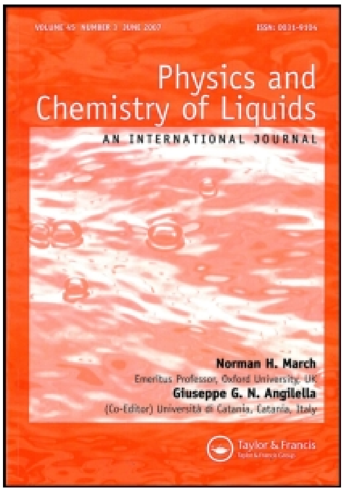

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Viscosity and density of binary mixtures of alcohols and polyols with three carbon atoms and water: equation for the correlation of viscosities of binary mixtures

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Viscosity and density of binary mixtures of alcohols and polyols with three carbon atoms and water: equation for the correlation of viscosities of binary mixtures

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Measurements have been made of the viscosity and density of binary mixtures of alcohols and polyols with three carbon atoms and water at 298.15 K and at atmospheric pressure, as a function of the mole fraction. Fits have been made of the experimental values corresponding to the excesses of molar volume (V^E), the deviations of viscosity ($\Delta\eta$), and the excesses of Gibbs free energy of activation (G^{*E}), by means of the Redlich–Kister equation. A new correlation equation is presented for studying the viscosity of such mixtures, and comparisons are made of the experimental values of viscosity *versus* the values obtained by means of the mentioned equation and the models of Heric and McAllister. Likewise, and with the purpose of corroborating the validity of the proposed correlation equation, the latter is applied to other reference binary mixtures.

Keywords: viscosity; density; binary mixtures; alcohols; polyols; water; empiric correlation equation of viscosities

1. Introduction

Alcohols, either alone or in solutions, are very widely used in the pharmaceutical, cosmetic, chemical, food, and other industries [1–6].

Among the physicochemical properties of such systems, mention should be made of their viscosity and density, among others. Knowledge of both of these parameters is important for understanding the molecular interactions among the components of the mixtures and thus optimising their application to processes such as mass transference, energy transference, etc. [7–10].

The viscosity of liquids is determined both by collisions among particles and by the force fields that determine the interaction among molecules. As a result, the theoretical description of viscosity is quite complex. In this context, many models have been proposed over the years, based on the theory of Eyring, or of an empirical or semi-empirical nature. However, such models are not always applicable to all types of mixtures [11–18].

In the present article, and with the aim of continuing and amplifying the study of the physicochemical properties of these systems (monoalcohols + water) [19], we report the experimental results on the viscosity η and density ρ of binary mixtures of alcohols, polyols with three carbon atoms and water, at 298.15 K atmospheric pressure.

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In the same way as the immense majority of the binary mixtures used in industry, these mixtures present the difficulty of nonlineal behaviour of viscosity. It is therefore necessary to secure rigorous data, with equations and models capable of providing a reliable estimation of the viscous behaviour of the mixtures.

A new correlation equation is thus proposed, based on lineal behaviour, and comparisons are made of the experimental values of the viscosity of such mixtures with the values calculated from the mentioned equation and the following correlation models.

Lastly, and with the purpose of corroborating the validity of the proposed correlation equation, the latter is applied to other reference binary mixtures.

2. Correlation equation and models

The proposed equation is based on the lineal behaviour of the binary mixtures:

$$\eta = x_1 \cdot \eta_1 + x_2 \cdot \eta_2, \tag{1}$$

where η is the viscosity of the mixture, η_1 and η_2 the viscosities of the pure components, and x_1 and x_2 are the mole fractions of the components of the mixture. By placing x_1 as a function of x_2, we have:

$$\eta = \eta_1 - (\eta_1 - \eta_2) \cdot x_2. \tag{2}$$

In this equation we introduce a correcting factor associated to the mole fraction x_2, resulting in:

$$\eta = \eta_1 - (\eta_1 - \eta_2) \cdot x_2 \cdot \left(\frac{1 + m_1 \cdot (1 - x_2)}{1 + m_2 \cdot (1 - x_2)}\right), \tag{3}$$

which meets the contour conditions of the experiment, i.e. if:

$$x_2 = 0 \rightarrow \eta = \eta_1,$$

$$x_2 = 0 \rightarrow \eta = \eta_2,$$

and where m_1 and m_2 are parameters to be fitted. When $m_1 = m_2 = 0$, the equation exhibits lineal behaviour.

The models used have been those of Heric [14] and McAllister [15], since they involve the same number of parameters as the proposed equation.

Heric:

$$\ln(\eta V) = x_1 \ln(\eta_1 V_1) + x_2 \ln(\eta_2 V_2) + x_1 x_2(\alpha_1 + \alpha_2(x_1 - x_2)), \tag{4}$$

where V is the molar volume, V_1 and V_2 the molar volumes of the pure components, and α_1 and α_2 the parameters to be fitted.

McAllister:

$$\begin{aligned} \ln \nu = {} & x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln Z_{12} + 3x_1 x_2^2 \ln Z_{21} + x_2^3 \ln \nu_2 \\ & - \ln(x_1 + x_2 M_2/M_1) + 3x_1^2 x_2 \ln(2/3 + M_2/3M_1) \\ & + 3x_1 x_2^2 \ln(1/3 + 2M_2/3M_1) + x_2^3 \ln(M_2/M_1), \end{aligned} \tag{5}$$

where ν is the kinematical viscosity, i.e., $\nu = \eta/\rho$; M_1 and M_2 are the molecular masses, and Z_{12} and Z_{21} the parameters to be fitted.

