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Competition between Redlich–Kister and improved Herráez equations of correlation viscosities in 1,4-dioxane + water binary mixtures at different temperatures

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Viscosity deviation $\Delta\eta$ has been investigated by using density and kinematic viscosity measurements for dioxane + water mixtures over the entire range of mole fractions at atmospheric pressure and in five temperatures (293.15, 298.15, 302.15, 306.15 and 309.15 K). This system exhibited very large positive values of $\Delta\eta$ due to increased hydrogen bonding interactions between unlike molecules in the cluster formation region and to very large differences between the molar volumes of the pure components. The results were fitted with the Redlich–Kister equations and the recently proposed Herráez equation. This last model was improved by fixing the first constant of the corresponding exponential function. Competition between the two models at different parameter numbers is discussed. We note that, in this system, where the viscosity versus molar fraction of dioxane presents a maximum, experimental data are in agreement with the two models when more than three parameters are employed.

Keywords: viscosity correlation; empirical equation; binary liquid mixture; 1,4-dioxane; Redlich–Kister equation; Herráez equation

1. Introduction

Physical and physico-chemical properties of liquid mixtures are important for understanding the thermodynamic behaviour. Most importantly, these properties may provide information about intermolecular interactions. This article is a continuation of our earlier works that include the study of the binary liquid mixture of 1,4-dioxane + water (D-W) [1,2]. In the previous papers, we have investigated excess molar volume V^E , shear viscosity deviation $\Delta\eta$ and excess Gibbs energy of the activation of viscous flow ΔG^*E for isobutyric acid + water (IBA-W) [3–6] and 1,4-dioxane + water (D-W) [1,2] systems over the entire range of mole fractions at different temperatures. The 1,4-dioxane + water solvent mixture is the most attractive, and a great deal of work has been well explored by many researchers

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[7–31] with different detailed experimental studies to understand the hydrogen bonding interactions and correlation length between unlike molecules in the cluster formation. In the frame of scientific research on binary liquid mixtures in chemical, pharmaceutical and foodstuff industries, the study of correlation models of excess quantities, especially the viscosity, is very interesting in applied chemistry to predict physico-chemical properties in the hydraulic calculations of fluid transport, for energy transference calculations [32], and in installation's plans of equipment and accessories. Hence, among the physical properties of fluids required for designing and optimising industrial processes, mention should be made of viscosity as one of the most important factor [32]. Viscosity of 1,4-dioxane + water mixtures results have been fitted to the Redlich–Kister (R-K) polynomial equation [33–34] and the recently proposed Herráez correlation equation [32] to derive binary coefficients and estimate the standard errors between experimental and calculated results. Calculated values are used to understand the nature of molecular interactions between the mixing components. Competition between the two models at different temperatures and parameters numbers will be discussed. Note that similar comparisons were made in previous paper [5] for isobutyric acid + water mixtures near and far away from critical temperatures. In this work [5], we have discovered that, at infinite dilution, the Herráez exponential function's values converge to a surprising single point (0.5) independent of temperature. Hence, in the present work, and according to Jones–Dole expansion [35–39], the recently proposed Herráez equation is improved by fixing the first constant of the corresponding exponential function to be equal to a justified (0.5) value.

2. Experimental details

Densities of the pure components and their compositions were measured on a vibrating tube densitometer, reproducible to $10^{-2} \text{ kg m}^{-3}$ (Anton Paar model DMA 5000) measuring with (0.005°C) temperature accuracy in a wide temperature range. The densitometer was calibrated with deionised and triple distilled water; the observed density was $9970.45 \text{ kg m}^{-3}$ at 25°C , which is close to literature [40]. The mixtures were prepared by mixing known masses of pure liquids in air tight, with care being taken to minimise the exposure to air, especially carbon dioxide. All measurements of mass were performed on an electronic balance accurate to 10^{-7} kg .

The shear viscosity coefficient η (10^{-3} Pa s) of the mixture, at different compositions and temperatures, is calculated as the product (Equation (1)) of the density ρ ($10^{-3} \text{ kg m}^{-3}$) and the kinematic viscosity ν ($10^{-4} \text{ cm}^2 \text{ s}^{-1}$):

$$\eta = \rho \cdot \nu, \quad (1)$$

which was calculated from the flow time using the following equation:

$$\nu = k \cdot (t - \theta), \quad (2)$$

where t is the flow time, k is a constant for a given viscosimeter (AVS/N-Chott-Gerate) and θ is the correction time. Ubbelohde viscosimeter of relatively long flow times (60–200 s) were used to minimise the time corrections. The viscosimeter was submerged in a thermally stabilised water bath with thermal regulation of the order of 0.001 K . The time given to attain thermal equilibrium for the content of viscometer was 15 min.

The flow time was measured with an accurate stopwatch to an accuracy of 0.01 s. The viscosimeter was calibrated separately with fluids of known density and viscosity (high-performance liquid chromatography grade), which is close to literature [41–42]. The reproducibility of measurements was 5×10^{-8} Pa s. Five to seven sets of readings for the flow times were taken for each pure liquid or liquid mixture and arithmetic mean was considered for the calculations.

Dioxane (Merk, ultra pure for analysis) was distilled under reduced pressure. The density of the dioxane was found to be $1027.95 \text{ kg m}^{-3}$ at 25°C (literature values $1027.80 \text{ kg m}^{-3}$ [41] and $1027.92 \text{ kg m}^{-3}$ [43]). Deionised and triple-distilled water with specific conductance $< 10^{-4} \text{ S m}^{-1}$ was used for the preparation of various compositions.

3. Viscosity results

At least 28 density and viscosity measurements were performed (with repetition) for each binary system, in the full mole fraction range ($0 \leq x_1 \leq 1$). Dynamic (shear) viscosities η (Pa s) of (D-W) mixtures at different compositions and temperatures were calculated from the density (ρ) and the kinematic viscosities (ν). The viscosity deviation was calculated by the following equation:

$$\Delta\eta = \eta - (x_1 \cdot \eta_1 + (1 - x_1) \cdot \eta_2), \quad (3)$$

where η , η_1 and η_2 are the viscosity of the mixture and the viscosity of pure 1,4-dioxane (1) and of pure water (2), respectively, and x_1 is the mole fraction of pure 1,4-dioxane (D). The experimental values of $\Delta\eta$ are also reported in Table 1. In Figure 1, we have reported the viscosity deviation $\Delta\eta$ against the mole fraction x_1 of the 1,4-dioxane (D) at different temperatures. On the other hand, the dioxane and water both have a proton acceptor group. Thermodynamic and physico-chemical properties of binary liquid mixtures of 1,4-dioxane with water have also been studied [2,18–29]. Therefore, the negative excess volume [1,2,15–17,25,28] is an indication of strong heteromolecular interaction in the liquid mixtures, and according to Fort and Moore [44] this can be attributed to specific interactions between dioxane and water molecules investigated in some recent structural studies [1,2,7–14] and non-specific interactions (dipole–dipole, dipole–induced-dipole, dispersion interactions), which depend on temperature [44,45]. Hence, there will be a significant degree of H-bonding, leading to strong correlation between the molecules; also the difference in the size of the molecules can somewhat play a role in this respect [15–18]. We can add that there exist specific interactions.

Viscosity deviations $\Delta\eta$ were positive over the whole range of mole fractions, quasi-linearly increase with mole fraction x_1 and slightly skewed in the middle region as shown in Figure 1. The values for $\Delta\eta$ are very large and exceed 50% at 293.15 K and tend to slightly increase with temperature. For the whole range of temperatures studied, an approximately skewed plateau on $\Delta\eta$ values is observed and the maximum of $\Delta\eta$ occurs at mole fraction in dioxane between 0.15 and 0.33, approximately.

The large positive $\Delta\eta$ can be interpreted qualitatively by considering the strength of intermolecular hydrogen bonding, molecular size and shape of the components. Also, it indicates the cluster structure stabilisation [1,7–9,46,47]. In fact, before this

Table 1. Viscosities (10^{-3} Pa s) and excess viscosities (10^{-3} Pa s) for the mixtures dioxane⁽¹⁾ + water⁽²⁾ at 293.15, 298.15, 302.15, 306.15 and 309.15 K.

