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Viscosity Arrhenius Activation Energy and Derived Partial Molar Properties in 1,4-Dioxane + Water Binary Mixtures from 293.15 to 323.15 K

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Abstract The knowledge and prediction of physicochemical properties of binary liquid mixtures is of great importance for understanding intermolecular interactions. Viscosities (η) have been investigated by using density (ρ) and kinematic viscosity (ν) measurements for 1,4-dioxane + water (D–W) mixtures over the entire range of mole fractions under atmospheric pressure, at 311.15, 316.15 and 320.15 K, in order to increase the studied temperatures range available from the literature and to improve the investigations. The viscosity Arrhenius activation energy of 1,4-dioxane + water mixtures was calculated from the present experimental viscosity measurements, and those presented in a previous work at only four temperatures, and for three temperatures in the present work, over the entire range of composition in the temperatures range from 293.15 to 323.15 K. Based on the partial molar activation energy from the Arrhenius equation for viscosity, interactions between water and 1,4-dioxane molecules are discussed. Comparison between some reduced Redlich–Kister functions covering the composition domain shows the existence of two distinct behaviors.

Keywords Binary liquid mixtures · Viscosity · Arrhenius activation energy · 1,4-Dioxane · Molecular interactions

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1 Introduction

Physical and chemical properties of binary liquid mixtures are important for understanding thermodynamic behavior and for designing and optimizing industrial processes.

This article is a continuation of earlier works that involve the study of 1,4-dioxane + water (D–W) binary liquid mixtures [1–6]. The 1,4-dioxane + water solvent mixture is interesting, and a great deal of good work has been reported by many researchers [7–14] with different experimental methods in order to understand the hydrogen bonding interactions and correlation length between unlike molecules in cluster formation. Studies of the physico-chemical properties of systems with 1,4-dioxane and water are important for understanding the influence of their intermolecular interactions. In the framework of scientific research on binary liquid mixtures in the chemical, pharmaceutical and foodstuff industries, the study of correlation equations for representing excess or deviation quantities is very interesting in applied chemistry. They are used to predict physicochemical properties for hydraulic calculations of fluid transport and for energy transference calculations, especially for viscosity [15]. Hence, in previous work [5], the viscosity of 1,4-dioxane + water mixtures results were fitted to the Redlich–Kister (RK) polynomial equation [16, 17] and the recently proposed Herráez correlation equation [15] in order to derive binary interaction coefficients and to estimate the corresponding standard deviations between experimental and calculated values. We have noted that, at infinite dilution of 1,4-dioxane in water, the Herráez exponential function's values converge to a surprising single point (0.5) independent of temperature, which was justified [5, 6] and considered to be an universal exponent characterizing predominant solute–solute interaction at infinite dilution of dioxane in water.

In this work we present a study of viscosity and Arrhenius behavior in 1,4-dioxane + water binary mixtures between 293.15 and 323.15 K. For this purpose, new experimental dynamic viscosity data (η) for the binary liquid mixtures of 1,4-dioxane + water at 311.15, 316.15 and 320.15 K are reported and used with data from previous works. The Arrhenius parameters (activation energy and pre-exponential entropic factor) of the pure components, and their binary mixtures, are determined as a function of temperature. The excess activation energy (ΔE_{a}) and the logarithm of the entropic factor deviation ($\Delta \ln A_S$) were correlated using reduced RK properties.

Note that the reduced Redlich–Kister functions relative to the Arrhenius parameters, which are equivalent to apparent molar properties, are more sensitive than the excess properties to interactions and give more information. In addition, by assuming that the activation energy is a thermodynamic quantity, partial molar activation energies have been determined to describe individual contributions of each pure component to the mixture for each composition.

2 Experimental Details

2.1 Materials

Dioxane (Merck, ultrapure for analysis) was distilled under reduced pressure. The density of the dioxane was found to be 1027.95 $\mathrm{kg{\cdot}m^{-3}}$ at 25 °C (literature values 1027.80 $\mathrm{kg{\cdot}m^{-3}}$ [18] and 1027.92 $\mathrm{kg{\cdot}m^{-3}}$ [19]). Deionized and triple distilled water with a specific conductance $< 10^{-4}$ $\mathrm{S{\cdot}m^{-1}}$ was used for mixture preparations of various compositions; its observed density is 997.045 $\mathrm{kg{\cdot}m^{-3}}$ at 25 °C, which is within 0.003 % of the literature value [20].

The mixtures were prepared by mixing known masses of pure liquids in air-tight containers, with care being taken to minimize exposure to air—especially carbon dioxide. All measurements of mass were performed on an electronic balance accurate to 1×10^{-7} kg.

2.2 Measurements

Densities of the pure components and their compositions were measured on a vibrating-tube densitometer, reproducible to 10^{-2} kg·m^{-3} (Anton Paar model DMA 4500), capable of 0.005 °C temperature accuracy over a wide temperature range. The densitometer needs to be carefully calibrated periodically with two liquids of different densities; we chose as standards triple-distilled water and methanol with density data taken from the literature [19, 20]. Comparison between experimental values and those of literature for the pure components are reported in previous work [21].

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

$$\eta = \rho \cdot \nu \tag{1}$$

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

$$\nu = k \cdot (t - \theta) \tag{2}$$

where t is the flow time, k is a constant for a given viscometer (AVS/N-Chott-Gerate), and θ is the correction time. Ubbelohde viscometers of relatively long flow times (60 to 200 s) were used to minimize the time corrections. The viscometer was submerged in a thermally stabilized water bath with thermal regulation of the order of ±0.001 K. The time given to attain thermal equilibrium for the viscometer and contents was 15 min. The flow time was measured with a stopwatch accurate to 0.01 s. The viscometer was calibrated with two liquids, acetone and n-hexane of known density and viscosity (high performance liquid chromatography grade) [18, 22]. The reproducibility of viscosity measurements was 0.00005 Pa·s. Five to seven sets of readings of the flow times were taken for each pure liquid or liquid mixture and their arithmetic mean was considered for the calculations. We note that both the densitometer and the viscometer were calibrated over a range of temperatures that cover all three studied temperatures. We also note that the density values for each composition and temperature permit both the calculation of the dynamic viscosity from the measured kinematic one and the conversion of concentration scales. The measured viscosities of the pure liquid components (water and 1,4-dioxane), presented here or in previous papers, are compared with literature data in Table 1. The experimental densities (ρ) of the binary water–dioxane mixtures at 311.15 K, 316.15 K and 320.15 K are listed in Table 2.