In all cases we used as estimation criterion the SD, S, defined by:

$$S = \sqrt{\frac{\sum_{i=1}^{n} \left\{\eta_{\text{exp}} - \eta_{\text{cal}}\right\}_i^2}{n-k}}, \tag{6}$$

where n is the number of points of the sample and k the number of parameters of the fitting equation or model.

3. Experimental section

The substances used in the mixtures were 1-propanol, 2-propanol, 1,2-propanediol, 1,3-propanediol and 1,2,3-propanetriol, supplied by Aldrich, and with a mass purity of >99.5% in all cases. The water used was distilled and deionised.

The mass of the mixtures was measured with a Mettler AT201 balance (precision $\pm 1 \cdot 10^{-5}$ g), and uncertainty in the mole fraction was estimated to be $<10^{-4}$.

The measurements of the densities of the pure components and of the binary mixtures was carried out using an Anton-Paar densitometer (model DMA 55) with an uncertainty of $\pm 10^{-5}\,\text{g}\,\text{cm}^{-3}$. The temperature of the measuring cell was maintained at (298.15 + 0.01) K using the Grant Thermostatic Water Bath.

A HAAKE viscometer (Rotovisco RV30) with NV sensor system was employed to measure the absolute viscosity, η, of the pure components and their binary mixtures at a temperature of 298.15 K. The measured viscosity values are accurate to ±0.001 mPa s. The mole fraction reproducibility was within ±0.0001 units. In all measurements, the temperature was maintained within ±0.01 K by the HAAKE Fuzzy logic circulator with a digital temperature setting.

Binary mixtures were prepared with the indicated compounds and distributed into three airtight containers. The measurements were carried out in triplicate, and in all cases showed a percentage dispersion of <1%.

4. Results and discussion

Table 1 shows the results of the experimental measurements of the viscosity and density of the pure components, which have been compared with the values found in the literature.

The experimental results for the viscosity η and density ρ of the mixtures at 298.15 K and at atmospheric pressure, as a function of the mole fraction x_2 are reported in Table 2.

The deviation of viscosity $\Delta\eta$ was defined by:

$$\Delta\eta = \eta - x_1 \cdot \eta_1 - x_2 \cdot \eta_2. \tag{7}$$

The excesses of molar volume V^{E} were defined by:

$$V^{\text{E}} = \frac{M_1 \cdot x_1 + M_2 \cdot x_2}{\rho} - \frac{M_1 \cdot x_1}{\rho_1} - \frac{M_2 \cdot x_2}{\rho_2}, \tag{8}$$

where ρ_1 and ρ_2 are the respective densities of the pure components.

Table 1. Viscosity and density of the pure components at 298.15 K and at atmospheric pressure.

	η (mPa s)		ρ (g cm^{-3})	
Compounds	This work	Literature	This work	Literature
Water	0.891	0.89025 [6] 0.890 [27]	0.99702	0.997047 [6] 0.99704 [27]
1-Propanol	1.946	1.9430 [6] 2.017 [26] 1.9369 [41]	0.80012	0.79960 [6] 0.7996 [26] 0.79950 [41]
2-Propanol	2.031	2.072 [26] 2.045 [40] 2.048 [42]	0.78104	0.7807 [26] 0.7813 [40] 0.7809 [30]
1,2-Propanediol	44.13	43.428 [27] 44.39 [32] 1.0330 [24]	1.03275	1.03277 [27] 1.0328 [6]
1,3-Propanediol	42.064	40.067 [27]	1.05001	1.04999 [27]
1,2,3-Propanetriol	938.025	934 [43]	1.25798	1.2613 [43] 1.25350 [28]

Table 2. Density, excesses of molar volume, viscosity, viscosity deviations and excesses of Gibbs free energy of activation for the indicated mixtures at 298.15 K and at atmospheric pressure.

x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (mPa s)	$\Delta\eta$ (mPa s)	G^{*E} (J mol^{-1})
Water (1) + 1-propanol (2)					
0.0000	0.99702	0.00000	0.891	0.000	0.0
0.0523	0.97012	−0.21350	1.734	0.788	1718.0
0.0997	0.95028	−0.38313	2.095	1.099	2212.1
0.1342	0.93634	−0.45254	2.303	1.270	2451.7
0.1986	0.91364	−0.53189	2.562	1.461	2693.3
0.3006	0.88657	−0.62714	2.705	1.497	2718.6
0.4003	0.86663	−0.67709	2.619	1.306	2467.6
0.4782	0.85367	−0.66960	2.498	1.102	2184.5
0.5394	0.84475	−0.63997	2.407	0.947	1945.9
0.6217	0.83419	−0.57293	2.306	0.759	1623.1
0.6856	0.82660	−0.47832	2.241	0.627	1371.9
0.8014	0.81530	−0.32061	2.116	0.380	875.8
0.9028	0.80693	−0.15816	2.032	0.189	443.0
1.0000	0.80012	0.00000	1.946	0.000	0.0
Water (1) + 2-propanol (2)					
0.0000	0.99702	0.00000	0.891	0.000	0.0
0.0439	0.97389	−0.25858	1.576	0.635	1466.5
0.0764	0.95871	−0.42299	2.198	1.220	2312.0
0.1497	0.92836	−0.69154	2.854	1.792	2962.4
0.2173	0.90486	−0.84799	3.097	1.958	3121.9
0.2855	0.88398	−0.90697	3.053	1.837	3009.2
0.4036	0.85656	−0.97084	2.862	1.511	2644.2
0.5000	0.83663	−0.82409	2.646	1.185	2234.0
0.5263	0.83199	−0.78210	2.581	1.090	2107.2

