

Study of Chemical Interactions in Binary mixture water-1,4-dioxane Neighbourhood and Associated Model Approach

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Abstract: We use our results of measurements of the activities coefficients of water and 1,4-dioxane at room conditions to analyse the interactions between molecules of water and 1,4-dioxane in different mixtures. Our study is based on "*Neighbourhood Model Approach*" at liquid state in correlation with solid state to calculate molar fractions of free molecules of water and of 1,4-dioxane in pure liquid state and to deduce the composition of the various mixtures. We calculate system composition in a basis of associate model (called). This model gives good results to interpreting interactions between molecules of water and of 1,4-dioxane.

Our model is inspired by resulting experimental recently published by our team, with measurements of the enthalpy of mixture: $\Delta_m h(X_D)$, present two maxima for molecular fraction of 1,4-dioxane $X_D = 0.1438$ and $X_D = 0.7805$, which correspond to arrangements between molecules of water and 1,4-dioxane of type $WD_{3.56}$, and $DW_{5.95}$ (D: 1,4-dioxane- W: water)

We use, for the study of the model suggested, a number of 4 neighbours' molecules in the first shell surrounding one molecule of water and 6 neighbours' molecules for one molecule of 1,4-dioxane. Our observations confirm well the results of works of many authors by different technical methods.

Keywords: Water, 1,4-dioxane, activities, structure, association, neighbourhood approach, liquid properties, associated model.

Introduction

The unique properties of water¹ can be attributed to the ability of water to form four hydrogen bonds with four other molecules, forming a tetrahedral structure. This local organization can give place to an open hexagonal network shell as well in the liquid phase in the solid phase. In addition, theoretical calculations concerning the stability of the aggregates or "clusters" of the water molecules^{2,3}, show that $(H_2O)_6$ are the most stable aggregate. This configuration resembles to the shape chair of a molecule of 1,4dioxane. It can integrate in the hexagonal network of the ice (Ih) which appears under the normal conditions. Moreover, other recent studies show that the addition of a non-electrolyte supports the formation of these clusters⁴⁻⁶.

Generally, it is allowed that a non-electrolyte modifies the local or total structure of water. This phenomenon is still the subject of several theoretical, structural and thermodynamic studies,

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in order to elucidate the process of mixture and solubility according to nature of the aqueous solution (hydrophobic or hydrophilic) and the concentration of water⁷⁻¹¹.

This study proposes to contribute to better understanding by precise thermodynamic measurements, the structure of the water-1,4-dioxane mixtures, especially in the mediums rich in water. We want in particular to check the assumption according to which the 1,4-dioxane in spite of its character of a not-polar not-electrolyte (permittivity = 2,235 with 25°C and P = 1 atm), does not present a hydrophobic character; on the contrary, it reinforces the total structure of water while being incorporated (like clusters (H₂O)₆) in the hexagonal network describes higher.

This assumption is suggested because resemblance which exists between physical properties of water and of 1,4-dioxane: (Boiling points and fusion points neighbours, respectively 100°C, 101,3°C and 0°C, -10°C, molar vaporization enthalpy relatively closes¹². 10 and 8,5 kcal.mol⁻¹). Molecule of 1,4-dioxane can give place to hydrogen bonds with the water molecules⁷. We can affirm that this assumption has as consequences:

a) A very light variation of partial molar volumes of water and 1,4-dioxane with the mixture composition: (about ±7 %): Partial molar volumes of water increase with molar fraction of 1,4-dioxane, from 18,07 to 16,80 cm³.mol⁻¹ and for 1,4-dioxane it increase from 80,38 to 85,71 cm³.mol⁻¹.

b) The existence of azeotrope at molar fraction X_D close to 0,5; thus, reflecting the structure associated (H bond) and quasi-regular (incorporation of the molecules of the 1,4-dioxane in the network) with the studied solutions. The checking of such a model implies also the determination of the molar partial enthalpy and the activity coefficients of water and the 1,4-dioxane according to Raoult¹³⁻¹⁴.

In this paper, we continue our earlier works studying 1,4-dioxane-water interactions in binary liquid mixture^{15,16,17,18} to understanding the cluster formation using simplistic chemical model¹⁹. We will use two models, called chemical and physical model²⁰ as following:

Presentation of models

We describe chemical interactions between molecules in a binary mixture water-1,4-dioxane based on measurements of the activities coefficients (reference to Raoult : pure solvent) at 25 °C given starting from the binary diagram liquid - vapour carried out with atmospheric pressure P = 1 atm , and at the temperature 25.00 °C by using the results of measurements of the enthalpy of mixture^{15,16}.

We propose a model in which the interactions are translated by water-water, 1,4-dioxane-1,4-dioxane and water-1,4-dioxane associations while resting on the principle of neighbourhood shell and the correlation between liquid state and solid state. Our model is inspired by resulting experimental recently published by our team¹⁵. Measurements of the enthalpy of mixture: Δ_{m,h} (X_D), present two maxima for molar fraction of 1,4-dioxane **X_D = 0.1438** and **X_D = 0.7805** which correspond to arrangements between molecules of water and 1,4-dioxane of type **WD_{3,56}** and **DW_{5,95}** (see Figure 1 and graph 1) (3.56 and 5.95 are X_D/X_W and X_W/X_D for maxima: 3.56 = 0.7805/0.2195 and 5.95 = 0.8562/0.1438). D: 1,4-dioxane, W: water.

If (3.56 ≅ 4 and 5.95 ≅ 6), we will use, thereafter, for the study of the model suggested a number of **4** neighbours' molecules in the first shell surrounding one molecule of water and **6** neighbours' molecules for one molecule of 1,4-dioxane.