x_1	η (10^{-3} Pa s)	$\Delta\eta$ (10^{-3} Pa s)	x_1	η (10^{-3} Pa s)	$\Delta\eta$ (10^{-3} Pa s)
293.15 K					
0.0000	1.0030	0.000	0.3560	2.1264	1.01522
0.00206	1.0279	0.02424	0.4203	1.9956	0.86484
0.00628	1.0693	0.06439	0.4996	1.8426	0.68778
0.01516	1.1551	0.14749	0.5367	1.7756	0.60949
0.03482	1.3260	0.31242	0.5999	1.6721	0.48684
0.05303	1.4820	0.46291	0.6479	1.6002	0.40034
0.07366	1.6509	0.62551	0.7309	1.5013	0.27617
0.08413	1.7366	0.70803	0.7621	1.4690	0.23440
0.1114	1.9243	0.88746	0.7953	1.4364	0.19174
0.1433	2.0834	1.0368	0.8686	1.3800	0.11303
0.1726	2.1740	1.1185	0.9092	1.3533	0.07398
0.2065	2.2282	1.1624	0.9760	1.3172	0.01759
0.2501	2.2330	1.1540	0.9855	1.3127	0.01021
0.3029	2.2019	1.1069	1.000	1.3069	0.000
298.15 K					
0.0000	0.8904	0.000	0.3560	1.8926	0.90047
0.00206	0.9128	0.02182	0.4203	1.8004	0.78992
0.00628	0.9453	0.05310	0.4996	1.6546	0.62148
0.01516	1.0166	0.12187	0.5367	1.5974	0.55365
0.03482	1.1639	0.26360	0.5999	1.5096	0.44785
0.05303	1.2991	0.39359	0.6479	1.4513	0.37579
0.07366	1.4483	0.53687	0.7309	1.3623	0.26308
0.08413	1.5219	0.60743	0.7621	1.3333	0.22517
0.1114	1.6808	0.75858	0.7953	1.3047	0.18709
0.1433	1.8169	0.88556	0.8686	1.2499	0.11134
0.1726	1.8922	0.95249	0.9092	1.2239	0.07373
0.2065	1.9440	0.99461	0.9760	1.1870	0.01775
0.2501	1.9530	0.99113	0.9855	1.1820	0.01004
0.3029	1.9342	0.95727	1.000	1.1761	0.00000
302.15 K					
0.0000	0.8148	0.00000	0.3560	1.7045	0.78853
0.00206	0.8373	0.02191	0.4203	1.6125	0.67827
0.00628	0.8685	0.05189	0.4996	1.5055	0.54877
0.01516	0.9277	0.10854	0.5367	1.4588	0.49155
0.03482	1.0548	0.23008	0.5999	1.3853	0.40003
0.05303	1.1770	0.34714	0.6479	1.3324	0.33348
0.07366	1.3036	0.46787	0.7309	1.2558	0.23338
0.08413	1.3746	0.53594	0.7621	1.2310	0.19965
0.1114	1.5178	0.67131	0.7953	1.2066	0.16586
0.1433	1.6412	0.78569	0.8686	1.1601	0.09851
0.1726	1.7151	0.85127	0.9092	1.1382	0.06510
0.2065	1.7623	0.88884	0.9760	1.1077	0.01558
0.2501	1.7600	0.87413	0.9855	1.1038	0.00904
0.3029	1.7530	0.85215	1.000	1.0989	0.000
306.15 K					
0.0000	0.7491	0.00000	0.3560	1.5575	0.70873
0.00206	0.7690	0.01930	0.4203	1.4812	0.61439
0.00628	0.7999	0.04907	0.4996	1.3895	0.50052
0.01516	0.8554	0.10205	0.5367	1.3495	0.45014

(continued)

Table 1. Continued.

x_1	η (10^{-3} Pa s)	$\Delta\eta$ (10^{-3} Pa s)	x_1	η (10^{-3} Pa s)	$\Delta\eta$ (10^{-3} Pa s)
0.03482	0.9612	0.20230	0.5999	1.2865	0.36947
0.05303	1.0696	0.30567	0.6479	1.2396	0.30909
0.07366	1.1890	0.41926	0.7309	1.1721	0.21837
0.08413	1.2471	0.47448	0.7621	1.1500	0.18751
0.1114	1.3723	0.59200	0.7953	1.1282	0.15644
0.1433	1.4818	0.69260	0.8686	1.0863	0.09397
0.1726	1.5496	0.75217	0.9092	1.0664	0.06269
0.2065	1.5880	0.78108	0.9760	1.0383	0.01587
0.2501	1.5995	0.78036	0.9855	1.0347	0.00964
0.3029	1.5958	0.76189	1.000	1.0291	0.000
309.15 K					
0.0000	0.7045	0.000	0.3560	1.4580	0.65490
0.00206	0.7208	0.01573	0.4203	1.3911	0.57018
0.00628	0.7467	0.04049	0.4996	1.3121	0.46922
0.01516	0.7958	0.08713	0.5367	1.2728	0.41961
0.03482	0.8999	0.18574	0.5999	1.2123	0.34164
0.05303	1.0015	0.28230	0.6479	1.1719	0.28794
0.07366	1.1099	0.38497	0.7309	1.1137	0.20673
0.08413	1.1642	0.43637	0.7621	1.0937	0.17807
0.1114	1.2785	0.54316	0.7953	1.0739	0.14911
0.1433	1.3766	0.63243	0.8686	1.0356	0.09052
0.1726	1.4364	0.68406	0.9092	1.0173	0.06097
0.2065	1.4813	0.71960	0.9760	0.9913	0.01643
0.2501	1.4899	0.71611	0.9855	0.9880	0.01048
0.3029	1.4888	0.70040	1.000	0.9815	0.000

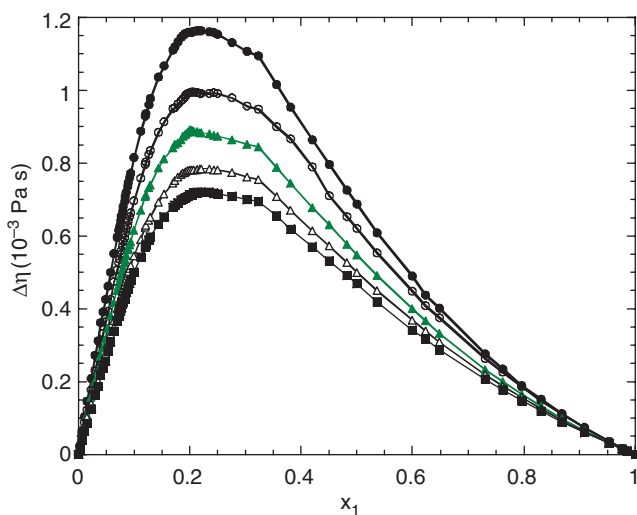


Figure 1. Viscosity deviation ($\Delta\eta$) in 10^{-3} Pa s, for the system of dioxane⁽¹⁾ + water⁽²⁾ mixtures vs. molar fraction x_1 in dioxane at the temperatures: (●): 293.15 K; (○): 298.15 K; (▲): 302.15 K; (Δ): 306.15 K; (■): 309.15 K.

range ($0.15 < x_1 < 0.33$), we must also consider the appreciable modification of liquid structure beyond 0.08 molar fraction in dioxane (30% weight) [1,8,15,48,49].

4. Empirical equations

The viscosity deviation values $\Delta\eta$ were correlated with composition using two procedures. Firstly, the R-K [33] expression (Equation (17)) is fitted in least-squares polynomial series of Legendre [50–57] polynomials (Equation (20)). Secondly, the Herráez [32] correlation equation using an exponent polynomial (Equations (21) and (22)) *versus* the mole fraction x_1 of dioxane at five different temperatures is proposed. Note that for all techniques, the goodness against the number of the adjustable parameters is discussed for different temperatures.

4.1. R-K equation

For the dioxane + water mixtures, the excess molar properties were correlated by the R-K [33] equation (Equation (4)), and fitted to a polynomial $\Delta\eta/(x_1(1-x_1))$ with $(2x_1-1)$ as a variable (Equations (4), (5) and (17)),

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

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

We note that in a previous paper [1,2], for the excess molar volume V^E , shear viscosity deviation $\Delta\eta$ and excess Gibbs energy of activation ΔG^{*E} of viscous flow, the concordance with experimental data requires more parameters ($n+1$ in Equation (4)), especially for $\Delta\eta$. Therefore, it is observed that the R-K ‘model’ does not reproduce the main features of the experimental data, even by using a high number of fitted parameters adjusted to describe V^E , $\Delta\eta$ or ΔG^{*E} for the D-W mixtures [1,2,34]. Also, for the mixtures that show a critical behaviour, the correlation fails [3–6]. This is not surprising, considering that the R-K model does not consider all the possible interactions occurring in the studied mixtures.

We can add that a comparison between excess properties y_j^{Ex} of isobutyric acid–water mixtures [3–6] and 1,4-dioxane–water mixtures [1,2] shows a strong similarity of their mutual curve’s shape (i.e. for the same physical magnitude). In fact, for the two mixtures, the excess molar volumes $V^E(y_1^{\text{Ex}})$ exhibit approximately the same minima coordinates and are not both practically affected by temperature. The same behaviour was observed for each pair of excess properties ($\Delta\eta$) or (ΔG^{*E}) for the two mixtures. We can deduce that this resemblance is due principally to the likeness of dioxane (D) and isobutyric acid (IBA) molecular weight (isomer) and close density values. Hence, this common feature leads to a like molecular size. Referring to water as a common second mixture component and which has a small molecular size, we can add that a strong specific interaction like hydrogen bonding, dipole–dipole and dipole-induced dipole interaction and cluster formation play an important role in this respect.

On the other hand, investigation of the reduced R-K excess molar properties $Q_{j,\text{exp},T}$ (Equation (5)) shows a completely different behaviour between each pair of

physical magnitudes in those two precedent mixtures. We can mention, for instance, the reduced R-K excess molar volume $Q_{1,\text{exp},T}$. Thereby, in isobutyric acid–water mixtures case [3,5], the function $Q_{1,\text{exp},T}(x_1) = V^E/(x_1(1-x_1))$ exponentially increases at lower concentration of IBA and then it varies smoothly when molar fraction x_1 in IBA increases, while in the case of 1,4-dioxane-water mixtures, $Q_{1,\text{exp},T}(x_1)$ decreases at lower concentration of dioxane and passes through a localised minimum [1,2], then it increases continuously.

In the same context, Desnoyers and Perron [34] stated that a rapid examination of the trends of the (y^{Ex}) dependence on x_1 suggests that many of these systems are similar but that the differences in interactions are mostly significant in the solution rich in component 2. Actually, even though one of the excess partial molar quantities was intentionally taken as identical for all the systems while the other one was varied, these systems are all basically different.

From the treatment of excess thermodynamic quantities for liquid mixtures exposed by Desnoyers and Perron [34], we can conclude that the excess quantity (y^{Ex}) gives an overall view of the origin of the nonideality in the mixture but can be quite misleading, especially with systems which show strong interactions at low concentrations. Desnoyers and Perron [34], suggest, in agreement with the original statements of R-K [33], that it is better to plot $y^{\text{Ex}}/(x_1(1-x_1))$ for this purpose. Also, the excess thermodynamic quantities have the advantage of illustrating the sign and magnitude of the nonideality, but $y^{\text{Ex}}/(x_1(1-x_1))$ gives a much better handle on the origin of the nonideality.

We can note that the reduced R-K excess property $y^{\text{Ex}}/(x_1(1-x_1))$ is more sensitive than (y^{Ex}) to interactions which occur at low concentrations [2,34].