3 Viscosity Results

The viscosities of the pure liquid components (water and 1,4-dioxane) are shown in Table 1.

At least 28 density and viscosity measurements were performed (with repetition) for each binary system at 311.15, 316.15 and 320.15 K over the full mole fraction range ($0 \le x_1 \le 1$). The experimental viscosities (η) of binary water–dioxane mixtures at 311.15, 316.15 and 320.15 K are listed in Table 2.

The components of this system, 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 been reported [2, 3, 11, 37]. Therefore, the observed negative excess volumes [1–3, 9, 10, 38] are an indication of strong heteromolecular interactions in the liquid mixtures and, according to Fort et al. [39], this can be attributed to specific interactions between dioxane and water molecules as investigated in some recent structural studies

Table 1 Comparison of experimental viscosities η (mPa·s) with the literature data for pure components at different temperatures from $T = (293.15 \text{ to } 323.15)$ K

T (K)	Water		1,4-Dioxane	
	Expt.	Lit.	Expt.	Lit.
293.15	1.0050 [4], 1.0030 [5]	1.0021 [24], 0.9990 [26], 1.0032 [27], 1.00219 [28], 1.0020 [35]	1.3125 [4], 1.3069 [5]	–
298.15	0.8903 [2], 0.9166 [3], 0.8904 [5]	0.8910 [12]	1.1766 [2], 1.1902 [3], 1.1761 [5]	1.1720 [12], 1.1810 [25], 1.1770 [36]
302.15	0.8148 [5]	–	1.0989 [5]	–
303.15	0.8007 [4]	0.8075 [24], 0.8005 [27], 0.7970 [29], 0.7931 [30], 0.7977 [35]	1.1127 [4]	1.0937 [31], 1.1000 [32], 1.086 [33], 1.101 [34]
306.15	0.7491 [5]	0.7540 [13]	1.0291 [5]	1.0220 [23]
309.15	0.7045 [5]	–	0.98150 [5]	–
313.15	0.6560 [4]	0.6660 [24], 0.6568 [27], 0.65277 [28], 0.6382 [30], 0.6532 [35]	0.96030 [4]	0.9425 [33]
316.15	0.61885	0.6240 [13]	0.88591	0.8710 [13]
323.15	–	0.5440 [13], 0.5470 [35]	–	0.8070 [14], 0.7870 [36]

[1, 2, 7, 8], and non-specific interactions (dipole–dipole, dipole-induced–dipole, dispersion interactions) that depend on temperature [39]. Hence, there will be a significant degree of H-bounding, leading to strong correlation between the molecules; also, the difference in the size of the molecules can play a role in this respect [13, 14, 38]. We add that specific interactions exist in this system.

The large positive viscosity deviation $\Delta\eta$ observed in previous works [9, 10, 38] can be interpreted qualitatively by considering the strength of intermolecular hydrogen bonding, molecular size, and shape of the component molecules. Also, it indicates cluster structure stabilization [1, 8, 40, 41]. In fact, below this range ($0.15 < x_1 < 0.33$), we must also consider the appreciable modification of liquid structure above 0.08 molar fraction in dioxane (30 % weight) [1, 8, 38].

4 Arrhenius Behavior

4.1 Pure Components

Simple Arrhenius viscosity behavior is observed when the dynamic viscosity (η) of the liquid system obeys to the well known Andrade equation:

$$\eta = A_S e^{\frac{E_a}{RT}} \tag{3}$$

where R is the perfect gas constant, E_a the molar Arrhenius activity energy and A_S the pre-exponential factor (also called the Arrhenius entropic factor) corresponding theoretically to

Table 2 Densities (10^3 kg·m^{-3}) and viscosities (10^{-3} Pa·s) for binary systems 1,4-dioxane (1) + water (2) against the mole fraction x_1 in dioxane at 311.15, 316.15 and 320.15

x_1	ρ (10^3 kg·m^{-3})			η (10^{-3} Pa·s)		
	311.15 K	316.15 K	320.15 K	311.15 K	316.15 K	320.15 K
0.0000	0.99297	0.99103	0.98934	0.68334	0.61885	0.57477
0.00206	0.99387	0.99218	0.99076	0.69772	0.62865	0.58551
0.00628	0.99528	0.99350	0.99198	0.71765	0.64877	0.59921
0.01516	0.99821	0.99622	0.99455	0.75777	0.69105	0.62767
0.03482	1.00412	1.00180	0.99988	0.85965	0.78246	0.70537
0.05303	1.00865	1.00615	1.00412	0.95643	0.86188	0.78196
0.07366	1.01272	1.00991	1.00764	1.0597	0.94332	0.86482
0.08413	1.01445	1.01154	1.00921	1.1073	0.98070	0.90371
0.1114	1.01789	1.01460	1.01193	1.2192	1.0649	0.99356
0.1433	1.02086	1.01727	1.01436	1.3105	1.1396	1.0655
0.1726	1.02265	1.01885	1.01578	1.3701	1.1877	1.1130
0.2065	1.02405	1.01992	1.01656	1.4092	1.2226	1.1437
0.2501	1.02505	1.02074	1.01726	1.4258	1.2418	1.1591
0.3029	1.02530	1.02077	1.01712	1.4159	1.2381	1.1579
0.3560	1.02491	1.02034	1.01670	1.3885	1.2152	1.1457
0.4203	1.02385	1.01913	1.01538	1.3386	1.1726	1.1179
0.4996	1.02208	1.01701	1.01295	1.2538	1.1100	1.0592
0.5367	1.02127	1.01621	1.01218	1.2260	1.0803	1.0396
0.5999	1.01972	1.01448	1.01030	1.1684	1.0331	0.99613
0.6479	1.01879	1.01344	1.00914	1.1299	1.0021	0.96861
0.7309	1.01722	1.01173	1.00731	1.0775	0.95965	0.93253
0.7621	1.01671	1.01119	1.00675	1.0931	0.94690	0.94950
0.7953	1.01612	1.01055	1.00606	1.0422	0.93482	0.90786
0.8686	1.01492	1.00923	1.00464	1.0044	0.91283	0.87929
0.9092	1.01437	1.00860	1.00394	0.98616	0.90365	0.86473
0.9760	1.01357	1.00790	1.00337	0.96200	0.89188	0.84297
0.9855	1.01347	1.00780	1.00326	0.95466	0.88984	0.83606
1.0000	1.01328	1.00758	1.00301	0.94969	0.88591	0.82763