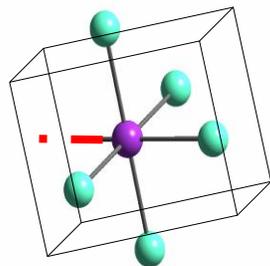


Figure 1 a): The **6** neighbours' molecules in the first shell surrounding one molecule of 1,4-dioxane

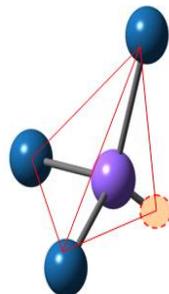
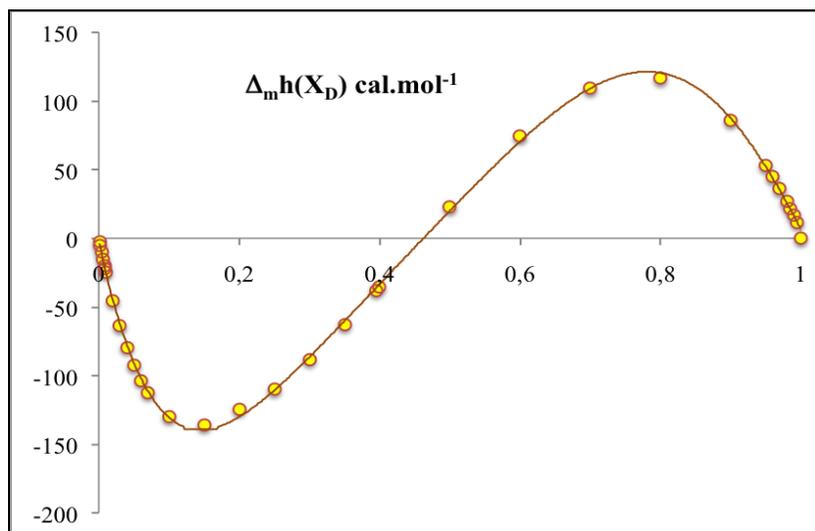


Figure 1 b): The **4** neighbours' molecules in the first shell surrounding one molecule of water

Figure 1: Neighbours shells for water and 1,4-dioxane- approach liquid-state solid-state



Graph 1: Enthalpy of mixture¹⁵: $\Delta_m h(X_D)$, present two maxima for molar fraction of 1,4-dioxane $X_D = 0.1438$ and $X_D = 0.7805$

(Brown line represents the fitting of experimental values represented by yellow circles)

Introduction of the liquid state properties

The liquid state has intermediate properties between the solid state and vapour state. It is viewed like a state of condensed vapour or decompressed solid. Near the freezing point, except for water and of Bismuth, the density of the liquids is lower than that their corresponding crystals; this property is explainable by the fact that while approaching the freezing point the molecules are arranged to form the crystal perfectly.

The structure of the liquid would be an imperfect crystalline structure where one finds site unoccupied. Many studies of the liquid state²¹⁻²⁴ confirm in their measurements this reasoning, show that by considering « c »: the number of molecules surrounding one molecule; « c » is smaller in the liquid state « c_{liq} » than in a crystalline state « c_{cr} » and decrease with the increase in temperature.

In the liquid state, we can imagine a number of « c » molecules surround the central molecule with missing one site by comparison with the corresponding crystal. Mobility is varying on this basis (as the theory of the liquids)²⁵⁻²⁷. Measurements of heat capacities also clarified the problem of the structure of the liquids²⁸⁻³¹.

Determination of the number of neighbours site « c » using the approximation of the potential energy.

When energies of interactions concern only the first layer of coordination, the average value of the potential energy of a molecule surrounded by a number « c » of close molecules is

$$U = (1/2) \cdot c \cdot \Phi \text{ where } \Phi \text{ is the interaction energy of only one pair of the molecules .}$$

We estimate c_{liq} the number of molecules at the liquid state and c_{cr} the number of molecules at the crystal state. We will express potential energies at liquid and solid state by following:

$$U_{cr} = 1/2 \cdot c_{cr} \cdot \Phi \quad (01)$$

$$U_{liq} = 1/2 \cdot c_{liq} \cdot \Phi \quad (02)$$

We deduce the potential energies from fusion and sublimation energies.

$$\Delta U_{fusion} = 1/2 (c_{liq} - c_{cr}) \Phi \quad (03)$$

$$\Delta U_{sublimation} = - 1/2 \cdot c_{cr} \cdot \Phi \quad (04)$$

In a first approximation, we can consider that:

$$\Delta U_{fusion} = L_f \text{ (latent heat of fusion) and}$$

$$\Delta U_{sublimation} = L_s \text{ (latent heat of sublimation) .}$$

We obtain:

$$c_{liq} = c_{cr}(1 - L_f / L_s) \quad (05)$$

The number of coordination in the liquid state is obtained by estimate starting from c_{cr} , L_f and L_s (see Table 1).

Table 1: Theoretical estimate of the number of coordination for the liquids

Substance	c_{cr}	L_f (calorie/mole)	L_s (Calorie/mole)	c_{liq}
Ne	12	80	588	10.37
CO	12	200.6	2083	10.84
CH ₄	12	225.5	2629	10.97
CO ₂	12	1913	6513	8.46
H ₂ O	4	1435.7	11325	3.49
1,4dioxane*	6	2842.1	11406	4.505

(*) c_{cr} for dioxane is deduced by Crystallographic data:

Crystallographic data relative to *1,4-dioxane*³²:

- Space Group: P2₁/n for phase I « monoclinical system » - Unit form by mesh: Z=2

- The cell parameters (for phase I) are: $a = 5.715 \text{ \AA}$; $b = 6.458 \text{ \AA}$; $c = 6.131 \text{ \AA}$
 $\alpha = 90.0^\circ$; $\beta = 99.89^\circ$; $\gamma = 90.0^\circ$

- Volume of the mesh: $V = 222.9 \text{ \AA}^3$

Models

Chemical and Physical models

In these models, interactions consist water-water, 1,4-dioxane -1,4-dioxane and water - 1,4-dioxane (associations between molecules). We simplify this model by following equilibriums, with:

W: represent the water molecule

D: represent the 1,4-dioxane molecule

p: represent the number of associated water molecules $p = c_{cr} + 1$ ($p = 5$)

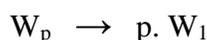
q: represent the number of associated 1,4-dioxane molecules $q = c_{cr}' + 1$ ($q = 7$)

X_{W1} : molar fraction of monomeric water in the mixture water-1,4-dioxane

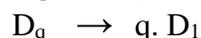
X_{D1} : molar fraction of monomeric dioxane in the mixture water- 1,4-dioxane

$X_{D_iW_j}$: molar fraction of the D_iW_j complex in the mixture water -1,4-dioxane

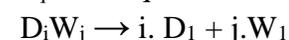
Equilibrium in pure water



Equilibrium in pure 1,4-dioxane



Equilibrium in water-1,4-dioxane mixture



The constants of equilibriums of association are:

$$K_w = X_{Wp}/(X_{W1})^p \quad (06)$$

$$K_D = X_{Dq}/(X_{D1})^q \quad (07)$$

$$K_{(i,j)} = X_{D_iW_j}/(X_{D1})^i. (X_{W1})^j \quad (08)$$

We call “**chemical model**” the model seen by an observer located inside the mixture. Once associations are established between the various molecules of the mixture, the formed entities form an ideal solution and we can write:

$$\mu_{W1} = \mu_{W1}^{\circ} + RT.\ln(X_{W1}) \quad (09)$$

and

$$\mu_{D1} = \mu_{D1}^{\circ} + RT.\ln(X_{D1}) \quad (10)$$

X_{W1} : molar fraction of the monomers (free) of water in the water-1,4-dioxane mixture.

X_{D1} : molar fraction of the monomers (free) of 1,4-dioxane in the water-1,4-dioxane mixture.

By writing $\Delta G = 0$ for various equilibriums we deduce:

$$\mu_{W1} = \mu_W \quad \text{and} \quad \mu_{D1} = \mu_D \quad (11)$$

$$\text{and} \quad X_{D1} = (\gamma_D^R \cdot X_D) \cdot X_{D1}^{\circ} \quad \text{and} \quad X_{W1} = (\gamma_W^R \cdot X_W) \cdot X_{W1}^{\circ} \quad (12)$$

With X_{D1}° : molar fraction of monomeric 1,4-dioxane in pure 1,4-dioxane

X_{W1}° : molar fraction of monomeric water in pure water

γ_D^R and γ_W^R are activity coefficients of 1,4-dioxane and water per reference to pure solvent (Raoult).

We also call “**physical model**” the model seen by an observer located outside the mixture where he saw n_W moles of water mixed with n_D moles of 1,4-dioxane. The interactions water-1,4-dioxane are translated by activities coefficients defined by chemical potentials such as:

$$\mu_W = \mu_W^{\circ R} + RT.\ln(\gamma_W^R \cdot X_W) \quad (13)$$

$$\mu_D = \mu_D^{\circ R} + RT.\ln(\gamma_D^R \cdot X_D) \quad (14)$$

X_D is the total molar fraction in mixture, $X_D = n_D / (n_D + n_W)$ and $X_W = 1 - X_D$, γ_W^R and γ_D^R are activities coefficients of water and 1,4-dioxane by reference to a pure substance (Raoult).

We will study limit case to the zones very rich in water ($X_D \approx 0$) and very rich in 1,4-dioxane ($X_D \approx 1$).

Aqueous zone

In the aqueous zone, we suppose that almost all 1,4-dioxane molecules were in the form of monomer $X_{Dq} \ll X_{D1}$ and thus the 1,4-dioxane number of moles in the mixture is reduced to the number of free monomers added to the number of the D_1W_j complex.

We propose a mixture composed by one mole of water and n_D mole of 1,4-dioxane. According to the chemical model formed of water X_{W1}° monomer mole and water X_{Wp}° mole crystallized (in W_p form) ($X_{W1}^{\circ} + X_{Wp}^{\circ} = 1$) and with $n_D \ll 1$.

$$\text{According to the chemical model} \quad n_W = X_{W1}^{\circ} + p \cdot X_{Wp}^{\circ} = X_{W1}^{\circ} + p \cdot (1 - X_{W1}^{\circ}) \quad (15)$$

The total number of moles for this mixture will be:

$$n_{\text{Total}} = n_{\text{D}} + n_{\text{W}} = n_{\text{D}} + X^{\circ}_{\text{W1}} + p \cdot (1 - X^{\circ}_{\text{W1}}) \quad (16)$$

The molar fraction of 1,4-dioxane for the physical model will be:

$$X_{\text{D}} = n_{\text{D}} / n_{\text{Total}} = n_{\text{D}} / [n_{\text{D}} + X^{\circ}_{\text{W1}} + p \cdot (1 - X^{\circ}_{\text{W1}})] \quad (17)$$

$$\sum X_{\text{DiWj}} \cong (X_{\text{D1}} + X_{\text{DWj}}) = n_{\text{D}} / (n_{\text{D}} + 1) \quad (18)$$

$$(17) \text{ and } (18) \text{ give us: } (X_{\text{D1}} + X_{\text{DWj}}) / X_{\text{D}} = [n_{\text{D}} + X^{\circ}_{\text{W1}} + p \cdot (1 - X^{\circ}_{\text{W1}})] / (n_{\text{D}} + 1) \quad (19)$$

by posing α the ratio of the molar fraction of the DW_j complex by X_{D1} ($\alpha = X_{\text{DWj}} / X_{\text{D1}}$) and taking account of (14):

$$\lim_{n_{\text{D}} \rightarrow 0} ((X_{\text{D1}} + X_{\text{DWj}}) / X_{\text{D}}) = X^{\circ}_{\text{W1}} + p \cdot (1 - X^{\circ}_{\text{W1}}) = \lim_{n_{\text{D}} \rightarrow 0} (1 + \alpha) \cdot X_{\text{D1}} / X_{\text{D}} = \lim_{n_{\text{D}} \rightarrow 0} (1 + \alpha) (\gamma_{\text{D}}^{\text{R}}) \cdot X^{\circ}_{\text{D1}} \quad (20)$$

