

Influence of Temperature and NaCl Impurities on Molecular Interactions in 1,4-Dioxane–Water Mixtures: A Grunberg–Nissan Model Analysis

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Abstract: The 1,4-dioxane-water system is of significant relevance in pharmaceutical development, Chemical Engineering and other industrial processes. In this study, we investigate the intermolecular interactions in 1,4-dioxane–water mixed solvent system under different temperatures and NaCl concentrations using the Grunberg–Nissan approach. As first step, the solubility parameters of the mixture is evaluated as a function of the water molar fraction (x_w) at 25 °C based on Hansen solubility parameters. The analysis shows that dispersion forces dominate for $x_w < 0.7$, whereas hydrogen-bonding interactions become predominant at $x_w \geq 0.7$. These findings are consistent with previous microscopic techniques. A new expression of the Grunberg–Nissan constant, d' , was established and calculated over the molar fraction of water at 25 °C, and thus the complexes formed from 1,4-dioxane and water are discussed. Furthermore, a theoretical expression for the temperature dependence of the Grunberg–Nissan constant was introduced to assess the influence of thermal effects on complex stability. The derivative, $\frac{\delta d'}{\delta T}$, is introduced to assess the thermal stability of the complex. Finally, the impact of ionic impurities (Na^+ and Cl^-) on the interaction between water and dioxane molecules was evaluated through a pseudo-Grunberg–Nissan constant, providing insights into how salt addition modifies mixture stability.

Keywords: mixed liquids, complex, Grunberg–Nissan constant, stability, temperature, ion.

INTRODUCTION

VISCOSITY is a fundamental parameter in analyzing transport phenomena in liquids. Measuring the viscosity of mixed liquids permits to evaluate interactions between dissimilar molecules. In fact, the simplest method is to calculate the Grunberg–Nissan constant d' at a given temperature and mixture composition.^[1] In a previous paper,^[2] we have shown a correspondence between the Grunberg–Nissan constant parameter variation and the complex formation varieties in water/methanol mixtures. Our observations were confirmed for ethylene glycol–water by other research groups.^[3] Ternary mixed-solvent systems involving chemical entities have attracted considerable scientific attention. Researchers aim to study the behaviour of these entities, whether in isolated form or in association. The chemical entities may include neutral

molecules, ions, polymers, polyelectrolytes, or surfactants. In this case, the observed phenomena are attributed to the physical properties of mixed solvents, particularly their viscosity. On the other hand, the effect of the presence of a chemical entity, considered as an impurity, on the interaction between dissimilar molecules in the mixture was examined for the polyvinylpyrrolidone/water/methanol mixture system.^[4] In this context, the system is considered as a quasi-binary system and a pseudo-Grunberg–Nissan constant, d'_p , was introduced to quantify the interaction between water and methanol in the presence of polyvinylpyrrolidone. This approach was extended and the effect of the presence of an impurity (neutral molecule, ion and polymer) was developed theoretically.^[5]

In 2012 Ouerfelli *et al.*^[6] reported viscosity data for 1,4-dioxane – water mixtures over the full range of mole fraction of 1,4-dioxane (D) ($0 \leq x_D \leq 1$) under atmospheric

pressure. The measurements were performed at 311.15, 316.15 and 320.15 K. Their work aimed to complete the studied temperature range (293.15 to 323.15 K) available in literature.^[7] In 2015, Tomaš *et al.*^[8] reported precise viscometric data for NaCl in water-1,4-dioxane mixtures. The studied mole fractions of 1,4-dioxane were $x_D = 0.05, 0.10, 0.15$ and 0.20 in the concentration range $0.05 \leq c / \text{mol dm}^{-3} \leq 0.30$. Measurements were taken at 9 temperatures (from 278.15 to 318.15 K at step of 5 K). The relative viscosity data, η_r , have been analysed and interpreted in terms of rearranged Jones-Dole equation, $(\eta_r - 1) - Ac^{1/2} = Bc$. In addition, from reported limiting ionic conductivity data including relative permittivity and viscosity data of solvent, the viscosity A-coefficients have been calculated from Falkenhagen and Vernon theory.^[9] All obtained value of B-coefficient are positive and bigger than values of A-coefficient in all solvent mixtures suggesting that ions-solvent are prevailing upon ion-ion interactions. Their study indicates that, in solutions with a low content of 1,4-dioxane, the structure-breaking effect of NaCl predominates, and ion-solvent interactions dominate. As the content of 1,4-dioxane increases, solvent-solvent interactions become more significant. This leads to a maximum in viscosity at $x_D = 0.25$, which can be attributed to strong interactions between 1,4-dioxane and water molecules. In the first part of this study, novel expressions of the Grunberg-Nissan and pseudo-Gunberg Nissan constants versus temperature are established and reported. Then, the stability under the effect of temperature of the formed complex between 1,4-dioxane and water molecules is examined. Finally, the effect of the Na^+ and Cl^- on the interaction between unlike molecules is also discussed in light of the theoretical developments.