In general, if the fitting equation requires more than four parameters, one should either suspect the presence of specific interactions such as association in the system, or systematic errors in the data [2,34].

In addition, the mathematical function $(x_1(1-x_1))$, as a function of molar fraction x_1 or x_2 , admits a maximum at equimolar mixture ($x_1 = x_2 = 1/2$). Hence, the factor $(x_1(1-x_1))$ is a dominant term in Equation (4) and tends to attract the abscissa of extremum of excess functions y_j^{Ex} to the middle of molar fraction interval (Figure 1). Therefore, the elimination of $(x_1(1-x_1))$ factor in the reduced R-K excess function $Q_{j,\text{exp},T}$ (Equation (5)) leads to the absence of this effect and gives a specific reduced function $Q_{j,\text{exp},T}$ characterising each property and gives evidence to the existence of an eventual phenomenon or a predominance interaction.

The experimental reduced excess viscosity $Q_{\text{exp},T}(x_1)$, Equation (5), is plotted in Figure 2 *versus* the mole fraction x_1 of (D).

$$Q_{\text{exp},T}(x_1) = \Delta\eta/(x_1(1-x_1)). \quad (5)$$

However, noteworthy changes in curvature were found for the studied shear viscosity deviation $\Delta\eta$ for dilute solutions of (D). It is not difficult to find an explanation for these anomalies:

(a) In the very dilute region, it can be associated with thermodynamic solvation equilibrium. In fact, in the high diluted region ($0 < x_1 < 0.035$, Figure 2), we must take into account the solvation of dioxane molecules by water ones and Cluster formation [1,2,7–20]. We add that the beginning of structure change of water in the region is observed [15]. Also, the significant degree of H-bonding between dioxane

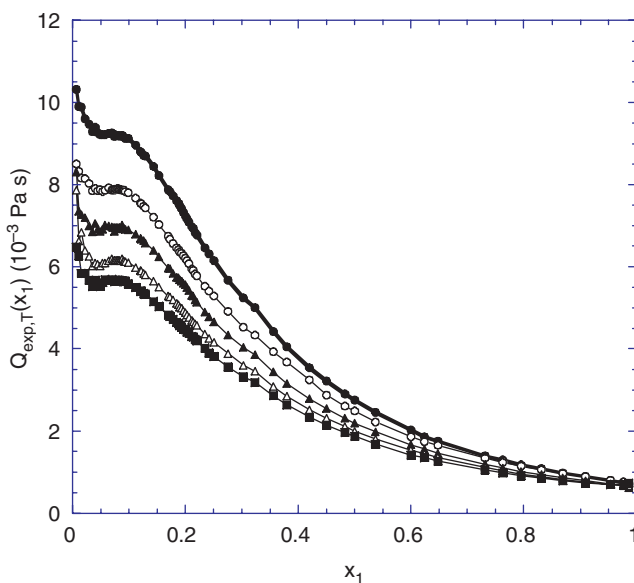


Figure 2. Experimental reduced R-K excess properties $Q_{\text{exp},T}(x_1)$ in 10^{-3} Pa s, for the ratio $\Delta\eta/(x_1(1-x_1))$ of the shear viscosity deviation (Equation (5)) for dioxane + water mixtures vs. molar fraction x_1 in dioxane at the temperatures: 293.15 K (●); 298.15 K (○); 302.15 K (▲); 306.15 K (△); 309.15 K (■).

and water molecules leads to strong correlation between the molecules; also the difference in the size of molecules can also play an important role in this respect [15–18].

(b) Moreover, if we adopt the Jones–Dole behaviour [35–37] for very dilute nonelectrolyte solution (Equation (6)), the experimental reduced R-K excess viscosity (Equation (5)) $Q_{\text{exp},T}(x_1)$ must be increased exponentially and diverges at infinite dilution ($x_1 \rightarrow 0^+$).

$$\eta = \eta_2(1 + A_{12} \cdot c_1^{1/2} + B_{12} \cdot c_1), \tag{6}$$

where c_1 represents the molarity of (D) (as a solute) in water (as a solvent) and A_{12} and B_{12} are the adjustable parameters corresponding to dioxane (1) diluted in water (2). We note that the A_{ij} coefficient arises from the ion-ion interaction, and the B_{ij} coefficient from the ion-solvent interaction [37].

Considering the molarity c_1 of dioxane in water as:

$$c_1 = x_1 \cdot \rho/M \tag{7}$$

and

$$M = M_2 \left(1 + \frac{M_1 - M_2}{M_2} \right) \cdot x_1, \tag{8}$$

where ρ is the density of mixture, M , M_1 and M_2 are the molar mass of the mixture and the molar mass of pure 1,4-dioxane (1) and of pure water (2), respectively.

Adopting the dependence of density (ρ) on molar fraction (x_1) investigated in literature [38,58] and using Equation (9), which was studied and discussed,

$$\rho(x_1) = \sum_{p=0}^{p=n} b_p(x_1)^p \quad (9)$$

we can then write at high dilution of (D) the following expansions:

$$\rho(x_1) = \rho_2(1 + b \cdot x_1) + o(x_1), \quad (10)$$

where $o(x_1)$ is the remainder of expansion, and

$$c_1 = \left(\frac{\rho_2}{M_2}\right) \cdot x_1 \cdot \left[1 + \left(b - \frac{M_2 - M_1}{M_2}\right) \cdot x_1\right] + o(x_1^2). \quad (11)$$

Consequently, the molarity c_1 in Equation (6) can be changed in molar fraction x_1 of (D) and leads to the following limited asymptotic expansion in the vicinity of zero:

$$\eta = \eta_2 \left[1 + A_{12} \cdot \left(\frac{\rho_2}{M_2}\right)^{1/2} \cdot x_1^{1/2} + B_{12} \left(\frac{\rho_2}{M_2}\right) \cdot x_1 + o(x_1)\right], \quad (12)$$

where ρ_2 and M_2 are the density and the molar mass of pure water, respectively.

Note that the viscosity (η_{id}) of ideal mixture can be expressed by Equation (13):

$$\eta_{id} = \eta_2 \left(1 + \frac{\eta_1 - \eta_2}{\eta_2}\right) \cdot x_1. \quad (13)$$

Considering Equations (3)–(5) and (13), the reduced R-K expression $Q_T(x_1)$ (at fixed temperature) can be improved in a limited asymptotic expansion in the vicinity of zero:

$$Q_{exp,T}(x_1) = \frac{\eta_2}{x_1^{1/2}(1-x_1)} \cdot \left[A_{12} \cdot \left(\frac{\rho_2}{M_2}\right)^{1/2} + \left(B_{12} \frac{\rho_2}{M_2} - \frac{\eta_1 - \eta_2}{\eta_2} \right) \cdot x_1^{1/2} + o(x_1^{1/2}) \right], \quad (14)$$

where the function $Q_T(x_1)$ is defined in the opened interval $]0,1[$ in molar fraction x_1 .

By the presence of the $x_1^{1/2}(1-x_1)$ -term in Equation (14), we can explain the divergence in Figure 2 of $Q_T(x_1)$ at high dilution ($x_1 \approx 0^+$), showing that the Falkenhagen parameter A_{12} [39] is not negligible in many nonelectrolyte mixtures. However, we can note that in the case of possible absolute absence of ion-ion interaction ($A_{12} = 0$), Equation (14) leads to Equation (15):

$$Q_{exp,T}(x_1) = \frac{\eta_2}{(1-x_1)} \cdot \left[B_{12} \left(\frac{\rho_2}{M_2}\right) - \left(\frac{\eta_1 - \eta_2}{\eta_2}\right) + C_{12} \cdot x_1^{1/2} + o(x_1^{1/2}) \right] \quad (15)$$

when C_{12} is the constant of the following order of limiting asymptotic expansion of Equation (15). In this case, the rapid change at very low concentration is not observed. However, we must be suspicious of an eventually completely missed divergence of $Q_T(x_1)$ at very high dilution ($x_1 \rightarrow 0^+$), when the number of measurements had been limited [34].

(c) The R-K correlation does not consider all possible interactions that occur in the studied mixtures, especially the structure-changing of water, at $x_1 \approx 0.08$ and

cluster formation [15–18]. In fact, around the ($x_1 \approx 0.15$) region, the interaction between (D) and (W) molecules is characterised by an increase of the viscosity and the correlation length.

We must classify this behaviour for the experimental reduced excess viscosity $Q_{\text{exp},T}(x_1)$ into two different composition regions, at $x_1 \leq 0.08$ and at very lower mole fractions, the variation of $Q_{\text{exp},T}(x_1)$ with x_1 is peculiar. The values of $Q_{\text{exp},T}(x_1)$ decrease and pass through a localised minimum, and then they pass through a localised maximum, as shown in Figure 2. This peculiar behaviour of $Q_{\text{exp},T}(x_1)$ against the mole fraction of (D) is also temperature dependent. In fact, the variation of $Q_{\text{exp},T}(x_1)$ is more pronounced at lower temperatures and the position of the localised minimum moves towards a lower mole fraction of (D) at increasing temperature and disappears around 315.15 K, which is far from eutectic temperature. We conclude that at higher temperatures, there will be a competition between molecular interactions and thermal agitation. Thermal agitation is dominant at temperatures higher than ≈ 315.15 K and *vice versa* at temperatures lower than ≈ 298.15 K. The $Q_{\text{exp},T}(x_1)$ curves in Figure 2 exhibit a weak increase when (D) is added to water, the maximum occurs at the eutectic composition ($x_c \approx 0.1429$) when temperature decreases. For higher concentrations of (D), $Q_{\text{exp},T}(x_1)$ decreases continuously but without having an extremum. This behaviour was observed at all of the studied temperatures. On the other hand, the absence of divergence of the experimental reduced R-K excess viscosity (Figure 2) at infinite dilution of water in (D) ($x_1 \rightarrow 1^-$) gives evidence for the negligible value of the A_{ij} coefficient. In fact, for nonelectrolyte solution, the absence of the ion–ion interaction leads to considering that the A_{ij} value is always zero. In the same context, the quasi-constancy of $Q_{\text{exp},T}(x_1)$ at very dilute range of water in (D) ($x_1 \approx 1$) permits to investigate the basic information on the solute solvent interaction (B_{21}) in the absence of the ion–ion interaction. Hence, in the basis of the extended conformal solution (ECS) theory [59,60], the $Q_{\text{exp},T}(x_1=1)$ is the regular viscosity term and denoted by η_{21} [37,38,59,60] and we can deduce the B_{21} coefficient for a nonelectrolyte binary solution given by Nakagawa [37] as:

$$B_{21} = M_1 \cdot [(\eta_2 - \eta_1) + \eta_{21}]/(1000\rho_1\eta_1) \quad (16)$$

where $\eta_{21} = Q_{\text{exp},T}(x_1=1)$, the subscript (1) and (2) denote (D) and water, respectively. The B_{21} coefficient is divided into two parts: B_{id} based on the contribution of ideal mixture (term in parenthesis in Equation (16)), and the B_n coefficient based on the net interaction between solute (W) and solvent (D) [37].