1,4-dioxane zone

The same reasoning made for water is reproduced for 1,4-dioxane brings us to the following relations:

by posing β the ratio ($\beta = X_{\text{DiW}} / X_{\text{W1}}$)

$$\lim_{n_{\text{W}} \rightarrow 0} ((X_{\text{W1}} + X_{\text{DiW}}) / X_{\text{W}}) = X^{\circ}_{\text{D1}} + q \cdot (1 - X^{\circ}_{\text{D1}}) = (1 + \beta) \lim_{n_{\text{W}} \rightarrow 0} (\gamma_{\text{W}}^{\text{R}}) \cdot X^{\circ}_{\text{W1}} \quad (21)$$

The adjustment of activities coefficients for 1,4-dioxane and water (see Table 2 and graph 2) in limit cases gives:
for $0 \leq X_{\text{D}} \leq 0,04$

$$\gamma_{\text{D}}^{\text{R}} = 3,986 \cdot 10^{11} x^6 - 4,529 \cdot 10^{10} x^5 + 1,989 \cdot 10^9 x^4 - 4,388 \cdot 10^7 x^3 + 5,329 \cdot 10^5 x^2 - 3,589 \cdot 10^3 x + 18,09$$

$$R^2 = 0,9996 \quad (x = X_{\text{D}})$$

for $0 \leq X_{\text{W}} \leq 0,05$

$$\gamma_{\text{W}}^{\text{R}} = 4,934 \cdot 10^{10} y^6 - 8,391 \cdot 10^9 y^5 + 5,716 \cdot 10^8 y^4 - 2,005 \cdot 10^7 y^3 + 3,858 \cdot 10^5 y^2 - 4,119 \cdot 10^3 y + 43,25$$

$$R^2 = 1 \quad (y = X_{\text{W}})$$

It is followed from there that:

$$\lim_{n_{\text{D}} \rightarrow 0} (\gamma_{\text{D}}^{\text{R}}) = 18,09 = 1 / (1 + \alpha) \cdot [X^{\circ}_{\text{W1}} + p \cdot (1 - X^{\circ}_{\text{W1}})] / X^{\circ}_{\text{D1}} \quad (22)$$

and

$$\lim_{n_{\text{W}} \rightarrow 0} (\gamma_{\text{W}}^{\text{R}}) = 43,254 = 1 / (1 + \beta) \cdot [X^{\circ}_{\text{D1}} + q \cdot (1 - X^{\circ}_{\text{D1}})] / X^{\circ}_{\text{W1}} \quad (23)$$

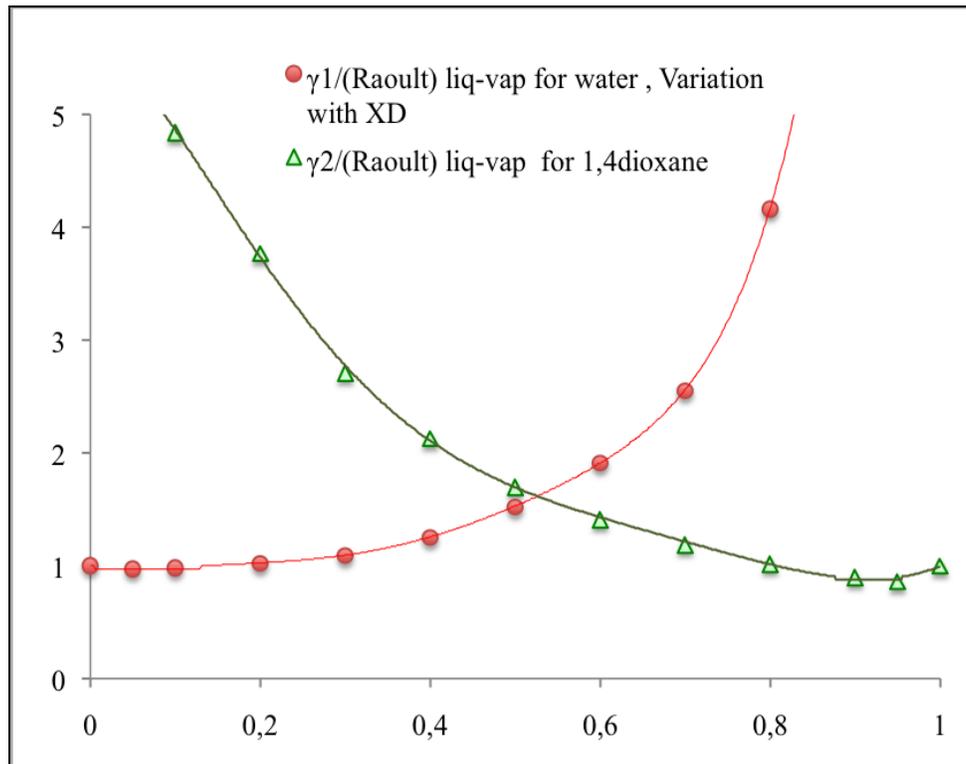
(22) and (23) form a system of equations which have four unknowns: X°_{D1} , X°_{W1} , α and β .