THEORETICAL DEVELOPMENTS

Effect of Temperature on the Interaction Between Dissimilar Molecules in Mixed Liquids

The Grunberg-Nissan constant d' is calculated using the viscosity measurements of two distinct liquids and their mixing at a well-defined molar fraction of liquid 1, x_1 . Positive values for d' indicate strong interactions between two components, whereas negative d' values indicate that the dispersion forces dominate the solution.^[15] Indeed, the Grunberg-Nissan constant characterizes the interactions between the mixture's molecules, which have a direct impact on the thermodynamic parameters. The Grunberg-Nissan constant d' can be expressed according to the following equation:^[1]

$$d' = \frac{\ln(\eta_m) - (x_1 \ln(\eta_1) + (1 - x_1) \ln(\eta_2))}{x_1(1 - x_1)} \quad (1)$$

where η_1, η_2 , and η_m , are respectively, the dynamic viscosities of liquids 1 and 2 and their mixture. The dynamic viscosity of simple liquids and their mixture obeys Arrhenius equation type. So, the dependence of the viscosities on temperature is given by Equations (2–4):

$$\ln \eta_1 = \frac{E_{a_1}}{RT} + \ln A_{s_1} \quad (2)$$

$$\ln \eta_2 = \frac{E_{a_2}}{RT} + \ln A_{s_2} \quad (3)$$

$$\ln \eta_m = \frac{E_{a_m}}{RT} + \ln A_{s_m} \quad (4)$$

where, R is the perfect gas constant. E_{a_1}, E_{a_2} , and E_{a_m} are respectively the activation energy of liquids 1, 2 and the mixture A_{s_1}, A_{s_2} , and A_{s_m} , are respectively, the Arrhenius entropic factor in liquids 1, 2 and the mixture. By combining Eqs. (1–4), the Grunberg-Nissan constant takes the following form:

$$d' = \frac{1}{x_1(1 - x_1)} \left[\frac{\Delta E_a}{RT} - \Delta \ln A_s \right] \quad (5)$$

where ΔE_a and $\Delta \ln A_s$, are given by the following expressions:

$$\begin{aligned} \Delta E_a &= E_{a_m} - \bar{E}_a \quad \text{and} \\ \bar{E}_a &= x_1 E_{a_1} + (1 - x_1) E_{a_2} \end{aligned} \quad (6)$$

$$\begin{aligned} \Delta \ln A_s &= \Delta \ln A_{s_m} - \Delta \ln A_{s_i} \quad \text{and} \\ \Delta \ln A_{s_i} &= x_1 \Delta \ln A_{s_1} + (1 - x_1) \Delta \ln A_{s_2} \end{aligned} \quad (7)$$

ΔE_a is the difference between the activation energy of the viscous flow of mixture E_{a_m} and the ideal activation energy E_{a_i} . In this context, ΔE measure to what extent the actual mixture deviates from the ideal in terms of energy barrier. If $\Delta E > 0$: the mixture requires more energy for molecular rearrangements which implies stronger specific interactions (e.g., hydrogen bonding, complexation, dipole-dipole interactions). If $\Delta E < 0$: the mixture requires less energy than predicted which indicates structure-breaking interactions

$\ln A_{s_i}$ is the **pre-exponential factor** in the viscosity expression (A_{s_m} : value for the mixture, A_i : ideal value) . Typically, this factor is an entropic factor that measures particle mobility. In this context, $\Delta \ln A_s$ determines the degree how much the **configurational entropy and molecular mobility factors** are far from ideal mixing.