Finally, from an analysis of the results, it is clear that the strong interactions and correlations between dioxane and water molecules in rich range of (W) are reflected in the reduced excess functions. It is obvious that the structure of water is very much affected by dioxane [15] and this phenomenon is more pronounced around the eutectic composition in a larger temperature range.

4.1.1. R-K polynomials

The R-K regressor is very powerful and frequently used to correlate vapour–liquid equilibrium data and excess properties. Nevertheless, it suffers from the important drawback that the values of the adjustable parameters $A_{n,p,T}$ change (Tables 2 and 3)

as the number of terms $(n + 1)$ in the series is increased, so that no physical interpretation can be attached to them [54–57].

$$Q_{n,T}(x_1)\mathfrak{S} = \sum_{p=0}^{p=n} A_{n,p,T}(2x_1 - 1)^p. \quad (17)$$

In order to evaluate the validity of the studied models, we have used 28 compositions in the whole range at five temperatures. The calculated results at different polynomial orders for each temperature are assessed adopting as a comparator element the χ^2 goodness-of-fit test used to optimise the fit, also called χ^2 minimisation and it is defined as the follows:

$$\chi^2 = \frac{1}{N - k} \cdot \sum_{i=1}^{i=N} \left(\frac{\eta_{i,\text{exp}} - \eta_{i,\text{cal}}(a_0, \dots, a_p, \dots, a_k)}{\sigma} \right)^2, \quad (18)$$

where $(N - k)$ is the number of degrees of freedom, N is the number of data points of the sample, k is the number of free parameters a_p of the fitting equation with n degree ($n = k + 1$) and σ is the standard deviation of η_i as defined in Equation (19).

Note that the fitted parameters a_p in Equation (18) are $A_{n,p,T}$ in R-K equation, $a_{n,p,T}$ in Legendre polynomial and $B_{n,p,T}$ in Herráez function, where p is the corresponding polynomial's order ($0 \leq p \leq k$).

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=N} (\eta_{i,\text{exp}} - \eta_{i,\text{cal}})^2}{N - k}} \quad (19)$$

where N is the number of points of the sample and k is the number of free parameters of the fitting equation ($n = k + 1$). The optimal parameters $A_{n,p,T}$ (Equation (17)) in correlating the viscosity deviation $\Delta\eta$ and corresponding chi-square minimisation χ^2 are listed in Table 2.

The reduced R-K polynomials $Q_{n,T}(x_1)$ were fitted with least-squares optimisation procedure in a series of monomials $(2x_1 - 1)^p$. The data analysis was performed using a fitting program *OriginPro 7.5* or *Kaleidagraph 4.1*.

We note that the positive constants $A_{n,0,T}$ decrease when temperature (T) or degree (n) of $Q_{n,T}(x_1)$ polynomial increases. In the same time, the variation of statistical parameters $R(\%)$ and χ^2 sited in Table 2 show that the goodness of the quality of data is improved.

4.1.2. Legendre polynomials

The Legendre polynomials can also be generated using Gram–Schmidt orthonormalisation in the open interval $]-1, 1[$ with the weighting function 1 (unit function) [50]. The Legendre polynomials are a basis for the set of polynomials, appropriate for use on the interval $]-1, 1[$. The first five Legendre polynomials $L_p(X)$ are listed in Table 3 when variable X is equal to $2x_1 - 1$.

The reducer R-K polynomials $Q_{n,T}(x_1)$ were fitted with least-squares optimisation procedure in a series of Legendre polynomials $L_p(2x_1 - 1)$ using a MATLAB 5.3 Software and Fortran Program:

$$Q_{n,T}(x_1) = \sum_{p=0}^{p=n} a_{n,p,T} L_p(2x_1 - 1). \quad (20)$$

Table 2. Variation of least-squares constants $A_{n,p,T}$ of the fits for the reduced R-K excess viscosity (Equation (17)) $Q_{n,T}(x_1)$ with temperature and the corresponding $R(\%)$ and χ^2 for each model of n degree (n varies from 1 to 5).

T (K)	$A_{n,0}$	$A_{n,1}$	$A_{n,2}$	$A_{n,3}$	$A_{n,4}$	$A_{n,5}$	R (%)	χ^2
$Q_{1,T}(x_1) = A_{1,0} + A_{1,1}(2x_1 - 1)$								
293.15	4.2538	-5.3333					96.215	1.093
298.15	3.7179	-4.4656					95.968	0.819
302.15	3.3380	-4.0878		0			94.399	0.978
306.15	3.0185	-3.6261					94.184	0.802
309.15	2.7421	-3.1452					95.577	0.449
$Q_{2,T}(x_1) = A_{2,0} + A_{2,1}(2x_1 - 1) + A_{2,2}(2x_1 - 1)^2$								
293.15	2.9597	-4.9474	2.8611				99.526	0.145
298.15	2.6579	-4.1496	2.3435				99.130	0.187
302.15	2.2683	-3.7689	2.3651		0		98.166	0.341
306.15	2.0239	-3.3295	2.1988				98.306	0.249
309.15	1.9516	-2.9095	1.7477				99.101	0.0968
$Q_{3,T}(x_1) = A_{3,0} + A_{3,1}(2x_1 - 1) + A_{3,2}(2x_1 - 1)^2 + A_{3,3}(2x_1 - 1)^3$								
293.15	2.9576	-5.0016	2.8683	0.07728			99.526	0.152
298.15	2.6578	-4.1516	2.3437	0.00292			99.130	0.196
302.15	2.2840	-3.3621	2.3111	-0.5803		0	98.226	0.344
306.15	2.0435	-2.8217	2.1314	-0.7243			98.424	0.242
309.15	1.9530	-2.8727	1.7428	-0.05247			99.102	0.101
$Q_{4,T}(x_1) = A_{4,0} + A_{4,1}(2x_1 - 1) + A_{4,2}(2x_1 - 1)^2 + A_{4,3}(2x_1 - 1)^3 + A_{4,4}(2x_1 - 1)^4$								
293.15	2.7829	-4.8906	4.2631	-0.08496	-1.4397		99.582	0.140
298.15	2.5345	-4.0733	3.3280	-0.1116	-1.0160		99.170	0.196
302.15	2.3070	-3.3768	2.1271	-0.5588	0.1899	0	98.228	0.361
306.15	2.1257	-2.8740	1.4748	-0.6479	0.6778		98.449	0.250
309.15	1.9096	-2.8451	2.0897	-0.09282	-0.3581		99.112	0.105
$Q_{5,T}(x_1) = A_{5,0} + A_{5,1}(2x_1 - 1) + A_{5,2}(2x_1 - 1)^2 + A_{5,3}(2x_1 - 1)^3 + A_{5,4}(2x_1 - 1)^4 + A_{5,5}(2x_1 - 1)^5$								
293.15	2.7784	-5.0386	4.3224	0.52546	-1.5055	-0.5018	99.583	0.147
298.15	2.5273	-4.3123	3.4237	0.87414	-1.1221	-0.8103	99.176	0.204
302.15	2.2801	-4.2597	2.4807	3.08184	-0.2022	-2.9929	98.320	0.359
306.15	2.0969	-3.8223	1.8545	3.26241	0.2566	-3.2146	98.583	0.240
309.15	1.9020	-3.0929	2.1890	0.92895	-0.4681	-0.8400	99.125	0.109

Table 3. R-K expression given by Equation (17) and Legendre polynomials given by Equation (20) as a function of polynomial order p .

Polynomial order, p	R-K, $(2x_1 - 1)^p$, Equation (17)	Legendre polynomial, $L_p(2x_1 - 1)$, Equation (20)
0	1	1
1	$2x_1 - 1$	$2x_1 - 1$
2	$4(x_1^2 - x_1 + 1/4)$	$6(x_1^2 - x_1 + 1/6)$
3	$8(x_1^3 - 3/2x_1^2 + 3/4x_1 - 1/8)$	$20(x_1^3 - 3/2x_1^2 + 3/5x_1 - 1/20)$
4	$16(x_1^4 - 2x_1^3 + 9/6 x_1^2 - 1/2x_1 + 1/16)$	$70(x_1^4 - 2x_1^3 + 9/7x_1^2 - 2/7x_1 + 1/70)$
5	$32(x_1^5 - 5/2x_1^4 + 20/8x_1^3 - 5/4x_1^2 + 5/16x_1 - 1/32)$	$252(x_1^5 - 5/2x_1^4 + 20/9x_1^3 - 5/6x_1^2 + 5/42x_1 - 1/252)$

Table 4. Variation of Legendre polynomial constants $a_{n,p,T}$ for the reduced R-K excess viscosity (Equation (20)) $Q_{n,T}(x_1)$ with temperature and the corresponding $R(\%)$ and χ^2 for each model of n degree (n varies from 1 to 5).