Knowing that $p = 5$ and $q = 7$, the resolution gives:

$$X^{\circ}_{\text{W1}} = 0,1274 \text{ et } X^{\circ}_{\text{D1}} = 0,248 \text{ for } (1 + \alpha) \text{ and } (1 + \beta) \cong 1 \text{ (Oswald dilution principle } ^{33,34})$$

$$[X^{\circ}_{\text{W1}} + p \cdot (1 - X^{\circ}_{\text{W1}})] = 4,49 \text{ identical to the value estimated in Table 1: } 4,49 (c_{\text{liq}}^{\text{W}} + 1)$$

$$[X^{\circ}_{\text{D1}} + q \cdot (1 - X^{\circ}_{\text{D1}})] = 5,51 \text{ identical to the value estimated in Table 1: } 5,505 (c_{\text{liq}}^{\text{D}} + 1)$$



Graph 2. Activity coefficients ^{29, 31} $\gamma_1 / (\text{Raoult})$ for water and $\gamma_2 / (\text{Raoult})$ calculated from binary diagram vapour-liquid ^{15,16} for mixture constituted by $\{X_D \text{ 1,4-dioxane} + (1 - X_D) \text{ water moles}\}$

Study of binary water-1,4-dioxane composition

The compositions of the various entities, based on equation (06), (07), (08) and (12) are calculated and summarized in Table 2, knowing that:

$$\text{Sum1} = X_{W1} + X_{D1} + X_{W5} + X_{D7}$$

$$\text{Rest} = 1 - \text{Sum1}$$

Table 2: Study of the mixture composition water-1,4-dioxane

X _w , liq	X _D , liq	γ_{w}^R (X _D ,liq)	γ_D^R (X _D ,liq)	X _{D1} , liq	X _{w1} , liq	X _{D7} , liq	X _{w5} , liq	Sum 1	Rest
0,999	0,001	0,996	12,72	0,003155	0,126764	4,0515E-14	0,85103	0,980948	0,019052
0,998	0,002	0,993	9,943	0,004932	0,126255	9,2478E-13	0,834103	0,965289	0,034711
0,996	0,004	0,989	8,449	0,008381	0,125495	3,7867E-11	0,80928	0,943156	0,056844
0,994	0,006	0,985	7,86	0,011696	0,124736	3,9014E-10	0,785116	0,921547	0,078453
0,992	0,008	0,983	7,505	0,01489	0,124232	2,1149E-09	0,76939	0,908512	0,091488
0,991	0,009	0,982	7,366	0,016441	0,123981	4,2318E-09	0,761634	0,902056	0,097944
0,99	0,01	0,981	7,246	0,01797	0,12373	7,8867E-09	0,753948	0,895648	0,104352
0,98	0,02	0,976	6,445	0,031967	0,121856	4,4461E-07	0,698554	0,852377	0,147623
0,97	0,03	0,975	5,941	0,044201	0,120489	4,2961E-06	0,660241	0,824935	0,175065
0,96	0,04	0,975	5,593	0,055483	0,119246	2,1093E-05	0,626902	0,801652	0,198348
0,95	0,05	0,974	5,367	0,066551	0,117883	7,5356E-05	0,59188	0,776389	0,223611
0,94	0,06	0,974	5,241	0,077986	0,116642	0,00022865	0,561377	0,756234	0,243766
0,93	0,07	0,972	5,189	0,090081	0,115165	0,0006273	0,526704	0,732577	0,267423
0,85	0,15	1,004	4,246	0,157951	0,108723	0,03196722	0,394988	0,693629	0,306371
0,8	0,2	0,997	3,770	0,186992	0,101614	0,10418509	0,281674	0,674465	0,325535
0,75	0,25	1,041	3,130	0,19406	0,099468	0,13508172	0,253151	0,681761	0,318239
0,7	0,3	1,096	2,712	0,201773	0,097741	0,17745275	0,231933	0,708900	0,291100
0,65	0,35	1,165	2,388	0,207278	0,096474	0,21425094	0,217279	0,735282	0,264718
0,605	0,395	1,242	2,150	0,210614	0,09573	0,23958248	0,209028	0,754955	0,245045
0,601	0,399	1,249	2,131	0,210867	0,095633	0,24160203	0,207972	0,756074	0,243926
0,5	0,5	1,512	1,697	0,210428	0,096314	0,23810531	0,215491	0,760339	0,239661
0,4	0,6	1,889	1,408	0,20951	0,096263	0,23093167	0,214922	0,751627	0,248373
0,3	0,7	2,587	1,191	0,206758	0,098875	0,21051099	0,245702	0,761846	0,238154
0,2	0,8	4,148	1,021	0,202566	0,105691	0,1823964	0,342897	0,833551	0,166449
0,1	0,9	8,479	0,902	0,201326	0,108022	0,17472276	0,382423	0,866494	0,133506
0,05	0,95	16,77	0,856	0,201674	0,106825	0,17684295	0,361689	0,847031	0,152969
0,04	0,96	18,7	0,858	0,204273	0,095295	0,19342643	0,204328	0,697323	0,302677
0,03	0,97	20,6	0,872	0,209768	0,078733	0,23292907	0,078662	0,600092	0,399908
0,02	0,98	22,55	0,898	0,21825	0,057457	0,30741358	0,016282	0,599403	0,400597
0,015	0,985	23,73	0,914	0,223272	0,045348	0,36048164	0,004986	0,634088	0,365912
0,01	0,99	25,52	0,932	0,228825	0,032512	0,42811842	0,000945	0,690400	0,309600
0,005	0,995	30,13	0,951	0,234669	0,019193	0,51077701	6,77E-05	0,764706	0,235294
0	1		1	0,248	0	0,75197978	0	0,999980	2,02E-05

To study the water-1,4-dioxane mixture composition, we represented the remainder (Rest) of associations other than W_5 and D_7 . The adjustment of the remainder by representation of the function $\ln(\text{Rest}/X_{D1}) = f(\ln(X_{W1}))$ gave us lines of slopes “n” the number of water molecules associated with a 1,4-dioxane molecule. The whole of the values of n found by adjustment by field are gathered in Table 3 following:

Table 3: Values of “n” the number of water molecules associated with a 1,4-dioxane molecule found by adjustment.