the viscosity at infinite temperature, and its also denoted as η_∞. Equation 3 can be rewritten in the following logarithmic form to give access to the E_a values:

$$\ln\eta = \ln A_S + \left(\frac{E_a}{R}\right)\cdot\left(\frac{1}{T}\right) \tag{4}$$

However, for the pure components (water or dioxane), plots of the logarithm of dynamic viscosity given in the literature [2–4, 12, 13, 23–36] against the reciprocal of absolute temperature are not linear when we consider a large temperature range. The E_a values are thus dependent on temperature. So, in order to obtain the true activation energy $E_a(T)$ as a function of temperature, we use the following equation:

$$E_a(T) = \frac{R\partial\ln\eta(T)}{\partial(\frac{1}{T})} \tag{5}$$

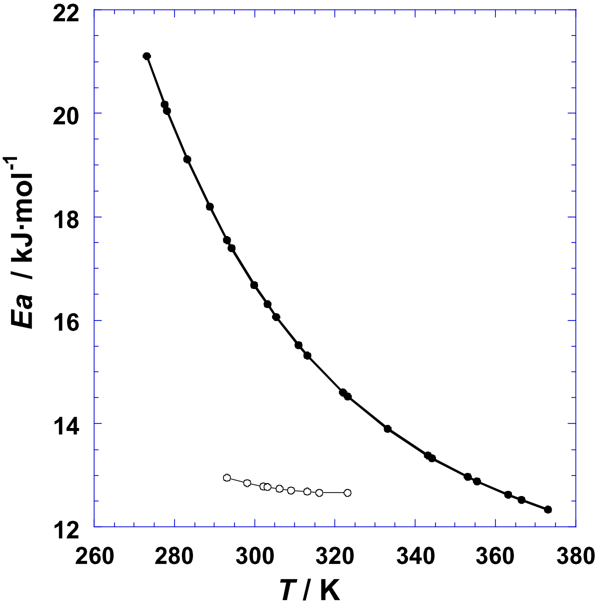


Fig. 1 Arrhenius activation energy E_a of the pure liquid components versus the absolute temperature T as given in this work, previous works [2–5], and from the literature [12, 13, 23–36]: (●) water, (○) dioxane

with the $\ln \eta(T)$ values fitted by a least-squares optimization procedure to a fourth-order polynomial in the reciprocal of the absolute temperature $(1/T)$.

The calculated values of E_a are plotted versus absolute temperature (T) in Fig. 1. It can be seen that E_a for pure water decreases appreciably with temperature, while that of pure dioxane varies only slightly. Hence, we can consider the viscosity of pure dioxane to follow approximately Arrhenius behavior, especially for a moderately large range of temperature (Fig. 1). In the same way, the calculated values of the entropic factor A_S (Eq. 4) for pure water and dioxane are plotted versus absolute temperature (T) in Fig. 2. We observe similar behavior for water: A_S varies appreciably with temperature while that of pure dioxane remains practically constant. In addition, we note that the magnitudes of the η_∞ values are in the order of the µPa·s, which leads us to the semi-empirical interpretation that the η_∞ values are highly correlated with the pure component's vapor phase viscosities. Figure 2 shows the viscosities of water vapor taken from the literature [42]. We can add that, opposite to the behavior of the liquid phase, the viscosity of the vapor increases with increasing temperature (Fig. 2). Consequently, the same behavior is also observed for the variation of the η_∞ values with temperature. In the same way, the Arrhenius activation energies can be closely related to the enthalpy of vaporization $\Delta_{\text{vap}}H$ of the pure component, and their viscosity can be predicted for both gases and liquids [1, 2, 6, 42]. In fact, some authors use Eq. 3 for expressing the viscosity of pure liquid component, but substitute for A_S the viscosity of the pure vapor of the same component at the same pressure and temperature [21]. Furthermore, the Arrhenius activation energy (E_a) for viscosity describes the energy needed for the liquid molecules to exceed the liquid-specific potential barrier. By using this energy of activation, the liquid molecules are able to move against the interval flow resistance that is caused by friction between the neighboring liquid molecules.

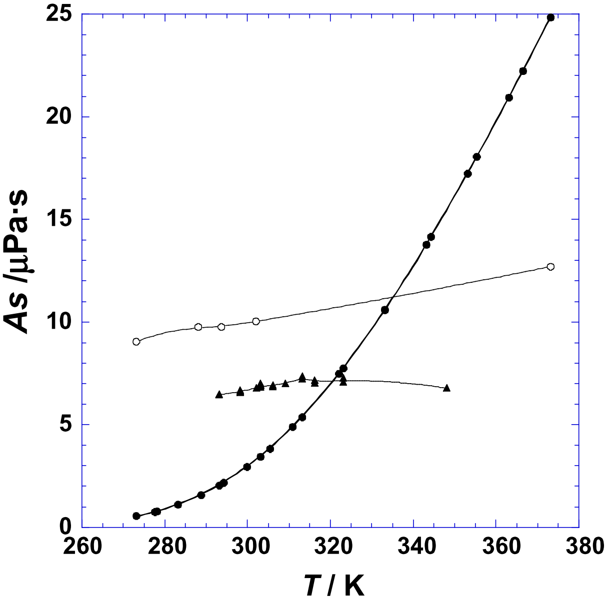


Fig. 2 Viscosity at infinite temperature (η_∞ or A_S) of pure liquid components, as given in this work, previous works [2–5], and from the literature [12, 13, 23–36]: (●) water, (▲) dioxane along with the viscosity of water vapor (in µPa·s), (○) [42], versus the absolute temperature (T)