(*continued*)

Table 2. Continued.

x_2	ρ (g cm^{-3})	V^E (cm^3 mol^{-1})	η (mPa s)	$\Delta\eta$ (mPa s)	G^{*E} (J mol^{-1})
0.5814	0.82324	−0.69628	2.489	0.935	1872.2
0.6897	0.80898	−0.52930	2.283	0.606	1343.9
0.7874	0.79878	−0.39210	2.177	0.388	914.6
0.8475	0.79318	−0.28969	2.106	0.249	631.0
1.0000	0.78104	0.00000	2.031	0.000	0.0
Water (1) + 1,2-propanediol (2)					
0.0000	0.99702	0.00000	0.891	0.000	0.0
0.0963	1.02174	−0.31862	2.775	−2.280	2158.7
0.1970	1.03360	−0.52541	5.634	−3.778	3108.5
0.3086	1.03920	−0.64819	9.397	−4.839	3388.1
0.3774	1.04061	−0.68127	12.168	−5.042	3381.7
0.4524	1.03994	−0.63882	15.524	−4.931	3256.6
0.5109	1.03905	−0.58572	18.218	−4.767	3068.8
0.5926	1.03797	−0.51000	22.240	−4.278	2726.0
0.6898	1.03681	−0.41413	27.156	−3.565	2198.3
0.8043	1.03511	−0.26523	33.022	−2.651	1449.3
0.8747	1.03427	−0.17626	36.977	−1.740	957.2
0.9013	1.03370	−0.12431	38.356	−1.512	754.3
0.9466	1.03332	−0.07237	41.099	−0.728	421.4
1.0000	1.03275	0.00000	44.136	0.000	0.0
Water (1) + 1,3-propanediol (2)					
0.0000	0.99702	0.00000	0.891	0.000	0.0
0.0743	1.01461	−0.10211	1.975	−1.975	1496.3
0.1661	1.03235	−0.30973	4.203	−3.527	2662.9
0.2338	1.03833	−0.36020	6.223	−4.294	3070.9
0.3007	1.04329	−0.42002	8.667	−4.605	3298.2
0.3965	1.04729	−0.44878	12.427	−4.789	3297.9
0.4726	1.04946	−0.45822	15.671	−4.678	3132.1
0.5649	1.05106	−0.44510	19.703	−4.447	2772.4
0.6713	1.05228	−0.41684	24.721	−3.809	2233.4
0.7492	1.05216	−0.34843	28.533	−3.205	1766.0
0.8137	1.05112	−0.23553	32.005	−2.388	1361.2
0.9004	1.05037	−0.11377	36.941	−1.022	775.8
0.9572	1.05023	−0.05371	39.938	−0.364	344.9
1.0000	1.05001	0.00000	42.064	0.000	0.0
Water (1) + 1,2,3-propanetriol (2)					
0.0000	0.99702	0.00000	0.891	0.000	0.0
0.0866	1.07781	−0.17689	2.708	− 79.369	1523.0
0.1636	1.12339	−0.26473	7.353	−146.887	2820.9
0.2269	1.15047	−0.31088	13.769	−199.750	3364.5
0.3134	1.17795	−0.34651	27.755	−266.865	3669.5
0.4390	1.20568	−0.36003	59.743	−352.573	3414.4
0.5124	1.21746	−0.34688	88.480	−392.561	3097.5
0.6378	1.23281	−0.29844	163.100	−435.491	2364.3
0.7036	1.23902	−0.25786	220.758	−439.491	1917.6
0.7684	1.24435	−0.21555	297.344	−423.651	1466.4
0.8478	1.24990	−0.15517	429.910	−365.483	911.7
0.9176	1.25398	−0.09066	604.839	−256.004	456.6
0.9561	1.25584	−0.04420	734.911	−161.974	219.8
1.0000	1.25798	0.00000	938.025	0.000	0.0

Table 3. Redlich–Kister coefficients A_i and SDs S of Equations (10) and (6) for (V^E) in the investigated system.

	V^E (cm^3 mol^{-1})				
System	A_1	A_2	A_3	A_4	S
Water + 1-propanol	−2.5866	−0.89435	−1.32840	1.3523	0.0030
Water + 2-propanol	−3.2615	−2.51800	−0.69845	−0.8275	0.0110
Water + 1,2-propanediol	−2.4311	−1.46000	−0.05709	−0.2666	0.0307
Water + 1,3-propanediol	−1.9659	−0.37341	0.97977	−0.4865	0.0906
Water + 1,2,3-propanetriol	−1.3871	−0.40737	−0.79434	0.6075	0.3172

Table 4. Redlich–Kister coefficients A_i and SDs S of Equations (10) and (6) for ($\Delta\eta$) in the investigated system.

	$\Delta\eta$ (mPa s)				
System	A_1	A_2	A_3	A_4	S
Water + 1-propanol	4.3027	6.0843	5.0600	−1.05440	0.0696
Water + 2-propanol	4.7949	8.1659	8.0910	−4.52480	0.0560
Water + 1,2-propanediol	−20.293	−5.3771	9.0356	−0.71000	0.0321
Water + 1,3-propanediol	−18.549	−8.6399	−10.812	15.4870	0.0578
Water + 1,2,3-propanetriol	−1515.2	994.46	−970.30	650.150	0.0188

The excesses of the Gibbs free energy of activation ΔG^{*E} were defined by:

$$\Delta G^{*^{\mathrm{E}}} = RT\left[\ln\left(\frac{\eta}{\rho}\cdot(x_1\cdot M_1 + x_2\cdot M_2)\right) - x_1\cdot\ln(\eta_1\cdot V_1) - x_2\cdot\ln(\eta_2\cdot V_2)\right], \tag{9}$$

where R is the universal gas constant and T the temperature of the experiment.

