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Endothermicity or exothermicity of water/alcohol mixtures

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Abstract

Excess enthalpies of mixtures of water with methanol, ethanol, 1- and 2-propanol, 1-, 2- and *tert*-butanol were determined by dilution calorimetry in the accessible range of mole fractions at 25°C. Ab initio RHF calculations were performed on the alcohols, their dimers and complexes with water. A full optimisation at the 6-31G level was used to obtain the properties of interest of these systems. The calculated H-bond energies are similar for all the studied alcohols. Nevertheless, a systematic stabilisation of the mixed dimers is found, especially for the secondary and tertiary alcohols. The formation of mixed H-bond chains is exothermic and does not follow the rules of the geometric mean. To a first approximation, the experimental excess enthalpies ΔH^e for all the systems follow the equation

$$\Delta H^e = C_{6/1}X_W^6X_A + C_{1/1}X_WX_A + C_{1/2}X_WX_A^2$$

The calorimetric results may be explained by the presence in water of two kinds of H-bonds differing by about 8.3 kJ mol^{-1} in energy. Upon dilution in water, the alcohol is inserted in a weak chain and renders the adjacent water-bond strong. As a consequence, the dilution of an alcohol in water is always exothermic. The dilution of water in an alcohol causes stabilisation of the H-bonds but has a negative effect on the non-specific cohesion. The effect of the non-specific forces increases in the homologous series, making the dissolution of water in the alcohols endothermic starting from propanol. The stabilisation of H-bonds formed by water at high dilution in the alcohols increases according to the sequence: primary < secondary < tertiary.

Introduction

Mixtures of liquids present a remarkable diversity in their properties, especially in their endo- or exothermic character. From the latter point of view, mixtures of water and alcohols exhibit a particularly strange behaviour that seems incomprehensible at first sight. Mixtures of water and methanol or of water and ethanol are exothermic over the whole concentration range. However, although the dissolution of small amounts of 1-propanol in water leads to an evolution of heat, the contrary is observed when small amounts of water are dissolved in this alcohol. The dissolution of butanol in water is limited to a few per cent, above which there exists a gap of miscibility. Nevertheless, this dissolution remains markedly exothermic. In contrast, the dissolution of small amounts of water in butanol absorbs heat from the surroundings.

Empirical models have been proposed to interpret the excess properties of the water/alcohol systems [1]. They are based on equilibria between association complexes. However, these models are fundamentally questionable, because, as we have demonstrated in recent works [2], the molecular

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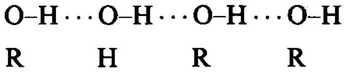
association in water and in alcohols is not an ergodic process, and that for non-ergodic phenomena the Guldberg and Waage equilibrium expression *does not hold.* According to Einstein [3], the thermodynamic probability is then ruled by fractions of time and not by concentrations. Some equation-of-state approaches have also been developed [4] and simulations either by Monte-Carlo techniques [5] or by molecular dynamics [6] have been presented. Quantum mechanical methods, although they are restricted to the study of single H-bonds, can provide useful information concerning the energy in the various homo and heterodimers. However, as will be shown in the present work, non-specific interactions also play an important role in the energy of mixing of water and alcohols.

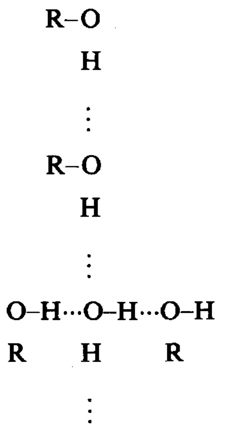
In this work we first present a general correlation giving for each of the binary systems of water with methanol, ethanol, the propanols and the butanols, the molar heat of mixing as a function of the mole fraction of the alcohol.

We also present a molecular interpretation of the terms. This interpretation is based on the fact that when one water molecule is dissolved in an alcohol, its two H atoms participate in two H-bonded chains which *differ markedly in strength.* After a first insertion leading to



$$\begin{array}{cccc} \text{O–H}\cdots & \text{O–H}\cdots & \text{O–H}\cdots & \text{O–H} \\ \text{R} & \text{H} & \text{R} & \text{R} \end{array}$$

the second H-atom can become involved in a second chain giving



The thermodynamics of the mobile disorder [2] employ not the concentrations of the entities in the liquid but the fractions of time during which the molecule is in a given state. Thus, for each water molecule the time is partitioned into three fractions: g° during which the water molecule is completely free from H-bonding, g_1 during which it is liberated from the weakest H-bond, and g_{12} where it is involved in two chains. These time fractions are ruled by the concentration of the possible insertion sites (this means by the total concentration of the oxygens) and by two insertion constants $K_{\text{ins.1}}$ and $K_{\text{ins.2}}$ related to the strength of the corresponding H-bonds. Thus:

$$g^{\circ} = 1/\{1 + K_{\text{ins.1}}(C_A + C_W)[1 + K_{\text{ins.2}}(C_A + C_W)]\} \tag{1}$$