4.2 The 1,4-Dioxane + Water Mixtures

Considering the 1,4-dioxane (1) + water (2) mixtures at fixed molar fraction (x_1), the plot of the logarithm of dynamic viscosity $\ln\eta$ versus the reciprocal of absolute temperature ($1/T$) is practically linear [6] over the full range of composition, and thus the Arrhenius parameters $E_a(x_1)$ and $A_S(x_1)$ are quasi-independent of temperature over the studied range (293.15 to 323.115 K). Using both graphical and least-squares optimization procedures, the slope of the straight line is equal to E_a/R and the intercept is equal to $\ln A_S$. Calculated values of (E_a) and ($\ln A_S$) are reported in Table 3 and plotted in Fig. 3. Inspection of the E_a values and those of the enthalpy (ΔH^*) of activation of viscous flow (Table 3), calculated from the Gibbs energy ΔG^* in previous work [43], shows that E_a and ΔH^* are very closely related. In this context, the variation of the Arrhenius activation energy E_a versus mole fraction (x_1) can give evidence for a change in the complex structure or a cluster formed in binary liquid mixtures as a function of temperature or mixture composition [43]. Thus, in the water-rich region, the rapid decrease of E_a shows a change of the structure of water as reported in the literature at 30 % w/w dioxane (i.e. $x_1 = 0.08$) [38], which corresponds approximately to the minimum of $\ln A_S$. Also, as indicated by Suzuki et al. [11], the rapid increase of $E_a(x_1)$ and the corresponding decrease of $\ln A_S(x_1)$ show that the hydrogen bonding network of water may be increased by the so-called hydrophobic hydration. Furthermore, the maximum of $E_a(x_1)$ at $x_1 \approx 0.2$ shows that there are two principal association-type structures delimited by the percent composition and corresponding to the cluster ($C_4H_8O_2{\cdot}4H_2O$ or $2C_4H_8O_2{\cdot}8H_2O$) discussed in previous works [1, 2, 6, 38, 44].

Nevertheless, values of $\ln A_S(x_1)$ permit us to calculate the values of the pre-exponential factor A_S (in µPa·s) that are plotted in Fig. 4. Since the A_S values are closely related to the viscosity of the system in its vapor phase, we observe high values of viscosity in the dioxane-rich region and we assume that bonding of dioxane molecules is more correlated and ordered in the vapor state. We add that in vapor–liquid equilibrium studies, the mixing enthalpy shows high positives values in this region [1, 2, 14]. In addition, the water–dioxane

Table 3 Arrhenius activation energy E_a (kJ·mol^{-1}), entropic factor of Arrhenius A_S (10^{-6} Pa·s), enthalpy of activation of viscous flow ΔH^* (kJ·mol^{-1}) and partial molar activation energy (kJ·mol^{-1}) for mixtures {1,4-dioxane (1) + water (2)} as a function of the mole fraction of dioxane x_1 in the temperature range (293.15 to 323.15 K)

x_1	E_a (kJ·mol^{-1})	ΔH^{*}[b] (kJ·mol^{-1})	A_S (10^{-6} Pa·s)	E_a1 (kJ·mol^{-1})	E_a2 (kJ·mol^{-1})
0.0000	16.1[a]	–	1.36[a]	–	–
	15.92	16.399	1.451	145.02	15.92
0.00206	16.17	16.420	1.354	135.39	15.96
0.00628	16.61	16.485	1.174	116.72	16.04
0.01516	17.33	17.080	0.935	83.92	16.37
0.03482	18.22	17.953	0.751	44.18	17.29
0.05303	18.54	18.124	0.738	29.34	17.95
0.07366	18.70	18.327	0.769	23.70	18.30
0.08413	18.75	18.441	0.788	22.84	18.37
0.1114	18.88	18.800	0.827	22.79	18.37
0.1433	19.01	18.978	0.843	22.90	18.36
0.1726	19.13	18.968	0.842	21.72	18.48
0.2065	19.18	18.743	0.849	18.93	19.27
0.2501	19.03	18.354	0.910	14.23	20.63
0.3029	18.51	17.759	1.105	9.290	22.51
0.3560	17.70	17.238	1.485	6.870	23.69
0.4203	16.62	16.458	2.175	7.370	23.33
0.4996	15.51	15.390	3.102	10.10	20.96
0.5367	15.18	15.004	3.468	10.98	20.05
0.5999	14.64	14.382	4.071	11.22	19.76
0.6479	14.20	13.953	4.667	10.71	20.62
0.7309	13.30	13.334	6.305	10.33	21.38
0.7621	12.97	13.150	7.490	10.59	20.60
0.7953	12.67	12.937	7.779	11.02	19.06
0.8686	12.24	12.702	8.852	11.70	15.80
0.9092	12.09	12.589	9.205	11.81	14.98
0.9760	12.15	12.478	8.775	12.43	0.930
0.9855	12.28	12.463	8.274	12.55	−5.730
1.0000	12.66	12.546	7.12	12.66	−20.17
	12.64[a]	–	7.384[a]	–	–

[a] Previous work. [6] (13 data points, 293.15 K–323.15 K)

[b] Previous work. [42] (28 data points, 293.15 K–309.15 K)

interaction has an H-bond character [1] and the observed maximum of E_a (Fig. 3) reflects the strong energy of hydrogen bonds between molecules [1, 7, 8, 16, 38]. Therefore, the distinct behaviors, limited approximately by the mole fraction $x_1 \approx 0.23$ of dioxane, are clearly shown when the correlation disorder–order is plotted in Fig. 5.