T (K)	$a_{n,0}$	$a_{n,1}$	$a_{n,2}$	$a_{n,3}$	$a_{n,4}$	$a_{n,5}$	R (%)	χ^2
$Q_{1,T}(x_1) = a_{1,0}L_0 + a_{1,1}L_1$								
293.15	4.2538	-5.3333					96.215	1.093
298.15	3.7179	-4.4656					95.968	0.819
302.15	3.3380	-4.0878		0			94.399	0.978
306.15	3.0185	-3.6261					94.184	0.802
309.15	2.7421	-3.1452					95.577	0.449
$Q_{2,T}(x_1) = a_{2,0}L_0 + a_{2,1}L_1 + a_{2,2}L_2$								
293.15	5.8208	-4.9475	5.7222				99.526	0.145
298.15	5.0014	-4.1496	4.6870				99.130	0.187
302.15	4.6333	-3.7689	4.7301		0		98.166	0.341
306.15	4.2227	-3.3296	4.3977				98.306	0.249
309.15	3.6993	-2.9095	3.4955				99.101	0.0968
$Q_{3,T}(x_1) = a_{3,0}L_0 + a_{3,1}L_1 + a_{3,2}L_2 + a_{3,3}L_3$								
293.15	3.9137	-4.9552	1.9122	0.03091			99.526	0.152
298.15	3.4390	-4.1499	1.5625	0.00117			99.126	0.196
302.15	3.0543	-3.7102	1.5407	-0.2320		0	98.224	0.344
306.15	2.7539	-3.2562	1.4209	-0.2897			98.424	0.242
309.15	2.5339	-2.9041	1.1619	-0.0209			99.102	0.101
$Q_{4,T}(x_1) = a_{4,0}L_0 + a_{4,1}L_1 + a_{4,2}L_2 + a_{4,3}L_3 + a_{4,4}L_4$								
293.15	3.9159	-4.9416	2.0194	-0.03398	-0.3291		99.582	0.140
298.15	3.4407	-4.1402	1.6381	-0.0446	-0.2322		44.275	0.196
302.15	3.0540	-3.7120	1.5266	-0.2235	0.04340	0	98.228	0.361
306.15	2.7529	-3.2627	1.3705	-0.2592	0.1549		98.449	0.250
309.15	2.5345	-2.9008	1.1886	-0.0371	-0.08185		99.112	0.105
$Q_{5,T}(x_1) = a_{5,0}L_0 + a_{5,1}L_1 + a_{5,2}L_2 + a_{5,3}L_3 + a_{5,4}L_4 + a_{5,5}L_5$								
293.15	3.9181	-4.9384	2.0213	-0.01284	-0.3441	-0.06370	99.583	0.147
298.15	3.4441	-4.1351	1.6413	-0.01049	-0.25648	-0.1029	99.176	0.204
302.15	3.0666	-3.6932	1.5382	-0.09743	-0.04622	-0.3800	98.320	0.359
306.15	2.7664	-3.2426	1.3830	-0.12375	0.05866	-0.4082	98.583	0.240
309.15	2.5380	-2.8955	1.1918	-0.00174	-0.1070	-0.1066	99.125	0.109

As mentioned by Peralta and coworkers [54–57], Legendre polynomials belong to the category of orthogonal functions such as Fourier, Bessel, Hermite and Chebyshev, which have the valuable feature that for a continuous series of observations the values of the coefficients do not change appreciably as the number of terms in the series is increased (Tables 3 and 4). This is an important property because if a physical explanation can be assigned to one of its coefficients, its value remains practically constant. For the case of discrete measurements, such as the determination of volumes of mixing and viscosities of mixtures, the values of the coefficients will vary, but slightly [54–57]. In addition, as shown in Table 3, the series of Legendre polynomials have the important characteristic that the structure of its first five terms is practically the same as that of the first five terms of the R-K expression. The mathematical procedure to transform a power series expansion, such as that of R-K,

into an orthogonal series has been described in detail by Tomiska [51,52]. Tomiska provides the iteration formulas for Legendre or Chebyshev's series of any order as well as the proof that the procedure is independent of the conversion coefficients from the actual excess property [54–57].

We note that the statistical parameters $R(\%)$ and χ^2 have the same values in Tables 2 and 4 for each fixed temperature (T) and polynomial degree (n) corresponding to R-K or Legendre. This can be explain by the closely dependence on the maximal monomial's order (p) used in the fit (Table 3).

4.2. Herráez equation

4.2.1. The proposed Herráez equation

In a recent paper [32], Herráez et al. propose a new empirical correlation equation (Equation (21)) which introduces a correcting polynomial (Equation (22)) as an exponential-acting upon the molar fraction of one of mixture components. We note that the viscosity excesses calculated with this model generally yield satisfactory results for many studied mixtures showing monotonous variation in viscosity values with molar fraction, but records deficient performance when distribution exhibits a maximum or minimum [32].

$$\eta(x_1) = \eta_2 + (\eta_1 - \eta_2) \cdot x_1^{P_{n,T}(x_1)}, \quad (21)$$

where $P_{n,T}(x_1)$ is a power polynomial with order (n) and ($n+1$) adjustable parameters $B_{n,p,T}$:

$$P_{n,T}(x_1) = \sum_{p=0}^{p=n} B_{n,p,T} \cdot x_1^p. \quad (22)$$

Nevertheless, out of curiosity we have examined this model in water–dioxane mixture in the whole range of composition (x_1) and at different temperatures (T). Note that this mixture shows a pronounced maximum of viscosity around the composition ($x_1 \approx 0.28$) which can exceed two times the value of those of pure components. The exponential values $B_{n,p,T}$ and constants of $P_{n,T}(x_1)$ polynomials (Equation (22)) calculated from Equation (23) were fitted with least-squares optimisation procedure in a series of monomials x_1^p in n^{th} -degree polynomials. The data analysis was performed using the fitting program *Kaleidagraph* 4.1. Results of $B_{n,p,T}$ are given in Table 5 and depicted. Hence, the Herráez $P_{n,T}(x_1)$ polynomials of Equation (22) can be inspected experimentally and graphically (Figure 3) using Equation (23):

$$P_{\text{exp},T}(x_1) = \frac{\ln\left(\frac{\eta_{\text{exp},T}(x_1) - \eta_2}{\eta_1 - \eta_2}\right)}{\ln x_1} \quad (23)$$

where η_1 and η_2 are the dynamic viscosity of pure components D and W, respectively, and $\eta_{\text{exp},T}(x_1)$ the dynamic viscosity of (D–W) mixtures at molar fraction x_1 in D and temperature T for $x_1 \in]0,1[$.

The variation of $P_{n,T}(x_1)$ versus molar fraction x_1 of (D) shows a monotonous decrease without any anomaly and occur to a minimum in very rich region in dioxane. However, at infinite dilution ($x_1 \rightarrow 0^+$), the $P_{\text{exp},T}(x_1)$ values converge to a surprising single point ($P_{\text{exp},T}(0) = 0.5$) independent of temperature (Figure 3)

Table 5. Variation of $B_{n,p,T}$ constants for the Herráez exponent polynomial (Equation (22)) $P_{n,T}(x_1)$ with temperature and the corresponding $R(\%)$ and χ^2 for each model of n degree (n varies from 1 to 5).

T (K)	$B_{n,0}$	$B_{n,1}$	$B_{n,2}$	$B_{n,3}$	$B_{n,4}$	$B_{n,5}$	R (%)	χ^2
$P_{1,T}(x_1) = B_{1,0} + B_{1,1}x_1$								
293.15	-0.18485 < 0	-1.7557					85.253	0.1405
298.15	-0.12126 < 0	-1.9206					89.616	0.1097
302.15	-0.10815 < 0	-1.6535		0			86.533	0.1112
306.15	-0.06608 < 0	-1.6249					87.936	0.0939
309.15	-0.03343 < 0	-1.5882					88.271	0.0867
$P_{2,T}(x_1) = B_{2,0} + B_{2,1}x_1 + B_{2,2}x_1^2$								
293.15	0.20655	-5.5755	4.1552				98.718	0.01365
298.15	0.21946	-5.2458	3.6172				98.813	0.01369
302.15	0.23842	-5.0358	3.6793		0		98.709	0.01183
306.15	0.24923	-4.7021	3.3474				98.636	0.01169
309.15	0.26629	-4.5133	3.1819				98.461	0.01249
$P_{3,T}(x_1) = B_{3,0} + B_{3,1}x_1 + B_{3,2}x_1^2 + B_{3,3}x_1^3$								
293.15	0.30323	-7.5382	9.6834	-3.8428			99.442	0.00622
298.15	0.32009	-7.2887	9.3712	-3.9998			99.537	0.00559
302.15	0.33094	-6.9140	8.9696	-3.6775		0	99.480	0.00499
306.15	0.34695	-6.6861	8.9355	-3.8844			99.556	0.00399
309.15	0.36858	-6.5898	9.0306	-4.0655			99.524	0.00405
$P_{4,T}(x_1) = B_{4,0} + B_{4,1}x_1 + B_{4,2}x_1^2 + B_{4,3}x_1^3 + B_{4,4}x_1^4$								
293.15	0.3696	-9.9174	22.493	-25.360	11.1548		99.820	0.00210
298.15	0.3842	-9.5865	21.743	-24.780	10.7730		99.862	0.00174
302.15	0.3936	-9.1596	21.060	-23.986	10.5284	0	99.871	0.00130
306.15	0.40168	-8.6476	19.496	-21.623	9.1962		99.874	0.00118
309.15	0.42497	-8.6110	19.913	-22.345	9.4763		99.881	0.00106
$P_{5,T}(x_1) = B_{5,0} + B_{5,1}x_1 + B_{5,2}x_1^2 + B_{5,3}x_1^3 + B_{5,4}x_1^4 + B_{5,5}x_1^5$								
293.15	0.39287	-11.268	34.254	-60.112	52.494	-17.075	99.871	0.00157
298.15	0.40502	-10.795	32.266	-55.876	47.763	-15.279	99.900	0.00132
302.15	0.41278	-10.274	30.760	-52.647	44.622	-14.083	99.911	0.00094
306.15	0.42138	-9.7913	29.455	-51.050	44.201	-14.459	99.920	0.00079
309.15	0.44113	-9.5493	28.083	-46.485	38.192	-11.861	99.913	0.00081

showing a fixed value of $B_{n,0,T}$ constant corresponding to the first monomial of $P_{n,T}(x_1)$ (Equation (22)). We can ascertain this discovery when we inspect the $B_{n,0,T}$ constant values in Table 5. In fact, except for anomalous negative values in first-degree polynomials, the fitted $B_{n,0,T}$ constant values start from a small positive value for increasing to the limit value (0.5) when degree (n) of polynomial increases especially at high temperatures (Table 5). Note that the same remark was made in our previous work [5], investigating viscosity in isobutyric acid + water mixtures.