For each mixture, the deviation of viscosity, $\Delta\eta$, the excesses of molar volume, V^E, and the excesses of Gibbs free energy of activation, G^{*E}, were fitted by the Redlich–Kister equation [20]:

$$Y = x_1\cdot x_2\sum_{i=1}^{n} A_i\cdot(x_1 - x_2)^{i-1}, \tag{10}$$

where $Y = V^E$, $\Delta\eta$ or G^{*E}.

The A_i coefficients of these fits are shown in Tables 3–5, and have been used to obtain the fitting curves, which are shown as a continuous line in Figures 1–3. For increased clarity, Figure 2 has been divided in two: Figure 2(a) and (b).

4.1. *Excess molar volume (V^E)*

Figure 1 shows that the values of V^E are negative for all the mixtures studied.

The minimum V^E corresponds to the mixture (water + 2-propanol), and the maximum to the mixture (water + 1,2,3-propanetriol).

Table 5. Redlich–Kister coefficients, A_i, and SDs, S, of Equations (10) and (6) for (G^{*E}) in the investigated system.

	G^{*E} (J mol^{-1})				
System	A_1	A_2	A_3	A_4	S
Water + 1-propanol	8110.2	7341.3	10,701.0	8110.1	0.0653
Water + 2-propanol	8672.5	8487.6	11,622.0	10781.0	0.0361
Water + 1,2-propanediol	12,282.0	7308.5	6373.9	3746.5	0.4475
Water + 1,3-propanediol	12,116.0	7281.9	4182.3	692.9	0.3163
Water + 1,2,3-propanetriol	13,060.0	9689.4	273.4	1251.3	0.0405

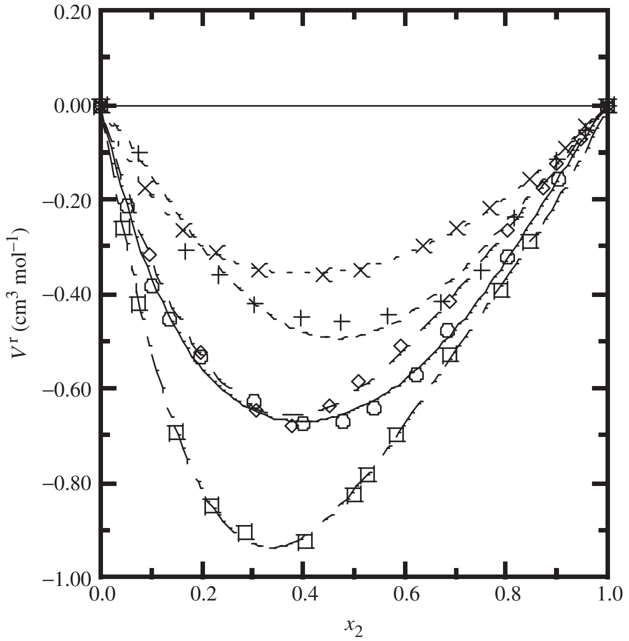

Figure 1. Plot of V^E against mole fraction x_2 at 298.15 K and at atmospheric pressure, for the mixtures of water with: ○, 1-propanol; □, 2-propanol; ◇, 1,2-propanediol; +, 1,3-propanediol; ×, 1,2,3-propanetriol. The points are measured, and the lines are calculated from Equation (10), using the parameters in Table 3.

Comparisons have been made of the experimental values of V^E with those reported in the literature [21–28]. Similar point distributions were found, with minimum values around mole fraction, $x_2 = 0.4$, the values of which are as follows for the systems analysed:

(a) (water + 1-propanol) −0.67709 cm^3 mol^{-1} for the study, *versus* −0.6533 cm^3 mol^{-1}, as mean of [21], [22] and [26];

(b) (water + 2-propanol) −0.97084 cm^3 mol^{-1} for the study, *versus* −0.97648 cm^3 mol^{-1}, as mean of [21], [22] and [26];

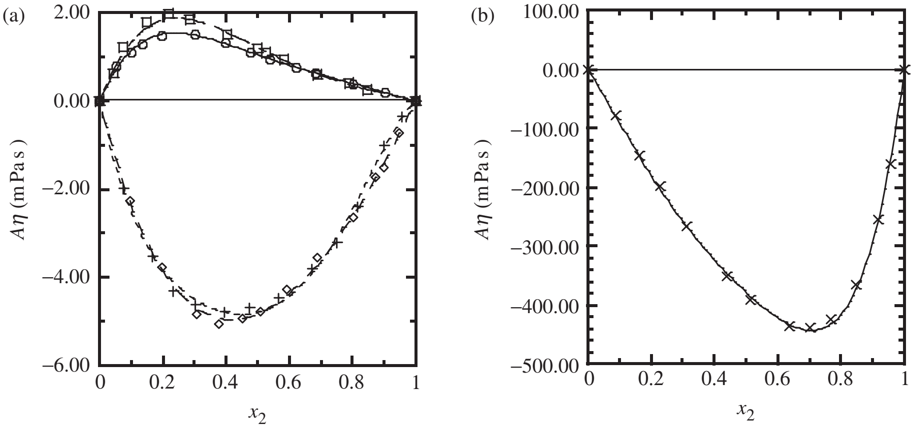

Figure 2. Plot of $\Delta\eta$ against mole fraction x_2 at 298.15 K and at atmospheric pressure, for the mixtures of water with: (a) ○, 1-propanol; □, 2-propanol; ◇, 1,2-propanediol; +, 1,3-propanediol. (b) ×, 1,2,3-propanetriol. The points are measured, and the lines are calculated from Equation (10), using the parameters in Table 4.