In addition, determination of the activation energy necessitates results at more temperatures for a high quality of fitting and accurate mathematical calculation of the derivative

Fig. 3 Arrhenius activation energy E_a and logarithm of the entropic factor $\ln A_S$ of viscosity (Eqs. 3 and 4) for dioxane + water mixtures versus the mole fraction x_1 of dioxane in the temperature range (293.15 to 323.15 K): (●) $\ln A_S$, (○) E_a (kJ·mol^{-1})

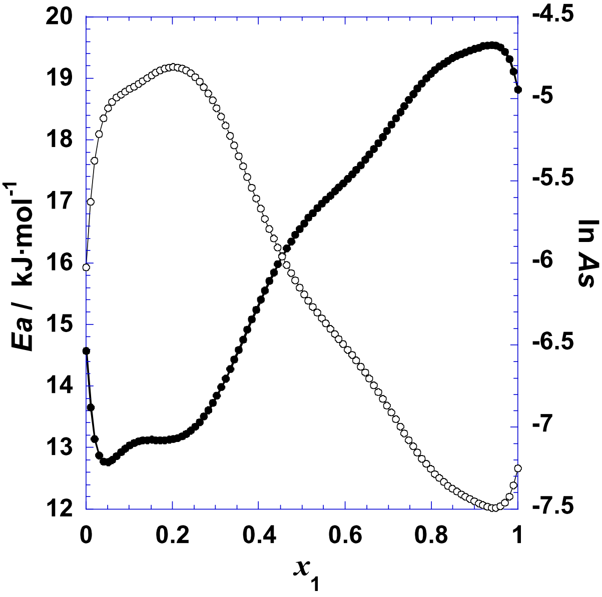
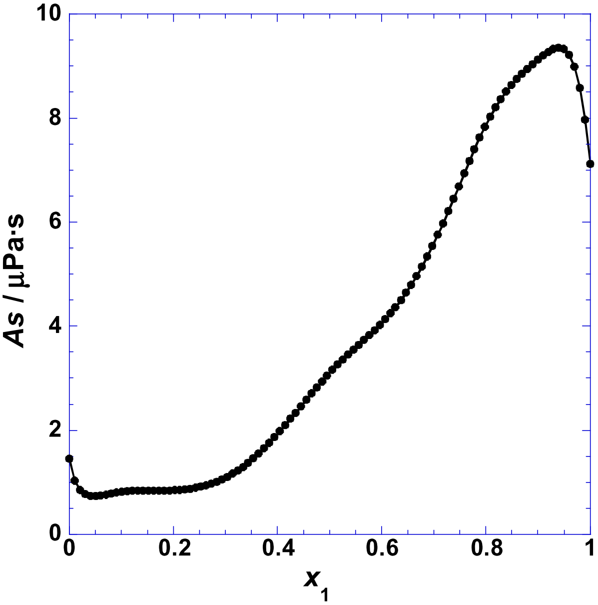


Fig. 4 Viscosity at infinite temperature (η_∞ or A_S) in μPa·s for 1,4-dioxane (1) + water (2) mixtures versus the mole fraction x_1 of dioxane in the temperature range 293.15 to 323.15 K



against the temperature. For this reason, we have added three new temperatures (311.15, 316.15 and 320.15 K) and more molar compositions for remediating the deficiency of data collected in a previous work at temperatures that show only one peculiar composition, $x_1 \approx 0.23$ [6]. Thus, in the present work, three peculiar compositions are observed showing interesting cluster varieties. Hence, we can locate the step for the breaking of water structure

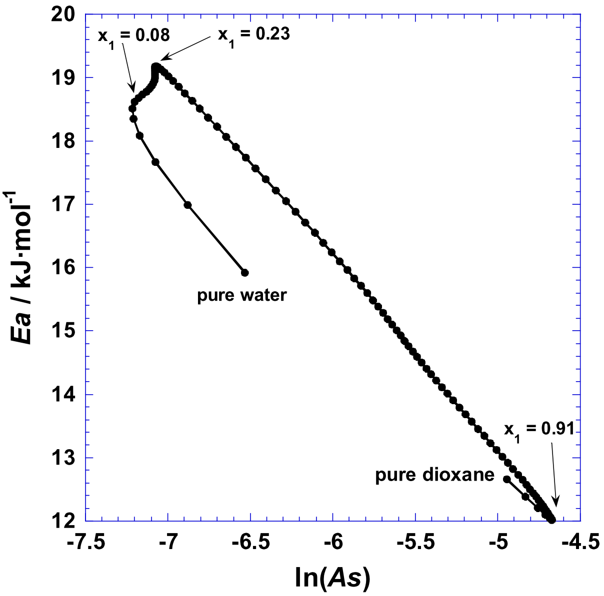


Fig. 5 Correlation between the Arrhenius activation energy (E_a) of viscosity and the logarithm of the entropic factor of Arrhenius ($\ln A_S$) for dioxane + water mixtures in the temperature range 293.15 to 323.15 K

mentioned above [38], by inspecting the strong curvatures at high dilution in the two ends of composition range at $x_1 \approx 0.08$ and at $x_1 \approx 0.91$ for the cluster ($10C_4H_8O_2 \cdot H_2O$).

4.3 The Reduced Redlich–Kister Functions

For the 1,4-dioxane + water mixtures, the excess activation energy (ΔE_a) and the logarithm of the entropic factor deviation ($\Delta \ln A_S$) were correlated by the Redlich–Kister (RK) [16] equation (Eqs. 6a and 6b):

$$\Delta Y = Y - x_1 Y_1 - (1 - x_1) Y_2 \tag{6a}$$

$$\Delta Y = x_1(1 - x_1) \sum_{p=0}^{p=n} A_p (2x_1 - 1)^p \tag{6b}$$

where Y_1 and Y_2 are the Y property of the pure components, x_1 is the mole fraction of dioxane, the A_p are adjustable parameters, n is the degree of polynomial expansion, and the property Y corresponds to the Arrhenius parameters of Eq. 4 (E_a or $\ln A_S$). The adjustable parameters A_p, obtained by fitting the equations to the experimental values with a least-squares algorithm, are given in Table 4 along with the standard deviation, σ, defined as follows:

$$\sigma = \left[\frac{1}{N - m} \sum_{i=1}^{i=N} \left(Y_i^{\text{exp}} - Y_i^{\text{calc}} \right)^2 \right]^{1/2} \tag{7}$$

where N is the number of experimental data and m is the number of parameters.