4.2.2. Improved Herráez equation

Considering Equations (21)–(23) and the limiting expansion of Equation (12), we can write the Herráez polynomial $P_{n,T}(x_1)$ in a limiting

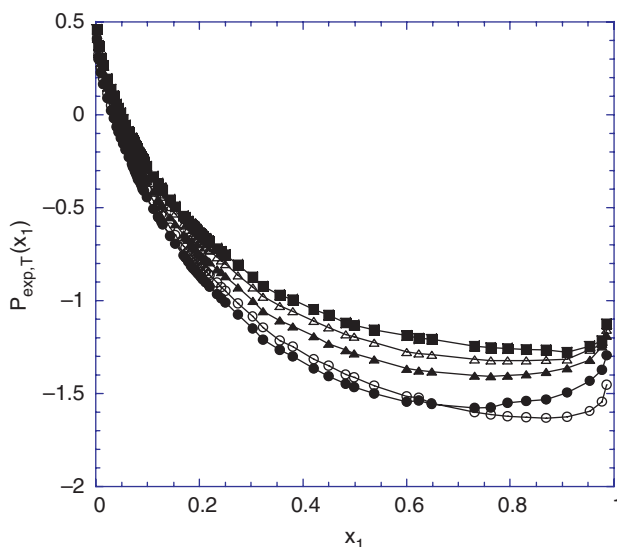


Figure 3. The experimental Herráez exponent polynomials (Equation (23)) $P_{\text{exp},T}(x_1)$ for dioxane + water mixtures vs. the mole fraction x_1 of IBA at the temperatures, 293.15 K (●); 298.15 K (○); 302.15 K (▲); 306.15 K (△); 309.15 K (■).

asymptotic expansion at high dilution of dioxane in water (i.e. in the vicinity of zero of x_1):

$$P_{\text{exp},T}(x_1) = \frac{1}{2} + \frac{\ln \left[\left(\frac{\rho_2}{M_2} \right)^{1/2} \cdot \left(\frac{\eta_2}{\eta_1 - \eta_2} \right) \cdot A_{12} \right] + \frac{B_{12}}{A_{12}} \cdot \left(\frac{\rho_2}{M_2} \right)^{1/2} \cdot x_1^{1/2} + o(x_1^{1/2})}{\ln x_1} \quad (24)$$

We can easily rediscover the limit value of $P_{n,T}(x_1)$ at infinite dilution in water as: $(\lim_{x_1 \rightarrow 0^+} P_{n,T}(x_1) = 1/2)$ and we can conclude that the first monomial of $P_{n,T}(x_1)$ is a fixed value independent of temperature and equal to 1/2 for the shear viscosity η (i.e. $B_{n,0,T} = 0.5$).

We can conclude that the Herráez model (Equations (21) and (22)) can be earning a fixed initial polynomial constant (B_0) such as 0.5 for viscosity. Hence, in the same degree of fitted polynomials we have a known parameter and we can consider it as a universal exponent B_0 . Hence, the improved Herráez equation for correlation viscosity can be written as

$$\eta = \eta_2 + (\eta_1 - \eta_2) \cdot x_1^{1/2} \cdot x_1^{x_1 \cdot H_{n,T}(x_1)} \quad (25a)$$

or:

$$\eta = \eta_2 + (\eta_1 - \eta_2) \cdot x_1^{0.5 + x_1 \cdot H_{n,T}(x_1)} \quad (25b)$$

where $H_{n,T}(x_1)$ is a power polynomial with order $(n - 1)$ and (n) adjustable parameters $B_{n,p,T}$:

$$H_{n,T}(x_1) = \sum_{p=1}^{p=n} B_{n,p,T} \cdot x_1^{p-1} \quad (26)$$

Table 6. Variation of $B_{n,p,T}$ constants for improved Herráez exponent polynomial (fixed $B_{n,0,T}=0.5$; Equations (22), (25) and (26)) $P_{n,T}(x_1)$ with temperature and the corresponding $R(\%)$ and χ^2 for each model of n degree (n varies from 1 to 5).

T (K)	$B_{n,0}$	$B_{n,1}$	$B_{n,2}$	$B_{n,3}$	$B_{n,4}$	$B_{n,5}$	R (%)	χ^2
$P_{1,T}(x_1) = B_{1,0} + B_{1,1}x_1$								
293.15		-2.7657					55.605	0.3417
298.15		-2.8368					69.697	0.2754
302.15	0.5	-2.5504		0			60.519	0.2698
306.15		-2.4598					64.719	0.2314
309.15		-2.3749					66.877	0.2087
$P_{2,T}(x_1) = B_{2,0} + B_{2,1}x_1 + B_{2,2}x_1^2$								
293.15		-6.8717	5.2617				96.181	0.03854
298.15		-6.4850	4.6749				96.679	0.03639
302.15	0.5	-6.1912	4.6656		0		96.370	0.03156
306.15		-5.8098	4.2929				96.336	0.02979
309.15		-5.5456	4.0631				96.352	0.02813
$P_{3,T}(x_1) = B_{3,0} + B_{3,1}x_1 + B_{3,2}x_1^2 + B_{3,3}x_1^3$								
293.15		-9.2577	13.285	-5.9707			98.626	0.01463
298.15		-8.8608	12.664	-5.9453			98.908	0.01261
302.15	0.5	-8.3913	12.064	-5.5056		0	98.780	0.01118
306.15		-8.0235	11.737	-5.5395			98.943	0.00907
309.15		-7.7382	11.436	-5.4868			99.048	0.00775
$P_{4,T}(x_1) = B_{4,0} + B_{4,1}x_1 + B_{4,2}x_1^2 + B_{4,3}x_1^3 + B_{4,4}x_1^4$								
293.15		-11.751	29.355	-34.798	15.461		99.534	0.00520
298.15		-11.215	27.837	-33.163	14.597		99.654	0.00418
302.15	0.5	-10.656	26.660	-31.688	14.042	0	99.649	0.00337
306.15		-10.030	24.670	-28.740	12.443		99.672	0.00294
309.15		-9.6663	23.862	-27.776	11.954		99.757	0.00207
$P_{5,T}(x_1) = B_{5,0} + B_{5,1}x_1 + B_{5,2}x_1^2 + B_{5,3}x_1^3 + B_{5,4}x_1^4 + B_{5,5}x_1^5$								
293.15		-13.488	47.238	-90.920	84.316	-28.980	99.708	0.00341
298.15		-12.764	43.778	-83.192	75.978	-25.834	99.781	0.00277
302.15	0.5	-12.081	41.330	-77.730	70.530	-23.775	99.785	0.00216
306.15		-11.421	38.984	-73.660	67.555	-23.196	99.810	0.00178
309.15		-10.769	35.217	-63.415	55.679	-18.403	99.849	0.00135

Results of the new $B_{n,p,T}$ fitted values are given in Table 6.

Nevertheless, we can add that in the case of nonelectrolyte solution when the Falkenhagen parameter [39] is null or takes very low values ($A_{12} = 0$), we can rewrite Equation (12) in a new limiting asymptotic expansion at high dilution solution and we then obtain:

$$P_{\text{exp},T}(x_1) = 1 + \frac{\ln\left[\frac{\eta_2}{\eta_1 - \eta_2} \cdot B_{12} \cdot \frac{\rho_2}{M_2}\right] + o(\sqrt{x_1})}{\ln x_1} \quad (27)$$

from which we can conclude that $(\lim_{x_1 \rightarrow 0^+} P_{n,T}(x_1) = 1)$.

Also, we can note that in the very rare case of nonelectrolyte solution when the parameters A_{12} and B_{12} (Equation (12)) are null or take very low values we can observe that $(\lim_{x_1 \rightarrow 0^+} P_{n,T}(x_1) = 2)$ for which we can cite, for example, the case of infinite dilution of 2-propanol in decane investigated by González *et al.* [23].

4.3. Discussion

The variation of reduced viscosity deviation $\Delta\eta/(x_1(1-x_1))$ with composition was used in every case to test the quality of the data; this function is extremely sensitive to experimental errors, particularly in the dilute ranges. In addition, its values at infinite dilution represent values of the equivalent of the partial excess physical magnitudes at infinite dilution ($x_1 \rightarrow 0^+$), [47], which can be also calculated from the adjustable parameters using:

$$\begin{aligned} Q_{n,T}(x_1 = 0) &= A_{n,0,T} - A_{n,1,T} + \dots + (-1)^p \cdot A_{n,p,T} + \dots + A_{n,n,T} \\ &= (\eta_1 - \eta_2) \cdot (1 + (\partial \ln(\eta - \eta_1)/\partial x_1)_T) \end{aligned} \quad (28)$$

and

$$\begin{aligned} Q_{n,T}(x_1 = 1) &= A_{n,0,T} - A_{n,1,T} + \dots + A_{n,p,T} + \dots + A_{n,n,T} \\ &= (\eta_1 - \eta_2) \cdot (1 - (\partial \ln(\eta - \eta_2)/\partial x_1)_T) \end{aligned} \quad (29)$$

for the R-K expression and:

$$\begin{aligned} Q_{n,T}(x_1 = 0) &= a_{n,0,T} - a_{n,1,T} + \dots + (-1)^p \cdot a_{n,p,T} + \dots + a_{n,n,T} \\ &= (\eta_1 - \eta_2) \cdot (1 + (\partial \ln(\eta - \eta_2)/\partial x_1)_T) \end{aligned} \quad (30)$$

and

$$\begin{aligned} Q_{n,T}(x_1 = 1) &= a_{n,0,T} - a_{n,1,T} + \dots + a_{n,p,T} + \dots + a_{n,n,T} \\ &= (\eta_1 - \eta_2) \cdot (1 - (\partial \ln(\eta - \eta_2)/\partial x_1)_T) \end{aligned} \quad (31)$$

for the Legendre polynomials.