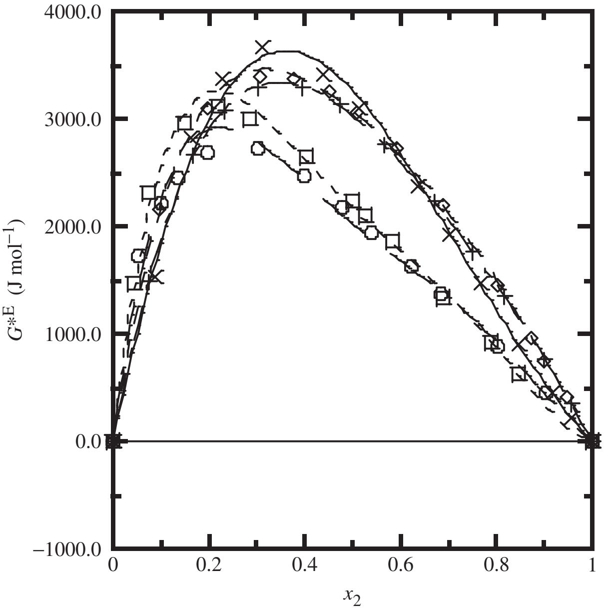

Figure 3. Plot of G^{*E} against mole fraction x_2 at 298.15 K and at atmospheric pressure, for the mixtures of water with: ○, 1-propanol; □, 2-propanol; ◇, 1,2-propanediol; + 1,3-propanediol; ×, 1,2,3-propanetriol. The points are measured, and the lines are calculated from Equation (10), using the parameters in Table 5.

(c) (water + 1,2-propanediol) $-0.68127\,\text{cm}^3\,\text{mol}^{-1}$ for the study, *versus* $-0.6783\,\text{cm}^3\,\text{mol}^{-1}$, as mean of [22], [23], [24] and [27];

(d) (water + 1,3-propanediol) $-0.45822\,\text{cm}^3\,\text{mol}^{-1}$ for the study, *versus* $-0.4318\,\text{cm}^3\,\text{mol}^{-1}$, as mean of [22] and [27]; and

(e) (water + 1,2,3-propanetriol) $-0.36139\,\text{cm}^3\,\text{mol}^{-1}$ for the study, *versus* $-0.390\,\text{cm}^3\,\text{mol}^{-1}$, for [28].

These differences may be due to the purity and volatility of the alcohols and the purity of the polyols.

The observed V^E values are the result of chemical and physical forces that may be broadly recognised as: (i) specific interactions appearing in the mixture between dissimilar molecules by dipole–dipole action; (ii) the breaking of liquid order on mixing with the second component; and (iii) nonspecific physical interactions and unfavourable interactions between unlike molecules. Generally, the first two factors contribute to the reduction in volume, while the latter two factors contribute to the expansion of volume [29]. From Table 2 and Figure 1, it is clear that the volume reducing factors are preponderant for all the studied mixtures.

4.2. *Deviations of the viscosity* ($\Delta\eta$)

The viscosity deviations may be generally explained by considering the following: (i) the difference in shape and size and of the component molecules and the loss of dipolar association in pure component may contribute to a decrease in viscosity of the mixtures; and (ii) specific interactions between unlike components such as hydrogen bond formation and charge transfer complexes may cause increases in viscosity of the mixtures [30].

In Figure 2(a) and (b), it is seen that $\Delta\eta$ is positive for the system water + (1-propanol, 2-propanol) and negative for the mixtures of water + (1,2-propanediol, 1,3-propanediol, 1,2,3-propanetriol).

The negative values of $\Delta\eta$ may be attributed to the dominance of dispersion forces between the mixing components of the binary liquid mixtures [31], while the positive values may be attributed to the presence of strong specific interactions between unlike components such as hydrogen bond formation and the formation of charge transfer complexes.

The minimum $\Delta\eta$ corresponds to the mixture of water + (1,2,3-propanetriol) and the maximum to the mixture of water + (2-propanol).

Comparisons have been made of the experimental values of $\Delta\eta$ with those reported in the literature [21,23,26,27,32,33]. Similar point distributions were found, with maximum and minimum values around the same mole fraction – the values of which are as follows for the systems analysed:

(a) (water + 1-propanol) presents a maximum at $x_2 = 0.3006$ with a value of $\Delta\eta = 0.461$ mPa s for the study, *versus* 1.490 mPa s, as mean of [21], [22] and [26];
(b) (water + 2-propanol) presents a maximum at $x_2 = 0.2173$ with a value of $\Delta\eta = 1.958$ mPa s for the study, *versus* 1.954 mPa s, as mean of [21], [22] and [26];
(c) (water + 1,2-propanediol) presents a minimum at $x_2 = 0.3774$ with a value of $\Delta\eta = -5.042$ mPa s for the study, *versus* -5.025 mPa s, as mean of [23], [27], [28] and [32];
(d) (water + 1,3-propanediol) presents a minimum at $x_2 = 0.3965$ with a value of $\Delta\eta = -4.789$ mPa s for the study, *versus* -4.785 mPa s, as mean of [23], [27], and [28]; and
(e) (water+1,2,3-propanetriol) presents a minimum at $x_2 = 0.7036$ with a value of $\Delta\eta = -439.491$ mPa s for the study, with a distribution point of $\eta = f(x_2)$ similar to [33].