Desnoyers et al. [17] showed that an examination of the trends of the dependence of ΔY on the mole fraction x_1 suggests that many of these systems are similar and that, in agreement with the original statements of RK, it is better to use the reduced RK property $Q_{\text{RK},Y}(x_1)$ (Eq. 8) for this purpose:

$$Q_{\text{RK},Y}(x_1) = \Delta Y / x_1(1 - x_1) \tag{8}$$

Table 4 The least-squares constants, A_p, for the fitting of the reduced Redlich–Kister excess property (Eq. 6b) $Q_{\mathrm{RK},Y}(x_1)$ with temperature, the corresponding standard deviation σ (%) for the Arrhenius activation energy E_a (kJ·mol^{-1}), and the logarithm of the entropic factor of Arrhenius $\ln(A_S/10^{-6}$ Pa·s) for 1,4-dioxane (1) + water (2) mixtures in the temperatures range (293.15 to 323.15 K)

Property	A_0	A_1	A_2	A_3	A_4	A_5	σ
$\ln(A_S/10^{-6}$ Pa·s)	7.1043	−30.241	−7.9358	67.889	34.181	−107.11	0.017
E_a (kJ·mol^{-1})	−0.99504	9.8054	5.3508	−29.141	−13.296	43.318	0.014

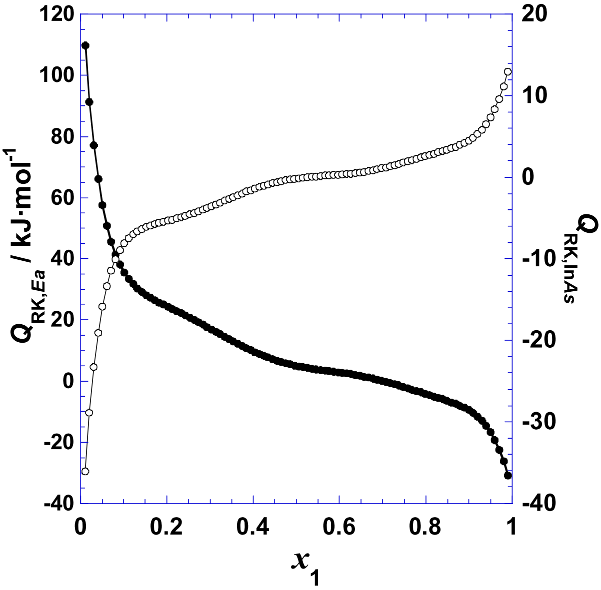


Fig. 6 Experimental reduced Redlich–Kister excess properties $Q_{\mathrm{RK},Y}(x_1)$ (Eq. 3) for dioxane + water mixtures versus molar fraction x_1 in dioxane in the temperature range 293.15 to 323.15 K, (●) $Q_{\mathrm{RK},E_\mathrm{a}}(x_1)$, (○) $Q_{\mathrm{RK},\ln A_S}(x_1)$

In fact, Redlich and Kister treated the data with a power series (Eq. 6b), putting greater weight on data near 0.5 mole fraction. As Desnoyers et al. [17] have shown, this is not always the best approach for binary mixtures having specific interactions such as association at low concentration. Therefore, elimination of the product factor $x_1(1-x_1)$ in Eq. 8 removes this effect and gives a specific reduced function $Q_{\mathrm{RK},Y}(x_1)$, characterizing the Y-property and also giving evidence for the existence of important interactions [6].

For the water–dioxane mixtures studied in this work, the experimental reduced RK function $Q_{\mathrm{RK},Y}(x_1)$ is plotted in Fig. 6 against the mole fraction x_1 of dioxane. We note that the functions $Q_{\mathrm{RK},E_\mathrm{a}}(x_1)$ and $Q_{\mathrm{RK},\ln A_S}(x_1)$ vary oppositely with the mole fraction x_1. In the first region discussed above ($x_1 < 0.2$), $Q_{\mathrm{RK},Y}(x_1)$ shows a rapid variation while in the second region ($x_1 > 0.2$) it changes moderately. We note that at infinite dilution of dioxane in water ($x_1 \approx 0^+$), $Q_{\mathrm{RK},Y}(x_1)$ diverges. Two assumptions are possible, either there are very strong solute–solute interaction at higher dilution, or this divergence is due to the Jones–Dole viscosity behavior of dioxane in water [6, 7, 43] which can be proved by using the limited asymptotic expansion of $Y(x_1)$ in x_1 near $x_1 = 0$, developed in previous work [6].

Furthermore, by elimination of the variable x_1, the plot of the reduced RK excess function $Q_{\mathrm{RK},E_\mathrm{a}}$ against the reduced function $Q_{\mathrm{RK},\ln A_S}$ (Fig. 7) leads us to conclude that we