In Equations (28)–(31) η_i is the shear viscosity of pure component i . The values of η_i are listed in Table 1 for each temperature. Equations (28) and (30) or (29) and (31) yield the same values of $Q_{n,T}(x_1=0)$ or $Q_{n,T}(x_1=1)$, respectively. Inspection of the results of Tables 2 and 4 proves with a good approximation the validity of Equations (28)–(31), particularly for fitting polynomials with fourth or fifth degree.

Considering the derivation function *versus* molar fraction x_1 of viscosity η at fixed temperature, in Herráez model, (Equation (21)) as:

$$(\partial\eta/\partial x_1)_T = (\eta - \eta_2) \cdot [\partial P_{n,T}(x_1)/\partial x_1 \cdot \ln(x_1) + P_{n,T}(x_1)/x_1] \quad (32)$$

we can easily find a relationship between the reduced R-K excess viscosity $Q_{n,T}(x_1=1)$ and the Herráez exponent polynomial $P_{n,T}(x_1=1)$ at the limit of $x_1=1$ (pure dioxane).

$$P_{n,T}(x_1 = 1) = 1 - Q_{n,T}(x_1 = 1)/(\eta_1 - \eta_2) = (\partial\eta/\partial x_1)_T/(\eta_1 - \eta_2). \quad (33)$$

As shown in Equation (33), at mutual infinite dilution (D in W or W in D) the limiting Herráez exponent polynomial values can be related to the viscosity derivation function as:

$$\begin{aligned} P_{n,T}(x_1 = 0) &= B_{n,0,T} = (x_1 \cdot \partial \ln(\eta - \eta_2)/\partial x_1)_T \\ &= -(x_1 \cdot \partial \ln(\eta - \eta_1)/\partial x_1)_T \end{aligned} \quad (34)$$

and

$$P_{n,T}(x_1 = 1) = B_{n,0,T} + B_{n,1,T} + \cdots + B_{n,p,T} + \cdots + B_{n,n,T} = (\partial \ln(\eta - \eta_2) / \partial x_1)_T = 1. \quad (35)$$

We can conclude that $B_{n,p,T}$ parameters have more mathematical than physical significance.

The value of χ^2 and $R(\%)$ (Equations (18) and (19), Table 5) have been calculated for Equations (17), (20) and (22) in order to compare the results with those obtained from Equations (3), (4) and (21). For many experimental data in the literature, authors show that in the representations where the function $\eta = f(x_1)$ exhibits monotonous variation (concave or convex distribution), can be well represented by correlation models only with one, two or three parameters [32,33,61–66]. That is why our choice was of adopting Equations (4) and (22) with a maximum of three parameters, because it is uncommon to introduce more than three parameters in the common correlation models. Nevertheless, when the function $\eta = f(x_1)$ presents a pronounced maximum or minimum, these proposed models record deficient performance and the correlation fails, especially for the binary mixtures that show a critical behaviour and near phase transition temperature [3,32]. In these mixtures we must manipulate Equations (4) and (22) with four parameters as a minimum.

Tables 2 and 4 present the coefficients of the fits of the correlation (Equations (17) and (20)) as well as and their corresponding common values of χ^2 and $R(\%)$. In the same way, Table 5 shows the coefficients of the fit $B_{n,p,T}$ and their corresponding χ^2 and $R(\%)$ values corresponding to Equation (22).

We see here that for the (D-W) mixtures, the Herráez proposed equation (Equation (22)) with three parameters or more gives better results than the R-K equation involving the same number of parameters. For a single or two parameters, the R-K equation affords better results.

As shown in Tables 2 and 4, at constant temperature, the chi-square minimisation χ^2 decreases when the degree (n) of reduced R-K function (Equation (17)) increases and becomes reasonable from the second degree. The χ^2 -value, strongly increases at low temperature showing the strong correlation between molecules in the mixture.

In the same way, as shown in Table 5 at constant temperature, the chi-square minimisation χ^2 decreases when the degree (n) of Herráez function (Equation (22)) increases and gives aberrant values ($\chi^2 > 0.4$) for the first degree's polynomial caused by the negative value of the $B_{1,0,T}$ coefficient (Table 5). Also χ^2 becomes reasonable ($\chi^2 < 0.015$) from the second degree and remains constant except at low temperature where we observe a small increase.

We can consider that the Herráez function $P_{\text{exp},T}(x_1)$, as a mathematical function, is a dimensionless number and represents physically a variable effective exponent which depends on the composition of mixture. Note that this function converges at infinite dilution ($x_1 \rightarrow 0^+$) to a common value (0.5) independent of temperature.

On the other hand, the reduced R-K function $Q_{\text{exp},T}(x_1)$ (Equation (5), Figure 2) can be considered as a physical function and can be showing different phenomena or behaviours, like the beginning of cluster formation or structure changing.

We remark that, preliminary fittings and calculations have shown that the concordance with experimental data requires more parameters (Figures 4–6). Many experimenters conclude the improvement of results only with the goodness of statistical parameters. In fact, they are satisfied with calculating standard deviation without examining the agreement of calculated data with the experimental one in each zone of their investigated domain, particularly for the satisfied value of corresponding standard deviation. As it indicates in the literature, for none of the systems does the precision warrant the use of more than four parameters [4], but these models with four parameters or less [32,33,61–66] did not reproduce the main features of the experimental data and the interpolation cannot cover all data points, especially far from the diluted range and near composition corresponding to maximum of viscosity at low temperature (Figures 4–6). In these intermediate regions, the interpolation fails, although the precision and statistical parameters (R , σ , χ^2 , etc.) shows a good representation and even in the majority of calculated points shows a good concordance with the experimental one. In fact, the goodness of statistical parameters provides global and middle indications. Also, even in the case of good quality of data points we can observe a relative viscosity discrepancy between the calculated and experimental one $((\eta_{\text{cal}} - \eta_{\text{exp}})/\eta_{\text{exp}})$, the composition corresponding to the maximum of viscosity exceeds 10% for some points even for high temperature.

However, we note that for the improved Herráez equation (Equation (22) and Figure 6), the fixed universal exponent B_0 to 0.5 value removes the observed aberration in first degree of polynomial, showing that it must be excelled in the case of monotonous variation in viscosity values with molar fraction [32].

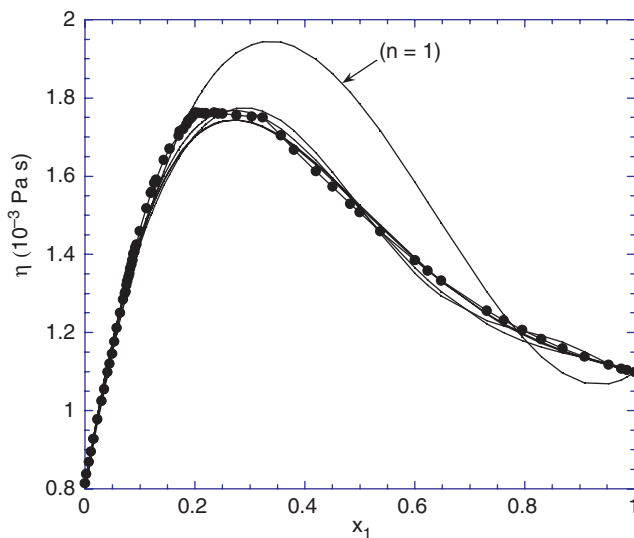


Figure 4. Comparison of experimental viscosity data at 302.15 K (●) with that calculated by R-K models (Equations (3)–(5)) for different fixed degrees (n) of $Q_{n,T}(x_1)$ polynomials (n varies from 1 to 5).

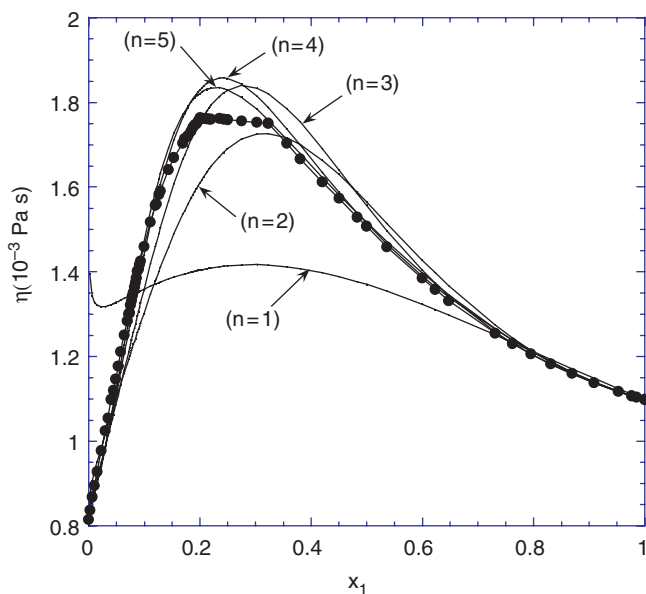


Figure 5. Comparison of experimental viscosity data at 302.15 K (●) with that calculated by Herráez models (Equations (21) and (22)) for different fixed degrees (n) of exponent polynomials $P_{n,T}(x_1)$ (n varies from 1 to 5).