Table 6. Coefficients m_1, m_2, α_1, α_2 and Z_{12}, Z_{21} obtained from the fits of Equations (3)–(5) with the corresponding SDs, S, calculated by Equation (6), for viscosity.

	Equation (3)			Equation (4)			Equation (5)		
System	m_1	m_2	S	α_1	α_2	S	Z_{12}	Z_{21}	S
Water + 1-propanol	1.31470	−0.90607	0.0329	3.9179	4.8244	0.3599	− 2.2450	−5.5496	0.3599
Water + 2-propanol	1.49220	−0.90324	0.0876	4.1933	5.5650	0.4305	−1.8470	−5.6713	0.4305
Water + 1,2-propanediol	−0.82410	−0.48235	0.0059	5.3100	3.6538	2.2191	−1.2689	−3.0418	2.2191
Water + 1,3-propanediol	−0.90351	−0.58472	0.0070	5.1604	3.2556	1.5113	−1.5531	−2.9292	1.5113
Water + 1,2,3-propanetriol	−0.98589	3.76980	0.0052	5.2994	3.9464	9.4598	−0.6509	−1.0074	4.4213

Table 7. Components of the mixtures used in the analysed files.

File	Mixture Component (1) + Component (2)	Ref.	File	Mixture Component (1) + Component (2)	Ref.
1	1,2-Dichlorobenzene + 1,4-Dioxane	[35]	22	$CHCl_2CHCl_2 + C_4H_8O$	[39]
2	1,4-Dioxane + Ethyl acetate	[35]	23	$CH_3CO_2C_4H_9 + C_4H_8O$	[39]
3	1-Butanol + 1,4-Dioxane	[35]	24	Methanol + 1,3-Dioxolane	[40]
4	1,4-Dioxane + Trichloroethylene	[35]	25	Ethanol + 1,3-Dioxolane	[40]
5	2-Chloroethanol + 1,4-Dioxane	[35]	26	1-Propanol + 1,3-Dioxolane	[40]
6	*N*,*N*-Dimethylacetamide + 1,4-Dioxane	[35]	27	2-Propanol + 1,3-Dioxolane	[40]
7	Diethylmalonate + 1,4-Dioxane	[35]	28	1-Butanol + 1,3-Dioxolane	[40]
8	2-Propanol + Octane	[36]	29	2-Butanol + 1,3-Dioxolane	[40]
9	2-Propanol + Decane	[36]	30	*t*-Butanol + 1,3-Dioxolane	[40]
10	2-Propanol + Dodecane	[36]	31	*i*-Amyl alcohol + 1,3-Dioxolane	[40]
11	2-Butanol + Octane	[37]	32	Water + Propane-1,2-diol	[41]
12	2-Butanol + Decane	[37]	33	Water + Propane-1,3-diol	[41]
13	2-Butanol + Dodecane	[37]	34	Water + Butane-1,2-diol	[41]
14	1-Pentanol + Phenetole	[38]	35	Water + Butane-1,3-diol	[41]
15	1-Hexanol + Phenetole	[38]	36	Water + Butane-1,4-diol	[41]
16	1-Heptanol + Phenetole	[38]	37	Water + Butane-2,3-diol	[41]
17	1-Octanol + Phenetole	[38]			
18	1-Nonanol + Phenetole	[38]			
19	1-Decanol + Phenetole	[38]			
20	$CCl_4 + C_4H_8O$	[39]			
21	$CHCl_3 + C_4H_8O$	[39]			

As has already been commented for V^E, these differences may be due to the purity and volatility of the alcohols and the purity of the polyols.

4.3. *Excesses of Gibbs free energy of activation* (G^{*E})

Figure 3 shows that the values of G^{*E} are positive for all the mixtures studied.

The positive values of G^{*E} indicate that intermolecular complexes are formed between the mixing components through hydrogen bonding. They also may be attributed to the size effect of the mixing component [31, 34].

The minimum G^{*E} corresponds to the mixture of water + 1-propanol, and the maximum to water + 1,2,3-propanetriol.

In order to conduct a correlation study of the viscosity η of the mixtures analysed, as a function of the mole fraction x_2, Equation (3) is presented and comparisons are made of the experimental values of viscosity *versus* those obtained from the mentioned equation and from Equations (4) and (5).

The results of the fits made with Equations (3)–(5) are given in Table 6.

From Table 6 it is deduced that of Equations (3)–(5), the best results are afforded by Equation (3), while Equations (4) and (5) yield the same results.