X_D Plage	n	complex
$0 < X_D \leq 0.05$	12.1	DW ₁₂
$0 < X_D \leq 0.06$	11.4	DW ₁₁
$0 < X_D \leq 0.07$	10.6	DW ₁₁
$0 < X_D \leq 0.15$	9.20	DW ₉
$0 < X_D \leq 0.20$	7.20	DW ₇
$0 < X_D \leq 0.25$	6.40	DW₆
$0 < X_D \leq 0.30$	6.10	DW₆
$0 < X_D \leq 0.35$	6.00	DW₆
$0 < X_D \leq 0.40$	5.85	DW₆
$0 < X_D \leq 0.50$	5.84	DW₆
$0 < X_D \leq 0.60$	5.86	DW₆
$0 < X_D \leq 0.70$	5.95	DW₆
$0 < X_D \leq 0.80$	6.10	DW₆
$0.004 \leq X_D \leq 0.80$	6.00	DW₆
$0.004 \leq X_D \leq 0.50$	5.74	DW₆
$0.006 \leq X_D \leq 0.50$	5.63	DW₆
$0.008 \leq X_D \leq 0.50$	5.47	DW ₅
$0.01 \leq X_D \leq 0.50$	5.12	DW ₅
$0.02 \leq X_D \leq 0.50$	4.85	DW ₅
$0.05 \leq X_D \leq 0.50$	4.50	DW ₅
$0.015 \leq X_D \leq 0.50$	3.70	DW ₄

Results and discussion

The adjustment of the remainder (Rest) shows well the dominating existence of the pseudo-complex **DW₆**; a molecule of 1,4-dioxane slips into the water supply network, since the remainder (Rest) is only the molar fraction of **DW₆** (see Graph 3).

This result was confirmed by measurements of heats of water-1,4-dioxane mixture, which presents a minimum corresponding to the formation of pseudo-complex **DW₆**. The partial molar enthalpy of water for the zone very rich in water is negative and tends for $X_W = 1$ towards -2,5 Kcal/mol. (by decreasing the interval of the X_D towards the mixtures very rich in water, the adjustment of the remainder (Rest) lead us to values exceeding much more 6 molecules of water (see Graph 2)). This observation makes us think that the 1,4-dioxane addition involves an

agglomeration of molecules of water around the 1,4-dioxane, which depends in fact on the 1,4-dioxane/water ratio.

These observations confirm well the results of work of many authors^{35,36}: Like G. R. Choppin³⁷ and Sirotkin³⁸ by IR (Infra-red - absorption spectrum) which affirm that the addition of 1,4-dioxane to water reinforces the structure of the water, work of Ying Guang Wu³⁹ which distinguished three critical compositions and four fields of composition

$X_D \leq 0,13$, there is presence of the complexes of the type DW_j ($j = 6,8$).

$0,13 \leq X_D \leq 0,3$ there is presence of small clusters formed (D_{1-3}, W_{7-21}),

$X_D > 0,3$ there is presence of D_n ($n \approx 10$), and we find disappearance of the clusters D_iW_j starting from $X_D > 0,7$.

In the same way, the study of water-1,4-dioxane structure and its mixtures by diffraction of the neutrons made by Imre Bako⁴⁰ shows that with the composition $X_D = 0,167$, the 1,4-dioxane molecules are incorporated in water edifice (adhesion of 1,4-dioxane to the structure of water). The study made by Toshiyuki Takamuku⁴¹ by the techniques of X-rays diffraction, mass spectrometry and relieving by NMR by zone of composition X_D announced the presence of water W_n clusters ($n = 6 - 43$) for $X_D = 0,01$ and by adding 1,4-dioxane until $X_D = 0,4$ the 1,4-dioxane molecules are incorporated to form clusters type D_mW_n ($m = 1 - 3, n = 1 - 16$). Recently study carried by V. Madhurima et al⁴² concluded that formation of clathrates is verified through contact angle measurements over various substrates and FTIR spectra.

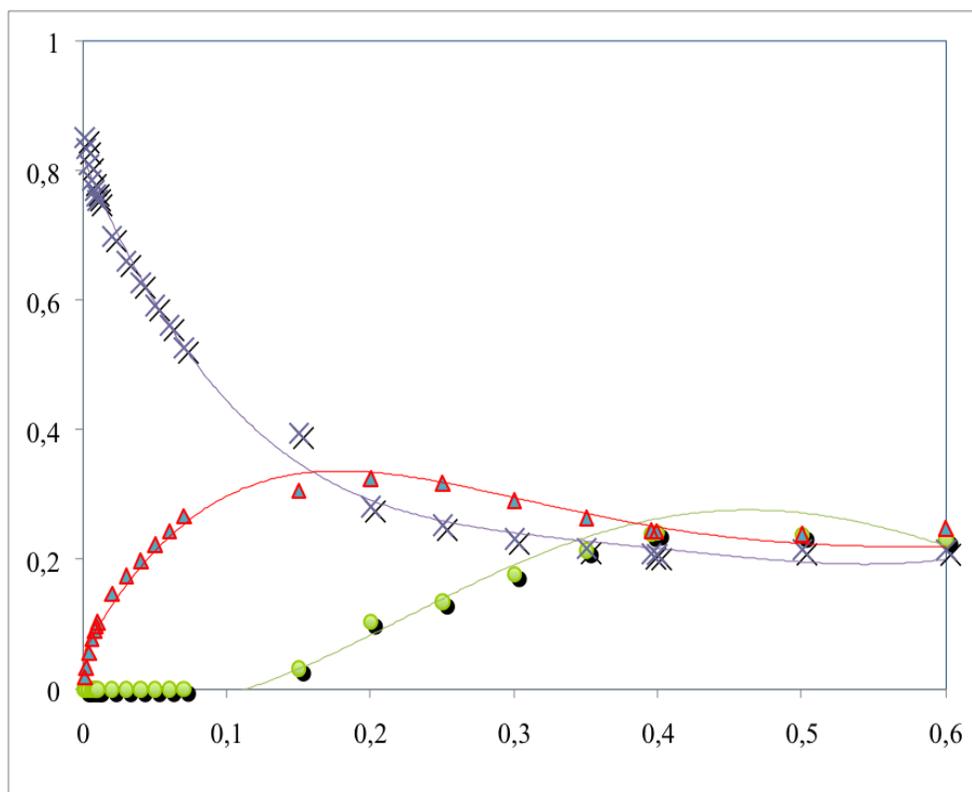
To recapitulate all these remarks, we say that the phenomenon of mixture proceeds as follows: By adding 1,4-dioxane to the water, 1,4-dioxane molecules leave the network of 1,4-dioxane and join the molecules water by hydrogen bonds while forming part of the water supply network and by forming associations of the D_mW_n type where DW_6 is dominating⁴³.