In order to quantify the effect of temperature on the interaction between dissimilar molecules in the mixture, the quantity $\frac{\delta d'}{\delta T}$ should be evaluated according Eq. (8):

$$\frac{\delta d'}{\delta T} = \frac{-\Delta E_a}{R x_1(1 - x_1) T^2} \quad (8)$$

According to Eq. (8), $\frac{\delta d'}{\delta T}$, increases when $E_{am} < \bar{E}_a$.

For the first time in the literature, the Grunberg-Nissan constant and the pseudo-Grunberg-Nissan constant take into account the activation energy in their expressions. This allows us to explicitly address the effect of temperature on the intermolecular interaction between different molecules and the effect of ion addition.

Effect of Impurity Addition on the Interaction Between Dissimilar Molecules in Mixed Liquids

To study the effect of an impurity addition to the mixed liquids, we assume that the ternary system behaves as a quasi-binary system for a limiting concentration of the impurity. Thus, a pseudo-Grunberg-Nissan constant, d'_p , at a mole fraction x_1 of liquid 1, was used^[5] to quantify the interactions between mixed liquids in the presence of an impurity as follows:

$$d'_p = \frac{\ln \eta_m^* - (x_1 \ln \eta_1^* + (1 - x_1) \ln \eta_2^*)}{x_1(1 - x_1)} \quad (9)$$

where η_m^* , η_1^* and η_2^* are the dynamic viscosities of the mixture and liquids 1 and 2 in presence of impurity, respectively. The viscosities dependence on temperature is given by Equations (10–12):

$$\ln \eta_1^* = \frac{E_{a1}^*}{RT} + \ln A_{s1}^* \quad (10)$$

$$\ln \eta_2^* = \frac{E_{a2}^*}{RT} + \ln A_{s2}^* \quad (11)$$

$$\ln \eta_m^* = \frac{E_{am}^*}{RT} + \ln A_{sm}^* \quad (12)$$

where E_{a1}^* , E_{a2}^* and E_{am}^* , are respectively, the activation energy of liquids 1, 2 and the mixture in presence of impurity. A_{s1}^* , A_{s2}^* and A_{sm}^* , are respectively, the Arrhenius entropic factor in liquids 1, 2 and the mixture in presence of impurity. By combining Eqs. (10–12) with Eq. (9), the pseudo-Grunberg-Nissan constant takes the following form:

$$d'_p = \frac{1}{x_1(1 - x_1)} \left[\frac{\Delta E_a^*}{RT} - \Delta \ln A_s^* \right] \quad (13)$$

where ΔE_a^* and $\Delta \ln A_s^*$, are given by the following expressions:

$$\Delta E_a^* = E_{am}^* - \bar{E}_a^* \text{ and } \bar{E}_a^* = x_1 E_{a1}^* + (1 - x_1) E_{a2}^* \quad (14)$$

$$\Delta \ln A_s^* = \ln A_{sm}^* - \ln A_{s1}^* \text{ and } \ln A_{s1}^* = x_1 \ln A_{s1}^* + (1 - x_1) \ln A_{s2}^* \quad (15)$$

These quantities are taken at the same temperature and impurity concentration C . The relative deviation of the

Grunberg Nissan constant due to the presence of the impurity, $\frac{\delta d'}{d'}$, can be calculated according to Eq. (16).

$$\frac{\delta d'}{d'} = \frac{d'_p - d'}{d'} \quad (16)$$

Effect of the Presence of Ion on the Interaction Between Dissimilar Molecules

In the case of an associative-electrolyte, the relative viscosity η_r , is connected to its concentration, c , by the following equation:

$$\eta_r = \frac{\eta}{\eta_0} = 1 + AC^{1/2} + BC \quad (17)$$

where A and B are the ion-ion and ion-solvent interactions, respectively. The last equation can be used for liquid1, liquid2 and the mixture. So, the relative viscosities of the associative electrolyte solution in mixed liquids, liquid1 and liquid 2 are given by the following equations:

$$\eta_{r,m} = \frac{\eta_m^*}{\eta_m} = 1 + A_m C^{1/2} + B_m C \quad (18)$$

$$\eta_{r,1} = \frac{\eta_1^*}{\eta_1} = 1 + A_1 C^{1/2} + B_1 C \quad (19)$$

$$\eta_{r,2} = \frac{\eta_2^*}{\eta_2} = 1 + A_2 C^{1/2} + B_2 C \quad (20)$$

where A_m , A_1 and A_2 are the interaction constant parameters ion-ion in mixed liquids, liquid1 and liquid 2, respectively. B_m , B_1 and B_2 are the interaction constant parameters for solute-mixed liquids, solute-liquid1 and solute-liquid2. Taking into account Eqs. (16–20) and (14), the quantity, $\frac{\delta d'}{d'}$, defined in Eq. (16), takes the following form:

$$\frac{\delta d'}{d'} = \frac{\ln \Gamma_i}{\ln \Gamma_0} \quad (21)$$

where Γ_i and Γ_0 , are respectively, given by Equations (22) and (23).

$$\Gamma_i \eta_{r,2} = \frac{\eta_{r,m}}{\eta_{r,1}^{x_1} \eta_{r,2}^{1-x_1}} \quad (22)$$

$$\Gamma_0 = \frac{\eta_m}{\eta_1^{x_1} \eta_2^{1-x_1}} \quad (23)$$

where η_m and $\eta_{r,m}$ are the dynamic viscosity of the mixture and the relative viscosity of the mixture. $\eta_1^{x_1}$ and $\eta_{r,1}^{x_1}$ are the dynamic viscosity of liquid 1 of molar fraction x_1 the relative viscosity of liquid 1 of molar fraction x_1 . $\eta_2^{1-x_1}$ and $\eta_{r,2}^{1-x_1}$ are the dynamic viscosity of liquid 2 of molar fraction $1 - x_1$ the relative viscosity of liquid 2 of molar fraction $1 - x_1$.

RESULTS AND DISCUSSION

The 1,4-dioxane-water Mixture

Solubility Parameters

The solubility parameters^[10] of a liquid, δ_d , δ_p and δ_h , respectively permit quantifying the contribution of the various interactions: dispersion, polar and hydrogen bonding. These parameters contribute to the solubility parameters, δ , which is defined as the internal pressure of the solvent and verifies the following equation:

$$\delta^2 = \delta_p^2 + \delta_d^2 + \delta_h^2 \quad (24)$$

For water and 1,4-dioxane, these parameters and the molar volume, V_m (Table 1) are reported in the literature at 25 °C.^[11] For mixed liquids the equivalent solubility parameters, δ_{md} , δ_{mp} , and δ_{mh} , are evaluated according to the following Eqs. (25–27):

$$\delta_{md} = \delta_{wd}\varphi_w + \delta_{1.4Dd}(1 - \varphi_w) \quad (25)$$

$$\delta_{mp} = \delta_{wp}\varphi_w + \delta_{1.4Dp}(1 - \varphi_w) \quad (26)$$

$$\delta_{mh} = \delta_{wh}\varphi_w + \delta_{1.4Dh}(1 - \varphi_w) \quad (27)$$

where δ_{wd} , δ_{wp} and δ_{wh} are respectively, the dispersion, polar and hydrogen bonding contribution to the solubility parameter of water. $\delta_{1.4Dd}$, $\delta_{1.4Dp}$ and $\delta_{1.4Dh}$ are respectively, the dispersion, polar and hydrogen bonding contribution to the solubility parameter of 1,4-dioxane. φ_w is the volume fraction of water in the mixture, this quantity is evaluated according to Equation (28):

$$\varphi_w = \frac{V_{m,w}}{V_{m,w} + V_{m,1.4D}} \quad (28)$$

where $V_{m,w}$ and $V_{m,1.4D}$ are respectively, the molar volume of water and 1,4-dioxane in the mixture. The volume fraction of water is connected to the molar fraction of water, x_w as follows:

$$\varphi_w = \frac{1}{1 + \frac{1 - x_w}{x_w} \frac{M_{1.4D}}{M_w} \frac{\rho_w}{\rho_{1.4D}}} \quad (29)$$

where M_w , $M_{1.4D}$, ρ_w and $\rho_{1.4D}$, are respectively, the molar mass of water and 1,4-dioxane, the density of water and 1,4-dioxane.