$$g_1 = K_{\text{ins.1}}(C_A + C_W)/\{1 + K_{\text{ins.1}}(C_A + C_W)[1 + K_{\text{ins.2}}(C_A + C_W)]\} \tag{2}$$

$$g_{12} = K_{\text{ins.1}}K_{\text{ins.2}}(C_A + C_W)^2/\{1 + K_{\text{ins.1}}(C_A + C_W)[1 + K_{\text{ins.2}}(C_A + C_W)]\} \tag{3}$$

where C_A and C_W are the molar concentrations of the alcohol and of water in the system, respectively. These equations lead to a correct evaluation of the influence of the concentration C_A of an alcohol added to cyclohexane or to another inert liquid on the solubility of water in these solvents. (Eqs. (1)–(3) are a revised version of relation (5) of ref. 7). However, the values of $K_{\text{ins.1}}$ and $K_{\text{ins.2}}$ used for the fitting of these data are profoundly different; $K_{\text{ins.1}}$ is of the order of magnitude of $10\,\text{dm}^3\,\text{mol}^{-1}$, whereas the second insertion constant $K_{\text{ins.2}}$ is only of the order of $0.3\,\text{dm}^3\,\text{mol}^{-1}$.

These results can be extrapolated to pure water ($C_W^{\circ} = 55.6\,\text{mol}\,\text{dm}^{-3}$). According to the above

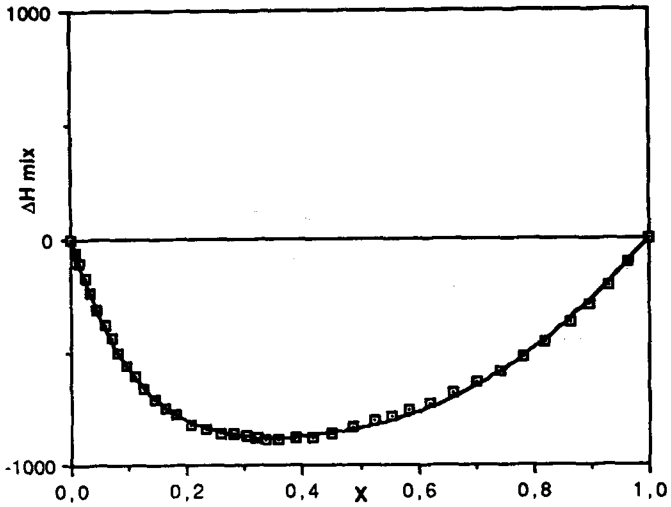


Fig. 1. Heat of mixing of water/methanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

equations, in the pure liquid at 25°C a given molecule is liberated from the weakest bond during 6% of the time. This result is confirmed by the fact that it corresponds to the percentage of free OH vibrators in pure water, as determined by Luck [8] from infrared data. The molecule is completely free of H-bonding during only 0.01% of the time.

Our discussion on the endo- or exothermicity of water/alcohol mixtures is essentially based on (i) the experimental enthalpies of mixing over the whole range of composition, and (ii) on the results of a quantum chemical study of the dimers and 1 : 1 complexes. The literature data on the molar energies of vaporisation are also used [9].

Experimental

Products used in this paper were all "for analysis"

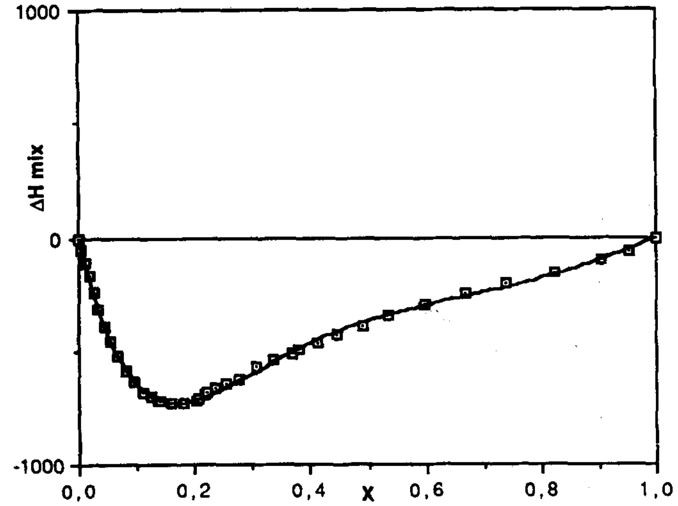


Fig. 2. Heat of mixing of water/ethanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