The energy result is a cooling of water resulting by too phenomenon:

Direct phenomena by a formation of associations between molecules of water and 1,4-dioxane molecules or indirect phenomena effect by the influence on the distribution structured water molecules and interstitial water molecules; this effect is seen in the variation of the densities of mixture and of viscosities. Study of density of the mixture shows that by adding 1,4-dioxane to water, the density increases. It is as if 1,4-dioxane molecules are stored within the cavities of the water. More the water /1,4-dioxane ratio is extremely more the associations' number is large.

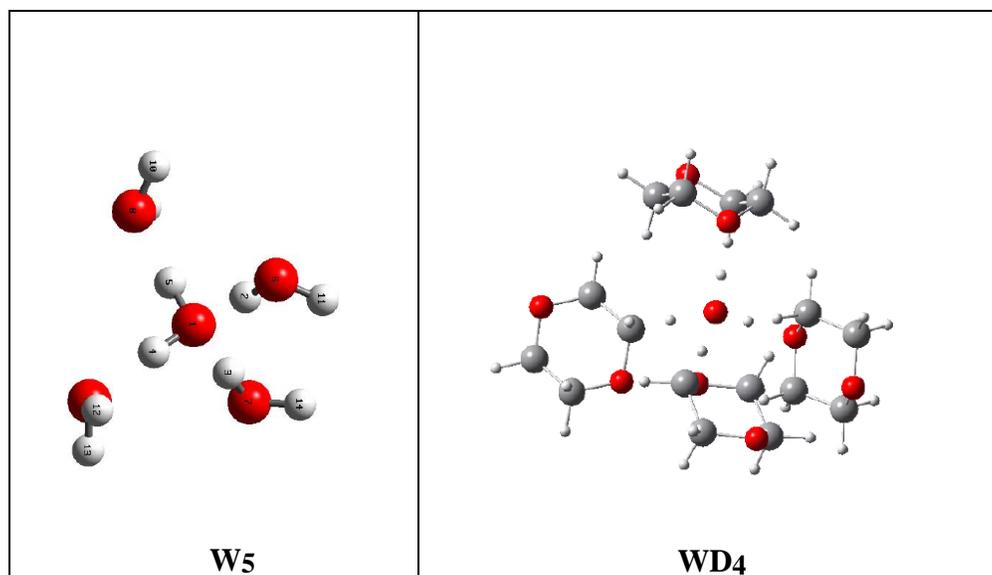
In this paper, we showed the importance of formal theory of associated solutions. We used a simple model with few parameters based on "**Neighbourhood Model Approach**" at liquid state in correlation with solid state, where different aspects of the theory of the association are applied. We obtained microscopic information in a base of chemical-physical study²⁰.

Graph 3 illustrates Distribution of the species in the mixture water-1,4-dioxane according zone $X_D = 0 - 0,6$



Graph 3. Distribution of the species in the mixture water - 1,4-dioxane with X_D :
Green circles represent D_7 , Gray crosses represent W_5 and Red triangles represent the Rest.
The solid lines represent the best adjustments in polynomial form for $X_{D_iW_j} = f(X_D)$.

Figure 2. illustrates the three principal clusters of water molecules and 1,4-dioxane molecules



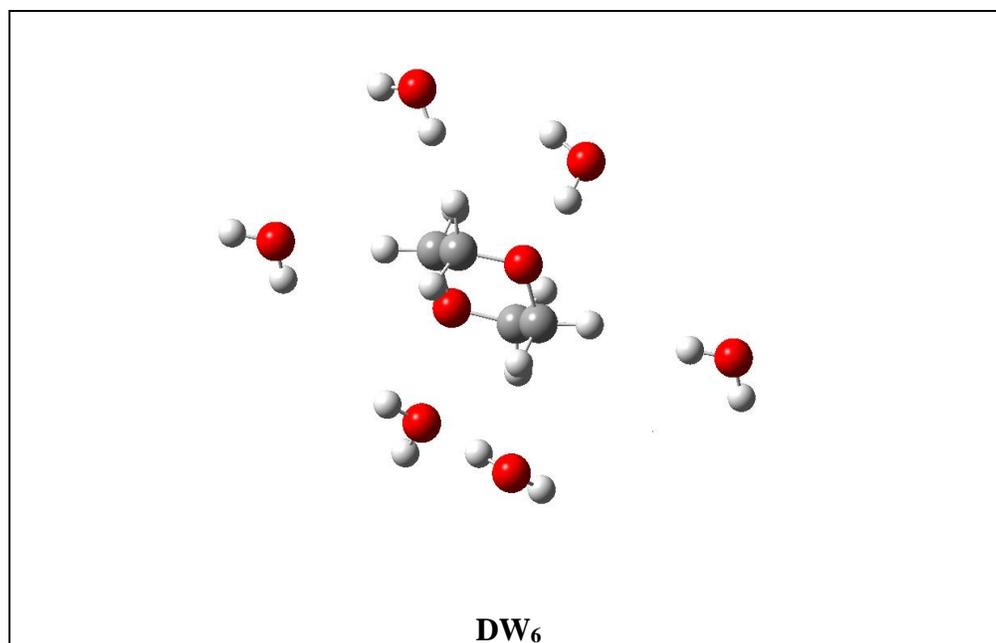


Figure 2. The three principal clusters* in water-1,4-dioxane mixture

* (Clusters are estimate using software: Gaussian 03)