Table 1. Solubility parameters and molar volume of water and 1,4-dioxane at 25 °C.^[10,11]

Solvent	Water	1,4-dioxane
$\delta_d / \text{M Pa}^{1/2}$	15.5	19.0
$\delta_p / \text{M Pa}^{1/2}$	16.0	1.8
$\delta_h / \text{M Pa}^{1/2}$	42.4	7.4
$\delta / \text{M Pa}^{1/2}$	47.9	20.5
$V_m / \text{cm}^3 \text{mol}^{-1}$	85.7	18.0

The data from Refs. [10,11] were used to determine the different solubility parameters from Eqs. (25), (26) and (27). Figure 1 shows the change in the solubility parameter of the 1,4-dioxane-water mixture, $\delta_m / \text{M Pa}^{1/2}$, the contribution of the dispersive forces, $\delta_{md} / \text{M Pa}^{1/2}$, polarisation forces, $\delta_{mp} / \text{M Pa}^{1/2}$, and hydrogen bonding, $\delta_{mh} / \text{M Pa}^{1/2}$, as a function of the molar fraction of water, x_w . For all mixture compositions, the contribution of the polarisation forces to the solubility parameter of the 1, 4-dioxane-water mixture is weak in the water-rich region mixture. However, the dispersion forces dominate the solubility parameter of the mixture; following the contribution of the hydrogen bonding forces dominates the solubility parameter of the mixture. In fact, when water mole fractions are low, $x_w < 0.6$, the mixture contains an excess of dioxane molecules, which reduces the probability of long-range hydrogen bonds. So, the behavior of the mixture is primarily controlled by nonpolar interactions in this composition range, particularly dispersion forces between dioxane molecules. However, when the water content exceeds $x_w > 0.6$, the system contains enough water molecules to create a long hydrogen bond network. Thus, hydrogen bonds prevail over other intermolecular interactions in this regime

The Grunberg Nissan Constant Parameter

The interaction between 1,4-dioxane-water binary mixtures is quantified using the Grunberg Nissan constant d' , as given by to the following Equation:

$$d' = \frac{\ln \eta_m - (x_w \ln \eta_w + (1 - x_w) \ln \eta_{1.4D})}{x_w(1 - x_w)} \quad (30)$$

where η_m, η_w and $\eta_{1.4D}$, are respectively, the dynamic

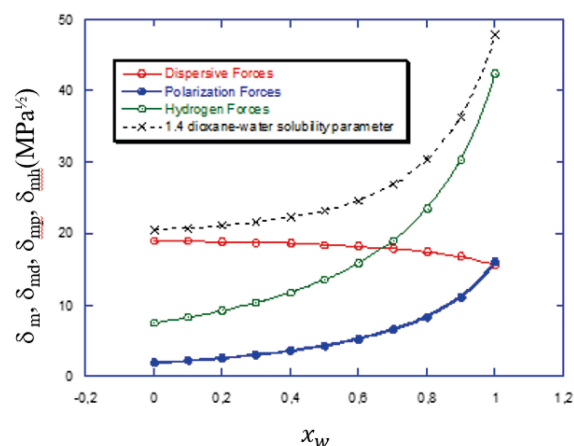


Figure 1. Solubility parameter of the 1,4-dioxane-water, $\delta_m / \text{M Pa}^{1/2}$, and its components: contribution of dispersive forces, $\delta_{md} / \text{M Pa}^{1/2}$, contribution of polarization forces, $\delta_{mp} / \text{M Pa}^{1/2}$ and hydrogen-bonding contribution, $\delta_{mh} / \text{M Pa}^{1/2}$, plotted versus the water molar fraction x_w . The results were obtained using Eqs. (25–27). Data sources: Refs. [10,11].

viscosity of the mixture at the molar fraction of water, x_w , the dynamic viscosity of water and 1,4-dioxane. Positive values for d' indicate strong interactions between two components, this usually indicates associative or structure-forming interactions (e.g., hydrogen bonding, complexation, strong dipole–dipole attractions). whereas negative d' values indicate that the dispersion forces dominate the solution, this suggests structure-breaking or weaker effective interactions (e.g., disruption of hydrogen-bond network, favourable packing that reduces friction).

