties than those of the Herráez et al. equation. In fact, the reduced Redlich-Kister function is a real thermodynamic quantity equivalent to an apparent molar quantity over the whole mole fraction range. Also, at the two limits of infinite dilution, this function gives the two excess standard thermodynamic quantities of the corresponding pure components, which depend only on solute-solvent interactions.

In addition, the introduced relative viscosity deviation and relative reduced Redlich-Kister equation reduce the temperature effect and can be also be good tools, like the reduced Redlich-Kister function $Q_{\exp,T}(x_1)$, for interpreting different types of interactions.

The Redlich-Kister equation offers better results than those of the Herráez et al. equation with the same number of parameters. In opposition to the indicated literature, as well as the Redlich-Kister equation, the Herráez equation can describe distributions showing an extremum in the viscosity of the mixtures, but with increasing number of parameters and taking mathematical precautions. Nevertheless, the Herráez equation can correlate the viscosities of binary mixtures with the same number of variable parameters as the Redlich-Kister equation when the corresponding first constant B_0 is fixed at 0.5 at all studied temperatures. In the case of some nonelectrolyte mixtures, the net absence of solute-solute interactions leads to a fixed value of the Herráez constant of 1.0 or more. The Herráez equation can be also adapted and generalized for the correlation of other physical properties of binary liquid mixtures, with a fixed initial polynomial constant for each type of physical quantity or property.

The first constant value B_0 is a mathematical tool for giving information about the existence of solute-solute or ion-ion interactions at infinite dilution and for interpreting the limiting behavior of the reduced Redlich-Kister excess properties.

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