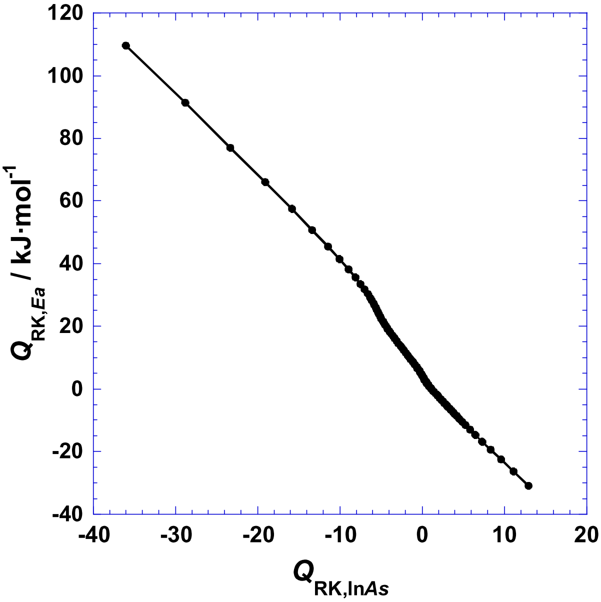


Fig. 7 Correlation between the experimental reduced Redlich–Kister functions $Q_{\mathrm{RK},E_\mathrm{a}}(x_1)$ and $Q_{\mathrm{RK},\ln A_S}(x_1)$ for dioxane + water mixtures in the temperature range 293.15 to 323.15 K

only need one of the two $Q_{\mathrm{RK},Y}(x_1)$ functions for giving practically a full interpretation. This is because of the strong correlation revealed by the quasi-linear dependence between the $Q_{\mathrm{RK},Y}(x_1)$ functions (Fig. 7). In the same context, we can interpret other behaviors implicitly using both of the two reduced RK functions $Q_{\mathrm{RK},E_\mathrm{a}}(x_1)$ and $Q_{\mathrm{RK},\ln A_S}(x_1)$ when we plot the Grunberg and Nissan [45] interaction parameter G_{12} (Eq. 9) at the temperature T:

$$\ln\eta = x_1\ln\eta_1 + x_2\ln\eta_2 + x_1x_2G_{12} \tag{9}$$

where the indexes 1 and 2 correspond to the pure components 1,4-dioxane (1) and water (2).

In fact, by considering the Arrhenius behavior (Eq. 4) for the viscosity shown in Eq. 9 for the mixtures, and approximately for the pure components, we can easily derive the following relationship:

$$G_{12,T}(x_1) = Q_{\mathrm{RK},\ln A_S}(x_1) + Q_{\mathrm{RK},E_\mathrm{a}}(x_1)/RT \tag{10}$$

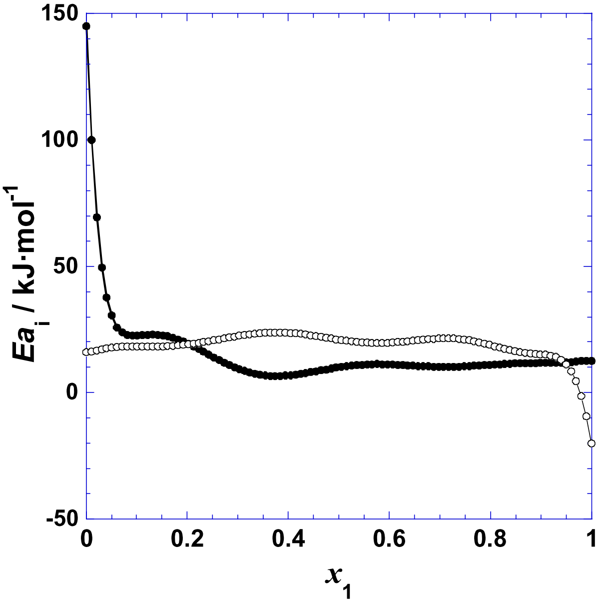
5 Partial Molar Activation Energy

Considering the quasi-equality between the Arrhenius activation energy E_a and the enthalpy of activation of viscous flow ΔH^* mentioned in Sect. 4.2 and Table 3, we can assume that $E_\mathrm{a}(x_1)$ is approximately a thermodynamic function and we can then define the partial molar activation energies $E_{\mathrm{a}1}$ and $E_{\mathrm{a}2}$ for dioxane and water, respectively, by the following equations:

$$E_{\mathrm{a}1}(x_1) = E_\mathrm{a}(x_1) + (1-x_1)\frac{\partial E_\mathrm{a}(x_1)}{\partial(x_1)} \tag{11}$$

$$E_{\mathrm{a}2}(x_1) = E_\mathrm{a}(x_1) - x_1\frac{\partial E_\mathrm{a}(x_1)}{\partial(x_1)} \tag{12}$$

Fig. 8 Partial Arrhenius activation energy E_a of viscosity (Eqs. 11 and 12) for 1,4-dioxane (1) + water (2) mixtures versus the mole fraction x_1 of dioxane in the temperature range 293.15 to 323.15 K: (●) $E_{a1}(x_1)$, (○) $E_{a2}(x_1)$



This calculation is interesting because the partial molar activation energy $E_{ai}(x_1)$ values give the individual contribution of each pure component (i) and their contribution at each binary mixture composition (x_1, x_2). Values of $E_{a1}(x_1)$ and $E_{a2}(x_1)$ are reported in Table 3 and depicted in Fig. 8 against mole fraction in dioxane (x_1).

The partial molar activation energy $E_{a1}(x_1)$ of dioxane exponentially decreases from a high value (about 150 kJ·mol^{-1}), and then varies slightly from $x_1 > 0.08$, taking on small values as pure dioxane is approached (about 12 kJ·mol^{-1}). This behavior suggests that at high dilution, the addition of dioxane to water forms and promotes the formation of clusters of water in which the dioxane strengthens the structure of water, until $x_1 \approx 0.08$ where the water structure changes [38, 43]. On the other hand, the partial molar activation energy of water $E_{a2}(x_1)$ varies slightly, having small values slightly greater than that of pure water (between 16 and 20 kJ·mol^{-1}), but which decrease rapidly to negative values in the very dioxane-rich region. We can assume that the hydrogen bonds can be broken in pure dioxane, but weak hydrogen bonds between water and dioxane molecules might be formed. Hence, the introduced molecules of dioxane in the water-rich region find considerable difficulty in becoming integrated into the layers' water molecules. Conversely, in the dioxane-rich region, the introduction of water molecules is facilitated by incorporating them in layers of dioxane molecules. We add that the large difference between the size and shape of molecules can play an important role in this interaction. We also note that the variation of $E_{ai}(x_1)$ between the pure component values and those at infinite dilution (Fig. 8) clearly shows that the excess molar activation energy $\Delta E_{a1}(x_1)$ of dioxane is negative, while that of water $\Delta E_{a2}(x_1)$ is positive over the full composition range. In fact, this is shown in Fig. 9 by the sign of the reduced RK partial molar activation energy $Q_{\mathrm{RK},E_{ai}}(x_1)$ (Eq. 8). In addition, the similar shape of the $Q_{\mathrm{RK},E_{ai}}(x_1)$ curves leads us to eliminate x_1 as a variable and to plot the correlation between the two partial molar activation energies $E_{a1}(x_1)$ and $E_{a2}(x_1)$ (Fig. 10). We conclude that the individual contribution of water and dioxane in the activation energy clearly show the delimitation of domains ($x_1 \approx 0.3737$) for water solvation in dioxane, and inversely, the limiting composition ($x_1 \approx 0.3737$) corresponds approximately to a cluster of