Using mixture viscosity measurements of 1,4-dioxane–water, reported in previous works,^[6,7] we applied the previously developed approach. In fact, authors^[6,7] have reported data on the effect of temperature on the viscosity of 1,4-dioxane–water in the 293.15 to 323.15 K temperature range. In fact, the viscosities of 1,4-dioxane and water and their mixture depend on temperature, T , according to the following equations:

$$\ln \eta_w = \frac{E_{aw}}{RT} + \ln A_{sw} \quad (31)$$

$$\ln \eta_{1,4D} = \frac{E_{a1,4D}}{RT} + \ln A_{s1,4D} \quad (32)$$

$$\ln \eta_m = \frac{E_{am}}{RT} + \ln A_{sm} \quad (33)$$

E_{aw} , $E_{a1,4D}$ and E_{am} are respectively the activation energy of the liquid water, 1, 4-dioxane and the mixture. A_{sw} , $A_{s1,4D}$ and A_{sm} , are respectively, the Arrhenius entropic factor in water and 1, 4-dioxane.

By combining Eqs. (30–33), the Grunberg-Nissan constant takes the following form:

$$d' = \frac{1}{x_w(1-x_w)} \left[\frac{\Delta E_a}{RT} - \Delta \ln A_s \right] \quad (34)$$

where ΔE_a and $\Delta \ln A_s$, are given by the following expressions:

$$\Delta E_a = E_{am} - \overline{E_a} \quad \text{and} \quad (35)$$

$$\overline{E_a} = x_w E_{aw} + (1-x_w) E_{a1,4D}$$

$$\Delta \ln A_s = \ln A_{sm} - \ln A_{si} \quad \text{and} \quad (36)$$

$$\ln A_{si} = x_w \ln A_{sw} + (1-x_w) \ln A_{s1,4D}$$

We report in Figures 2 and 3, respectively, the variation of ΔE_a and $\Delta \ln A_s$, versus water molar fraction, x_w . Empirical equations connecting ΔE_a and $\Delta \ln A_s$, to water molar fraction x_w are proposed. The empirical parameters A_i and B_i were determined by regression of the experimental data using the least squares method. The best fit was obtained with a polynomial-type functional dependence between the variables (i : the order of the polynomial):

$$\Delta E_a / \text{kJ mol}^{-1} = \sum_{i=0}^6 A_i x^i \quad (37)$$

$$\Delta \ln A_s / 10^{-6} \text{Pa s} = \sum_{i=0}^9 B_i x^i \quad (38)$$

where, A_i and B_i , are free parameters. The obtained results are reported in Table 2. We report in Figure 4, the variation of the Grunberg-Nissan, d' , versus water molar fraction for the temperature. Borowski *et al.*^[12] have detected five complex varieties on the 1,4-dioxane–water mixture by IR and Raman measurements. In a previous work, Guettari *et al.*^[13] have shown a correspondence between the variation of the Grunberg-Nissan constant and complex varieties in water/methanol mixture. This proposition was confirmed for ethylene glycol–water mixture.^[3,14] As reported in Figure 4, the Grunberg-Nissan constant variation of 1,4-dioxane–water versus water molar fraction presents five parts. According to our previous finding, we confirmed the existence of five distinct complex varieties between water and 1,4-dioxane.

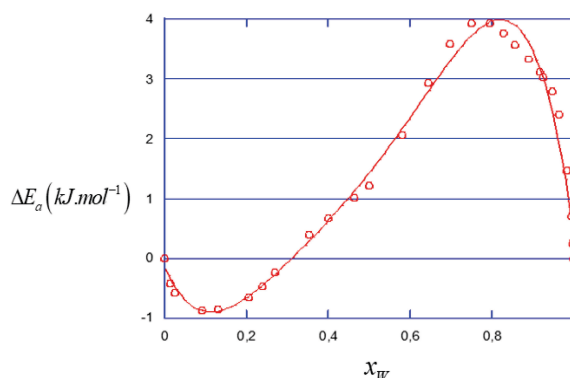


Figure 2. The activation energy for the mixing of water and 1,4-dioxane, according to Eq. (35). References of the data used [6,7].