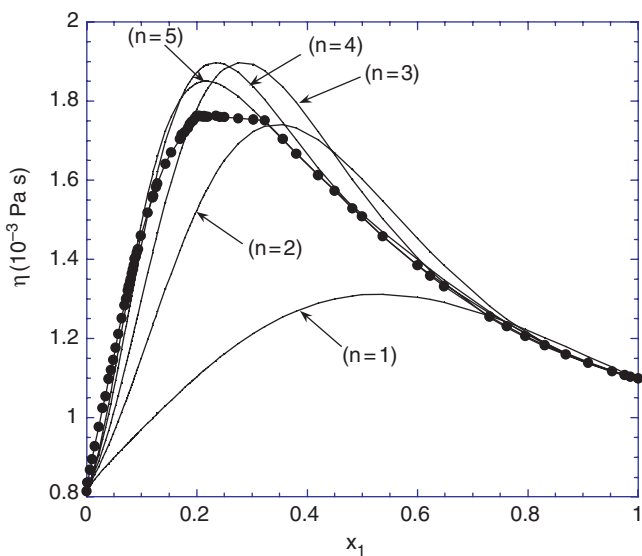


Figure 6. Comparison of experimental viscosity data at 302.15 K (●) with that calculated by the improved Herráez models (Equations (25) and (26)) for different fixed degrees (n) of exponent polynomials $P_{n,T}(x_1)$ (n varies from 1 to 5).

5. Adapted Herráez equation

However, the physical properties of mixtures have the principal common feature that their values tend towards its pure ones (y_1 or y_2) at infinite dilution (when $x_1 \rightarrow 0$ or 1). So, we can use the same approach that Herráez used in viscosity (Equations (21) and (22)), to adapt and generalise his proposed equation to any physical properties (y) other than the shear viscosity (η).

$$y(x_1) = y_2 + (y_1 - y_2) \cdot x_1^{P_{n,T}(x_1)}, \quad (36)$$

where y , y_1 and y_2 are the investigated property of the mixture and the property of pure components (1) and (2), respectively, and x_1 is the mole fraction of pure component (1). $P_{n,T}(x_1)$ is a power polynomial with order (n) and ($n + 1$) adjustable parameters $B_{n,p,T}$:

$$P_{n,T}(x_1) = \sum_{p=0}^{p=n} B_{n,p,T} \cdot x_1^p. \quad (37)$$

Henceforth, we can use a similar equation (Equation (36)) for investigating a property (y) of the mixture. Note that the choice of index (1) in x_1 -variable for the first component must respect the mathematical definition's domain of the exponential function (Equation (36)). In fact, all the y -values of mixtures in the whole range must be absolutely majored or minored by the selected y_2 -value at the considering fixed temperature T .

Inspecting some physical properties at fixed temperature T of different binary liquid mixtures in the literature, we have represented the corresponding experimental Herráez polynomial $P_{\text{exp},T}(x_1)$ applying Equation (38) for $x_1 \in]0,1[$

$$P_{\text{exp},T}(x_1) = \frac{\ln\left(\frac{y_{\text{exp},T}(x_1) - y_2}{y_1 - y_2}\right)}{\ln x_1}. \quad (38)$$

However, we have found that at infinite dilution the $P_{\text{exp},T}(x_1)$ -values converge to single point (0.5 or 1) or more independent of temperature. Hence, we can categorise the different physical properties into two types; such as viscosity-type for 0.5-limit (Figure 7) and density-type for 1-limit (Figure 8); except in very rare and particular case we can observe a value greater than the precedent habitual values.

6. Conclusion

In the case of distributions of viscosity data as a function of mole fraction presenting a maximum or minimum, the two investigated models show deficient performance for one and two degrees of their corresponding polynomials, especially at low temperature. We must record high values of chi-square minimisation χ^2 which increase at low temperature. This divergence is more pronounced in the R-K model than Herráez one. Likewise, the concordance with experimental data fails around composition corresponding to maximum of viscosity. The R-K polynomial constants offer more physical explanation of binary mixture properties than those of Herráez.

Starting from three degrees, the two models begin to reproduce the experimental data points. The R-K model offers better results than those of Herráez with the same

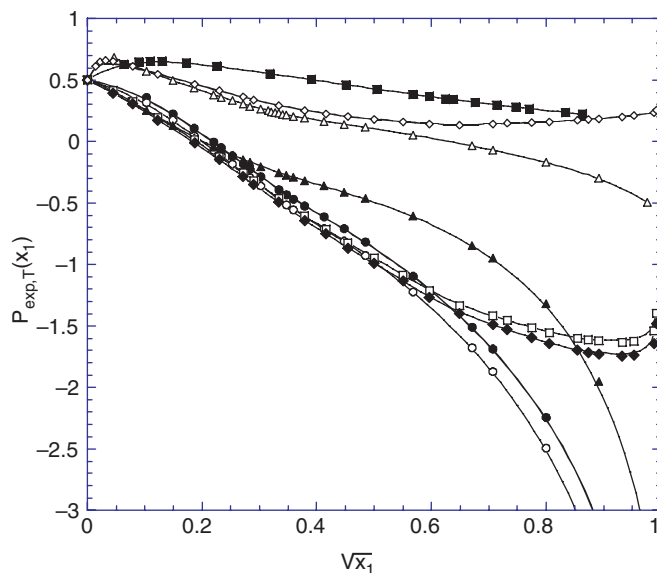


Figure 7. Experimental Herráez exponent polynomials $P_{\text{exp},T}(x_1)$ (Equations (38), (39) and (22)) for some properties of viscosity-type Herráez magnitudes in different systems of binary liquid mixtures vs. square root of molar fraction x_1 in IBA or D, (●): kinematic viscosity ν of IBA+W at 313.15 K [3,5]; (○): shear viscosity η of IBA+W at 313.15 K [3,5]; (▲): electrical conductivity σ in IBA+W at 313.15 K [6]; (Δ): Gibbs energy of activation of viscous flow ΔG^* of IBA+W at 313.15 K [3,5]; (■): Heat capacity C_p of IBA+W at 308.15 K [67]; (□): shear viscosity η in D+W at 298.15 K [2]; (◆): kinematic viscosity ν in D+W at 298.15 K [2]; (◇): Gibbs energy of activation of viscous flow ΔG^* of D+W at 298.15 K [2].

number of parameters. The R-K polynomial is more sensitive to experimental point's number whereas the Herráez model offers a good smoothed interpolation without any oscillation between data points even in the case of a few experimental samples numbers. In opposition to that indicated in literature [32], as well as R-K model, the Herráez one can describe distribution showing a maximum or minimum in viscosity values of mixture but with increasing of parameters number and taking mathematical precaution (boundary conditions, overvalue, undervalue, etc.).

Nevertheless, the Herráez model can be excelled in describing correlation viscosities in binary mixtures, with the same number of variable parameters than R-K model, when the corresponding first constant is fixed to 0.5 for all studied temperatures. We must take care that in the case of some nonelectrolyte mixtures the net absence of the ion-ion interaction when the Falkenhagen parameter A_{ij} [39] is absolutely null, leads to a fixed value of Herráez model to (1.0) or more [43]. In the same context, the Herráez model can be also adapted and generalised in other correlation physical properties of binary liquid mixtures and can be earned a fixed initial polynomial constant for each physical magnitude like the Gibbs energy of activation of viscous flow (0.5), density, molar volume (1.0), electrical conductivity of binary solvent mixtures (0.5), refractive index (1.0), electrical permittivity (1.0), speed of sound, etc. Note that this first constant-value (B_0) is justified in this work and can be considered as a universal exponent for each type of physical property in

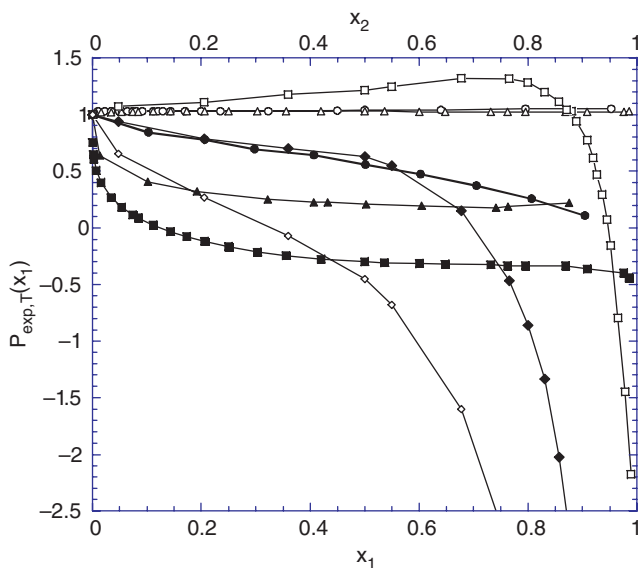


Figure 8. Experimental Herráez exponent polynomials $P_{\text{exp},T}(x_1)$ (Equations (38), (39) and (22)) for some properties of density-type-Herráez magnitudes in different systems of binary liquid mixtures; (a) vs. molar fraction x_1 in IBA or D, (●): refractive index n of density ρ of IBA+W at 313.15 K [4]; (○): molar volume V in IBA+W at 313.15 K [3]; (▲): refractive index n of D+W at 298.15 K [2]; (Δ): molar volume V of D+W at 298.15 K [2]; (■): density ρ in D+W at 298.15 K [2]; (b) vs. molar fraction x_2 in W, (□): density δ of IBA+W at 313.15 K [3,5]; (◆): entropy of activation of viscous flow ΔS^* of IBA+W at 313.15 K [3,5]; (◇): enthalpy of activation of viscous flow ΔH^* of IBA+W at 313.15 K [3,5].

binary mixtures. In the next work, different physical magnitudes in binary liquid mixtures will be classified into two categories.

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