Fig. 9 Experimental reduced Redlich–Kister excess properties $Q_{\mathrm{RK},E_{ai}}(x_1)$ (Eq. 3) for dioxane + water mixtures versus the mole fraction x_1 of dioxane at the temperatures 293.15 K to 323.15 K: (●) $Q_{\mathrm{RK},E_{a1}}(x_1)$, (○) $Q_{\mathrm{RK},E_{a2}}(x_1)$

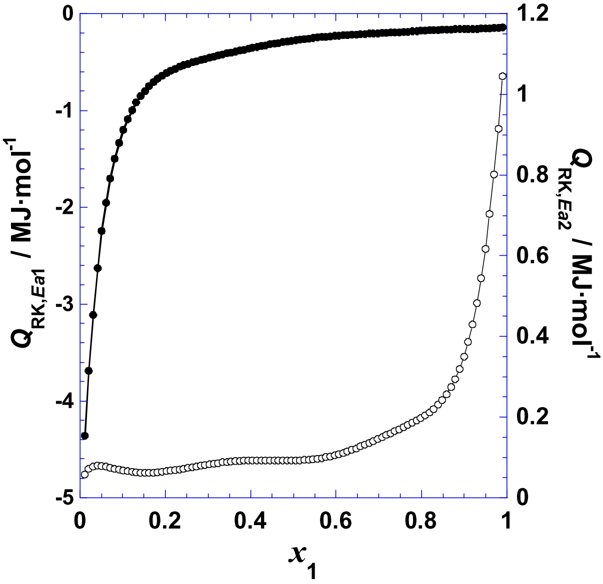
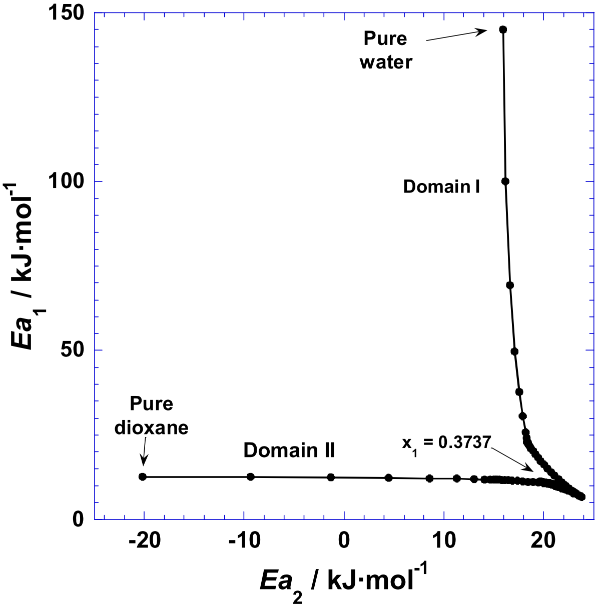


Fig. 10 Correlation between the partial Arrhenius activation energies $E_{a1}(x_1)$ and $E_{a2}(x_1)$ for dioxane + water mixtures in the temperature range 293.15 to 323.15 K



$10C_4H_8O_2 \cdot 17H_2O$. Also, the universal exponent B_0 of the Herráez equation [15] at infinite dilution, investigated in previous works [5, 6], shows that B_0 has a value of 0.5 for dioxane in water and 1.0 for water in dioxane. We can conclude that at very high dilution the solute–solute interactions are present in the case of dioxane in water ($x_1 \approx 0^+$) while they are absent in the case of water in dioxane ($x_1 \approx 1^-$).

6 Conclusions

New experimental data of dynamic viscosities for the binary liquid mixtures of 1,4-dioxane + water at temperatures 311.15, 316.15 and 320.15 K and at many mole fraction compositions are reported, in order to extend the collection of temperatures carried out in previous works and in the literature, for improving the correlation of the Arrhenius activation energy against temperature.

Arrhenius parameters of pure components (water and dioxane) were determined as a function of temperature and can be predicted. The pre-exponential entropic factor, equivalent to the viscosity at infinite temperature, is very closely related to that of the same system in its vapor phase. Also, the activation energy in Arrhenius's equation is almost equal to the enthalpy of activation of viscous flow and it is correlated with its enthalpy of vaporization.

Correlation between these two Arrhenius parameters for binary mixtures can give evidence for the existence of distinct composition regions with different behaviors. Therefore, there is a significant degree of H-bonding leading to strong correlation between the molecules. Also, the difference in the size of the molecules can play an important role in this behavior.

The reduced Redlich–Kister functions relative to the Arrhenius parameters, which are equivalent to apparent molar properties, are more sensitive than the excess properties to interactions and give more information. Thus, assuming that the activation energy is a thermodynamic quantity, we have determined the partial molar activation energy to elucidate the interaction contributions of each pure component of the mixture at each composition.

This original treatment of partial molar activation energy showed the existence of two main distinct domains separated from the cluster ($10C_4H_8O_2{\cdot}17H_2O$) which was also observed by spectroscopic investigations reported in the literature. We can add that the studied mixtures present important deviations, as a consequence of their structures and interactions. These aqueous binary systems are complex systems with strong hydrogen bond and dipole–dipole interactions.

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