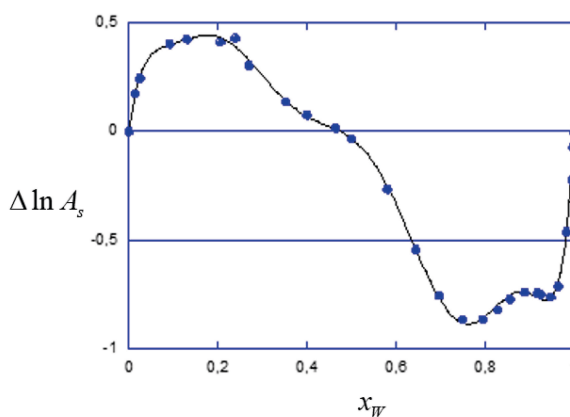


Figure 3. Variation of the entropic deviation parameter, $\Delta \ln A_s$, for the mixing of water and 1,4-dioxane, with the water molar fraction, x_w , as given by Eq. (36). Data sources: Refs. [6,7].

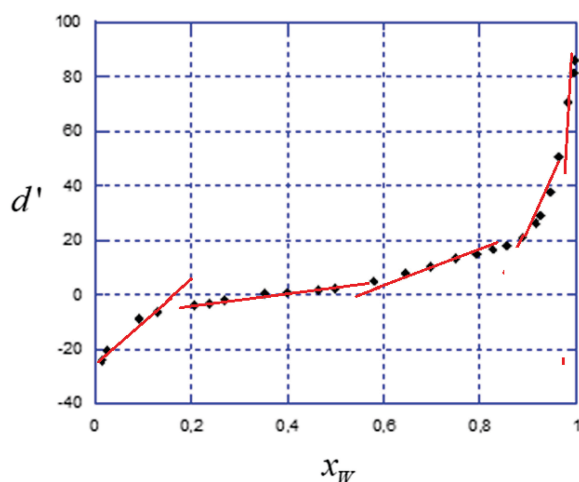


Figure 4. Dependence of the Grunberg-Nissan constant, d' , on the water molar fraction, x_w , for the mixing of water and 1,4-dioxane at 298.15 K, calculated using Eq. (34). Data from Refs. [6,7].

Temperature Effect on the Stability of Complex in 1,4-dioxane-water Mixture

The variation of Grunberg-Nissan constant under temperature effect, $\frac{\delta d'}{\delta T}$, allows us to discuss the interaction between dissimilar molecules and so the stability of the formed complex in the mixture. Considering Equation (39), $\frac{\delta d'}{\delta T}$, takes the following form:

$$\frac{\delta d'}{\delta T} = \frac{-\Delta E_a}{R_{x_w}(1-x_w)T^2} \quad (39)$$

The sign of this quantity depends directly on the sign of ΔE_a defined in Equation (35). This allows us to study the temperature effect on the interaction between dissimilar molecules in the mixture. In fact, when $\frac{\delta d'}{\delta T} = 0$, temperature doesn't affect the complex formed between water and 1,4-dioxane. An increment of the interaction between dissimilar molecules is detected when $\Delta E_a < 0$ and so the formed complex becomes stable. However, when $\Delta E_a > 0$ a decrement of the interaction between water and 1,4-dioxane is observed and the stability of the complex is affected. In fact, $\frac{\delta d'}{\delta T}$ is evaluated over water composition and temperature. As this quantity depends

Table 2. The fitting parameters A_i , $0 \leq i \leq 5$ according to Eq. (37).

A_0	A_1	A_2	A_3	A_4	A_5	R^2
0.14864	-15.615	103.84	-246.41	296.47	-137.74	0.99

Table 3. The fitting parameters B_i , $0 \leq i \leq 9$ according to Eq. (38).

B_0	B_1	B_2	B_3	B_4	B_5	B_6
-0.0031356	15.759	-270.67	2531.7	-13353	40800	-73660

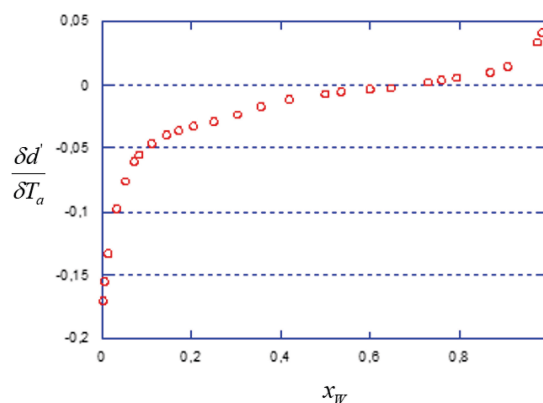


Figure 5. Average values of the increment $\frac{\delta d'}{\delta T_a}$ in the temperature range 273.15 – 318.15 K as a function of the water molar fraction, x_w for the system water-1,4-dioxane, obtained from Eq. (39).