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References

- 1 - A. Ben-Naim, *Water and aqueous solutions*, Plenum Press, New York, London, **1974**.
- 2 - R.J. Wawak, M.M. Wimmer and H.A. Scheraga, *J. Phys. Chem*, **1992**, 96, 5138-5138.
- 3 - J.K. Gregory and D.C. Clary, *J. Phys. Chem*, **1997**, 101, 6813.
- 4 - Anna Sikorska , Bogumil B. Linde ; *Chemical Physics*, **2008** , 354 , 148-154.
- 5 - Józef Mazurkiewicz a, Piotr Tomasiak ; *J. Mol. Liquids*, **2006** , 126 , 111-116.
- 6 - Hartmut Krienke, Gudrun Ahn-Ercan, Josef Barthel; *J. Mol. Liquids*, **2004**, 109, 115-124.
- 7 - J. Rex Goates and R. J. Sullivan, *J. Chem. Phys*, **1958**, 62 (2), 188-190.
- 8 - J. M'halla, T. Ben Dhia et M. Chemla, *J. Chim. Phys*, **1982**, 79, 442-450.
- 9 - R. Bury. A. Mayaffre and C. Treiner. Can., *J. Chem.*, **1978**, 56, 2940-2940.
- 10 - Y. Koga, *J. Phys. Chem*, **1996**, 100, 5172-5181.
- 11 - J.M'halla et S. M'halla, *J. Chim. Phys*, **1999**, 96, 1450-1478.
- 12 - G.J. Janz and R.P.T. Tomkins, *Nonaqueous Electrolytes Handbook*, Academic Press, Vol, I, New York, London, **1972**.
- 13 - I. Prigogine et R. Defay, *Traité de Thermodynamique*, Ed Desoer, Liege, **1950**.
- 14 - P. Souchay, *Thermodynamique Chimique*, Ed Masson, Paris, **1968**, pp. 142-161.
- 15 - J.M'halla , Rafik BESBES et S. M'halla *J. Soc. Chim Tunisie*, **2001**, 4, n°10, 1300-1315.
- 16 - R. Besbes, N. Ouerfelli and H. Latrous ; *J. Mol. Liquids*, **2009** , 145 , 1-4.
- 17 - N. Ouerfelli, O. Iulian, R. Besbes , Z. Barhoumi and N. Amdouni , *Phys. Chem. Liq* , **2012**, Vol. 50, No. 1, January-February , 54-68.

- 18 - N. Ouerfelli, Z. Barhoumi, R. Besbes and N. Amdouni , *Phys. Chem. Liq .* **2011**, Vol. 49, No. 6, November-December, 777-800.
- 19 - J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice Hall PTR, USA ,**1999**, chapter 7, 307-415.
- 20 - A. Apelblat, *J. Mol. Liquids*, **2006**, 128, 1-31
- 21 - Debye and Mencke, *Physikal. Z*, **1930**, 31, 797-798.
- 22 - Kirkwood, *J. Chem. Physics*, **1935**, 3, 300-313.
- 23 - Gringrich, *Rev. Mod. Phys*, **1943**, 15, 90-110.
- 24 - Zernike and Prins, *Z. Physik*, **1927**, 41, 184-185.
- 25 - Altar, *J. Chem. Physics*, **1936**, 4, 577-587.
- 26 - Fürth, *Proc. Camb. Phil. Soc*, **1941**, 37, 252-276.
- 27 - Ree,T.S., Ree, T., Eyring ,H., and Perkins , R., *J. Phys . Chem* , **1965** , 69 , 3322-3328.
- 28 - Bernal, *Trans. Faraday Soc*, **1937**, 33, 27-40.
- 29 - Eucken, *Z. Elektrochem*, **1948**, 52, 255-269.
- 30 - Staveley, Tupman and Hart, *Trans. Faraday Soc*, **1955**, 51, 323-342.
- 31 - Harrison and Moelwyn. Hughes, *Proc. Roy. Soc*, **195**, A239, 230-246.
- 32 - T.Koritsanszky & al , *J. Am. Chem. Soc*, **1991** , 113 n°24 , 9148-9154.
- 33 - W. Ostwald, *Zeitschrift für Physikalische Chemie*, **1897**, 22, 289-330.
- 34 - T.Threlfall, "Structural and thermodynamic explanations of Ostwald's Rule". *Organic Process Research and Development* **2003**, 7 (6): pp.1017-1027.
- 35 - N.A.M. Besseling and J. Lyklema, *J. Phys. Chem B*, **1997**, 101, 7604-7611.
- 36 - T. Takamuku and al, *J. Mol. Liquids*, **1999**, 83, 163-177.
- 37 - G.R. Choppin & al, *J. Chem. Physics*, **1971**, 56, 5890-5898.
- 38 - V.A. Sirotkin & al, *Journal of structural chemistry*, **2000**, 41, n° 6, 997-1003.
- 39 - Y.G. Wu & al, *J. Mol. Liquids*, **2001**, 94, 273-282.
- 40 - I.Bako & al , *Chem. Physics Letters* , **1999** , 303 , 315-319.
- 41 - T.Takamuku & al , *J. Mol. Liquids*, **2003** , 103-104 , 143-159.
- 42- V. Madhurima, Debarun Dhar Purkayastha and N.V.S Rao, *J. Colloid Interface Sci.*, **2011**, 357, issue 1, 229-233.
- 43 - G. Ahn-Ercan, H. Krienke and G. Schmeer; *J. Mol. Liquids*, **2006**, 129, 75-79.