From the results in Table 6, and in order to corroborate the validity of Equation (3), we used 37 files from a recent literature review [35–41] (Table 7), studying the viscosity of different binary mixtures of liquids at atmospheric pressure and over different

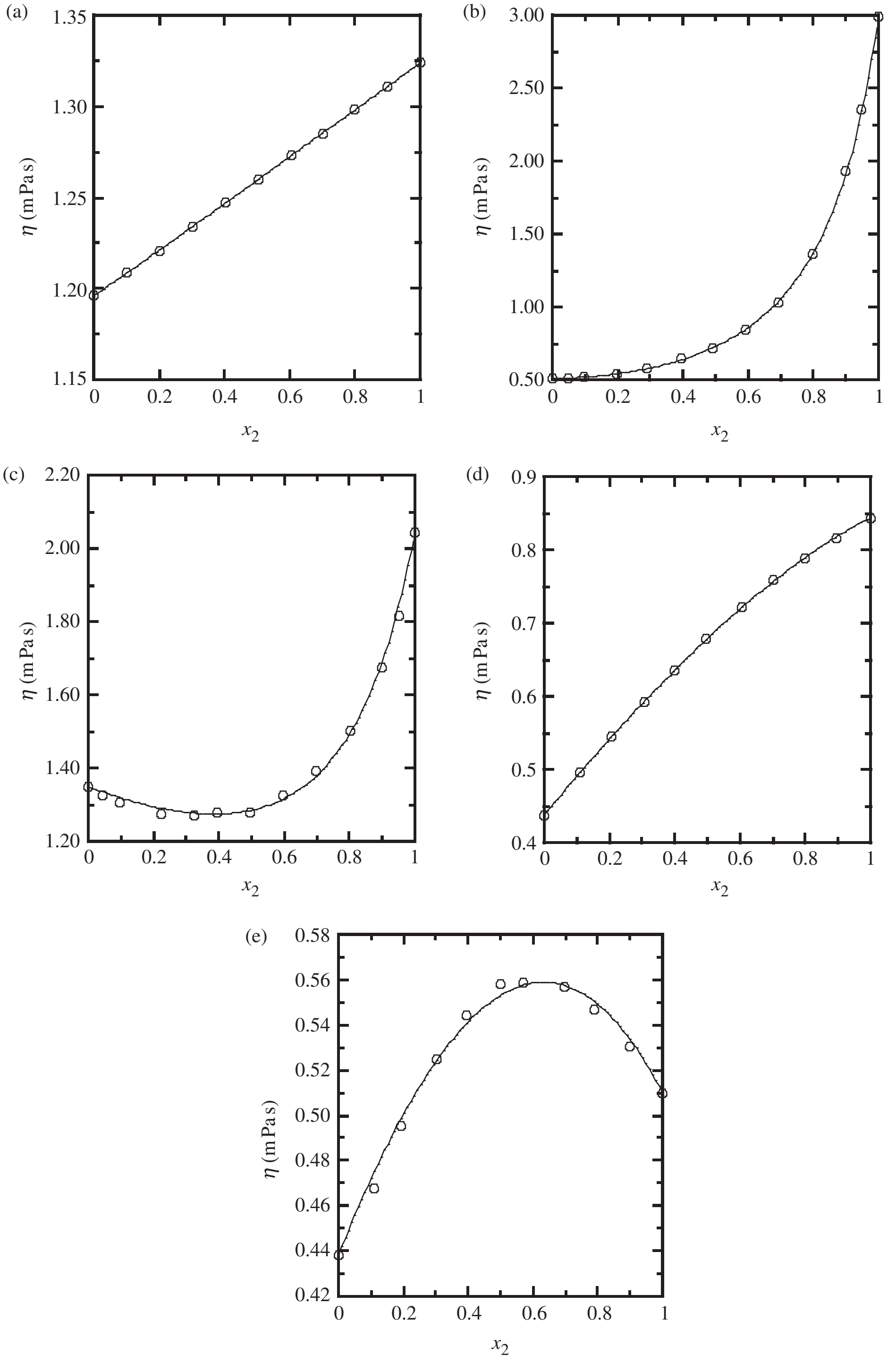

Figure 4. Distribution of points $\eta = f(x_2)$ corresponding to: (a) (File 1); (b) (File 11); (c) (File 10); (d) (File 20); and (e) (File 21). The lines are calculated from Equation (3).

Table 8. Coefficients of the fits for Equations (3)–(5), with the corresponding SD, S, calculated from Equation (6), mean SDs, $\overline{S}$, and SDs, $S_{\max}$, and $S_{\min}$, for viscosity.