less on temperature, the average value $\frac{\delta d'}{\delta T_a}$, over the studied temperature range is calculated and reported in Figure 5. The obtained results show that this quantity is small compared to d' at 25 °C. The relative deviation of d' under temperature effect $r_d = \frac{100}{d'} \left| \frac{\delta d'}{\delta T_a} \right|$ is evaluated over molar water composition x_w . The obtained results show that $0.08\% \leq r_d \leq 2.6\%$, the last observation shows that temperature range doesn't affect the stability of formed complex between water and 1,4-dioxane.

Effect of ion addition (Na^+ , Cl^-) on the stability of 1,4-dioxane-water complex

In order to examine the effect of ion addition on the interaction between water and 1,4-dioxane, the relative deviation of the Grunberg-Nissan due to ion additions is calculated according to Eq. (40):

$$\frac{\delta d'}{d'} = \frac{\ln \Gamma_i}{\ln \Gamma_0} \quad (40)$$

where Γ_i and Γ_0 , are respectively, given by Equations (41) and (42):

$$\Gamma_i = \frac{\eta_{r,m}}{\eta_{r,w}^{x_w} \eta_{r,1.4D}^{1-x_w}} \quad (41)$$

$$\Gamma_0 = \frac{\eta_m}{\eta_w^{x_w} \eta_{1.4D}^{1-x_w}} \quad (42)$$

Table 4. Relative deviation of the Grunberg-Nissan test, $r_d = 100 \left| \frac{\delta d'}{d'} \right|$, due to the addition of ions (NaCl) of different concentrations $C / \text{mol dm}^{-3}$, and for different compositions of water-1,4-dioxane.

$C / \text{mol dm}^{-3}$	x_w			
0	0.95	0.9	0.85	0.8
0.0512	0.46	0.38	0.23	0.17
0.1025	0.94	0.77	0.46	0.29
0.2059	1.88	1.53	0.90	0.50
0.258	2.33	1.89	1.11	0.59
0.3102	2.78	2.25	1.31	0.67

The quantity, $r_d = 100 \left| \frac{\delta d'}{d'} \right|$, is calculated for the added salt concentration at 293.15 K. The obtained results are reported in Table 4 show a maximum relative deviation of 2.78 %. The maximum relative deviation permits to deduce that the stability of the formed complex between water and 1,4-dioxane is not significantly reduced by addition of salt in the studied composition range.

CONCLUSIONS

In this work, we developed a theoretical study to investigate the evolution of molecular interactions in 1,4-dioxane–water mixtures under the influence of temperature and the addition of Na^+ and Cl^- ions. The analysis was based on the Grunberg–Nissan theory, applied to viscosity data for 1,4-dioxane–water mixtures reported in the literature.^[6,7] The main findings of this work can be summarized as follows:

- The solubility parameters of water-1,4-dioxane mixture values show a dominance of dispersion forces in the poor water region, however hydrogen bonding forces dominate the interaction in high-water-content region of the mixture.
- The correspondence between complex varieties and the variation of the Grunberg Nissan constant was examined, showing five complex varieties in the mixture of water and 1,4-dioxane.
- The concept of pseudo-Grunberg-Nissan was used to study the effect of temperature and salt addition, considered as an impurity, between dissimilar molecules in water-1,4-dioxane mixture.
- The expression of the Grunberg-Nissan under temperature effect was established, and the stability of formed complex was discussed showing minor effects of temperature on the complex formed between water and 1,4-dioxane.
- The stability of complex formed between water and 1,4-dioxane is not affected by temperature and

impurity addition (ion salt) in the reported concentration and mixture composition.

Despite the simplicity of the theoretical approach, this study provides a formalism for analyzing the influence of any impurity (electrolyte, polymer, etc.) on the interactions within a solvent mixture. The only requirement is the availability of experimental data within the selected temperature range. The significance of the results of this work could be expandable in order to apply the developed expressions and extend the physicochemical parameters such as the impurity concentration range and the temperature range of study. For this, it will be important perspective a modeling work to illustrate the findings using molecular modeling.

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