	Equation (3)			Equation (4)			Equation (5)		
File	a_1	a_2	S	α_1	α_2	S	Z_{12}	Z_{21}	S
1	−0.72625	−0.71440	0.0002	0.04905	−0.00531	0.0002	0.05127	0.08971	0.0002
2	−0.12814	1.40490	0.0067	−0.45079	−0.10817	0.0062	−0.32436	−0.54002	0.0062
3	−1.77550	1.42890	0.0155	−1.34900	−0.20168	0.0172	0.24511	0.14060	0.0172
4	−0.45468	−0.44885	0.0003	0.28083	−0.06194	0.0003	−0.15565	−0.47297	0.0003
5	−0.88612	0.22512	0.0090	−0.52435	0.26672	0.0086	0.56790	0.17316	0.0086
6	2.78800	2.58670	0.0002	0.01855	−0.00342	0.0003	0.24601	0.20367	0.0003
7	−0.87412	−0.77399	0.0007	0.20028	0.02254	0.0020	0.50329	0.31775	0.0020
8	−0.97404	3.44330	0.0040	−1.51350	−0.45184	0.0092	−0.16859	−0.28875	0.0092
9	−1.30030	3.42290	0.0084	−1.00980	−0.47712	0.0128	0.12150	0.13262	0.0128
10	−2.92240	3.02790	0.0087	−0.46828	−0.30540	0.0122	0.46809	0.54558	0.0122
11	−0.82332	4.62320	0.0076	−1.97630	−0.72698	0.0100	−0.14379	−0.20993	0.0100
12	−1.13290	4.44090	0.0056	−1.65290	−0.76227	0.0159	0.15110	0.14663	0.0159
13	−1.77430	4.41190	0.0028	−1.18320	−0.76006	0.0142	0.36629	0.59531	0.0142
14	−1.37540	1.05210	0.0186	−1.34910	0.13635	0.0226	0.64272	0.14413	0.0226
15	−1.21700	1.30390	0.0106	−1.47220	0.16392	0.0137	0.69639	0.21873	0.0137
16	−1.10900	0.95618	0.0111	−1.34770	0.56933	0.0117	1.08180	0.22965	0.0117
17	−0.69322	1.56870	0.0158	−0.99840	0.15692	0.0134	1.21780	0.56476	0.0134
18	−0.85482	1.50800	0.0181	−1.14110	0.44758	0.0148	1.40950	0.50456	0.0148
19	−0.62976	1.12250	0.0160	−0.28636	0.26401	0.0110	1.78520	0.89679	0.0110
20	0.79305	0.35333	0.0019	0.43418	−0.07648	0.0019	−0.58477	−0.56821	0.0019
21	5.02360	0.19712	0.0071	0.61685	0.01654	0.0055	−0.74856	−0.64703	0.0055
22	3.56660	2.85610	0.0115	1.04050	−0.20650	0.0038	−0.08946	−0.14078	0.0038
23	−0.25576	−0.44379	0.0033	0.28316	−0.07849	0.0028	−0.38949	−0.46438	0.0028
24	1.93430	−0.04111	0.0148	0.29847	−0.02098	0.0145	−0.49959	−0.53986	0.0145
25	−0.89423	1.52300	0.0238	−0.66199	−0.27447	0.0220	−0.27613	−0.68482	0.0220
26	−0.91913	2.45150	0.0204	−1.31870	−0.26291	0.0225	−0.32289	−0.59887	0.0225
27	−0.75351	4.73490	0.0157	−1.53680	−0.90228	0.0154	−0.54783	−0.37543	0.0154
28	0.04759	−0.80992	0.0135	−1.42310	−0.61472	0.0223	−0.95868	−0.28955	0.0223
29	−0.62443	5.29060	0.0109	−1.83680	−0.92002	0.0210	−0.43862	−0.31874	0.0210
30	−0.95077	4.33030	0.0135	−2.12470	−0.64438	0.0166	−0.27483	−0.40872	0.0166
31	−0.40575	2.60240	0.0207	0.62042	−0.41390	0.0174	0.36286	0.21032	0.0174
32	−0.69008	−0.29116	0.0128	5.40510	−4.61310	0.1366	2.53210	4.26080	0.1366
33	−0.89825	−0.56135	0.0110	5.03770	−2.96300	0.0445	2.56910	3.85180	0.0445
34	−0.66433	−0.32286	0.0134	6.57450	−6.83540	0.1993	−1.84960	9.39600	0.1993
35	−0.84058	−0.37582	0.0261	7.18140	−6.33600	0.1836	3.06910	5.64500	0.1836
36	0.15317	0.69427	0.0553	7.38860	−8.93680	0.3447	2.06830	6.47950	0.3447
37	−0.64028	0.02893	0.0465	5.22270	−3.83570	0.1295	2.73220	3.89990	0.1295
						$\bar{S}$			
			0.0130			0.0378			0.0378
						$S_{\min}$			
			0.0002			0.0002			0.0002
						$S_{\max}$			
			0.0553			0.3447			0.3447

temperature ranges. Although the number of files is not very extensive, they comprise the five different types of distributions $\eta = f(x_2)$ that can be found in studies of this kind, and which are presented in Figure 4. For greater clarity, however, we decided to divide this figure into Figure 4(a)–(e). The distributions shown in Figure 4(a)–(e) have been fitted by Equation (3).

The files shown in Table 7 have been fitted by means of Equations (3)–(5), and the results of these fits are reported in Table 8.

Table 8 in turn yields the following results: in 62% of the cases Equation (3) offers better results than Equations (4) and (5) and in 8% the same results. In addition, the mean SD for Equation (3) is 0.01303, *versus* 0.03784 in the case of Equations (4) and (5).

5. Conclusions

From the current study it is concluded that negative values of V^E correspond to all the mixtures analysed. The minimum V^E corresponds to the mixture (water + 2-propanol) and the maximum V^E to the mixture (water + 1,2,3-propanetriol).

The $\Delta\eta$ values are positive for the mixtures of water + (1-propanol and 2-propanol), and negative for the rest of the mixtures analysed. The minimum $\Delta\eta$ corresponds to the mixture (water + 1,2,3-propanetriol), and the maximum to (water + 2-propanol).

The G^{*E} values are positive for all the mixtures analysed, and the maximum corresponds to the mixture (water + 1,3-propanediol).

Regarding the study of viscosity, it is seen that for the mixtures of water + (alcohols, polyols with three carbon atoms), Equation (3) offers better results for the SD S than Equations (4) and (5).

As to the files presented, Equation (3) likewise offers better results than Equations (4) and (5).

Moreover, both for the binary mixtures of water + (alcohols, polyols with three carbon atoms) and for the reference files, Equation (3) offers better results for the mean SD $\overline{S}$ than Equations (4) and (5).

In view of the above, Equation (3) can be regarded as an adequate correlation equation for studying the viscosity of binary mixtures of liquids.

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