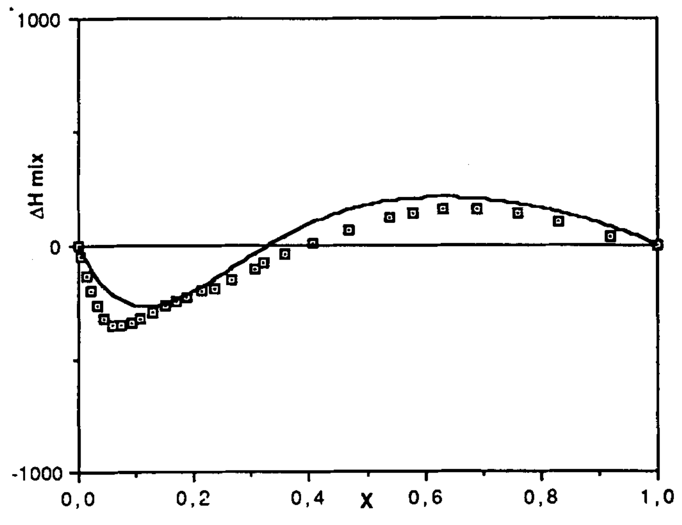


Fig. 3. Heat of mixing of water/1-propanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

quality products. Methanol and both propanols were provided by BDH, ethanol by Fluka, 1-butanol by Prolabo, 2-butanol by Baker and *tert*-butanol by Jansen. These products were not purified further and various mixtures were prepared by weight with distilled deionised water.

The heats of mixing were measured using a Parr solution calorimeter calibrated by the measure of the well-known heat exchange produced by the mixture of methylacetate with cyclohexane ($C_{p\,app}$) [10]. Temperature was recorded on an x–t recorder and ΔTs were obtained graphically from the charts.

Heat capacities of the pure compounds were taken from the review on alcohols by Zwolinski [9]. Heat capacities of the mixtures were obtained,

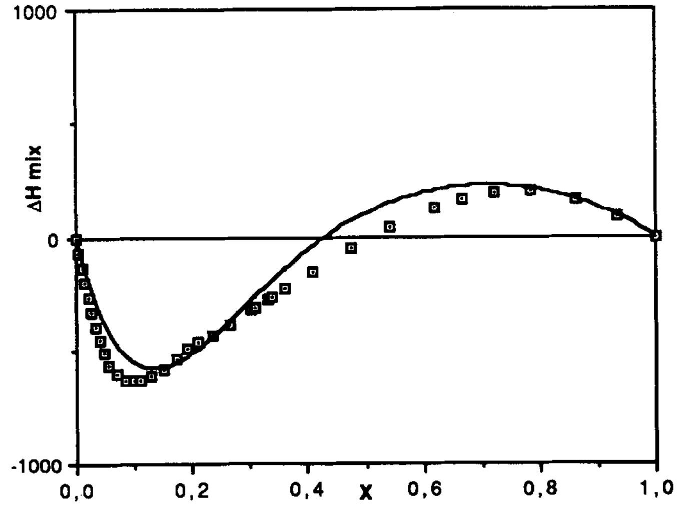


Fig. 4. Heat of mixing of water/2-propanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

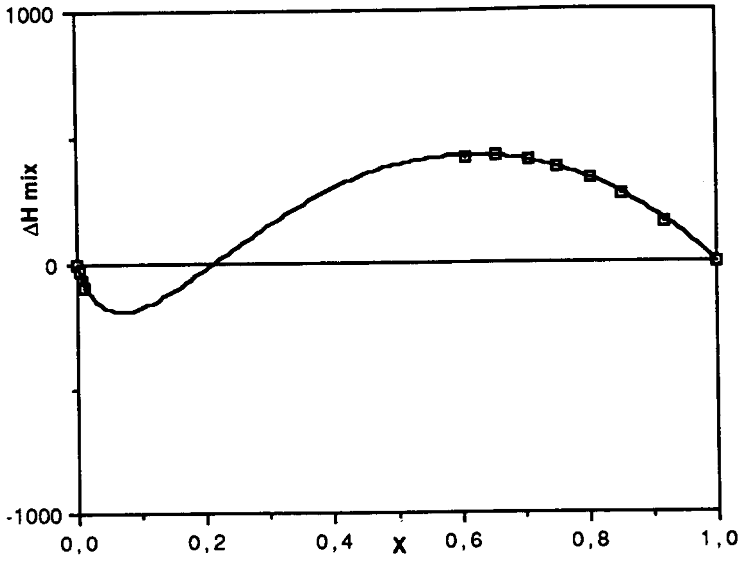


Fig. 5. Heat of mixing of water/1-butanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

assuming additivity, from the pure compounds by the relation:

$$C_{\mathrm{p\,mix}} = n_{\mathrm{W}} C_{\mathrm{pW}} + n_{\mathrm{A}} C_{\mathrm{pA}} + C_{\mathrm{p\,app}} \tag{4}$$

All measurements were made at 25°C except for *tert*-butanol for which the temperature was raised above its melting temperature to 28°C.

Enthalpy data were obtained by successive addition of small amounts of solute starting from either the pure compound or mixtures of known composition. In this way, the complete range of mixing was scanned and the various explored regions were allowed to overlap to ensure the reliability of the measurements. The experimental excess molar enthalpies of mixing are represented by the dots in Figs. 1–7.

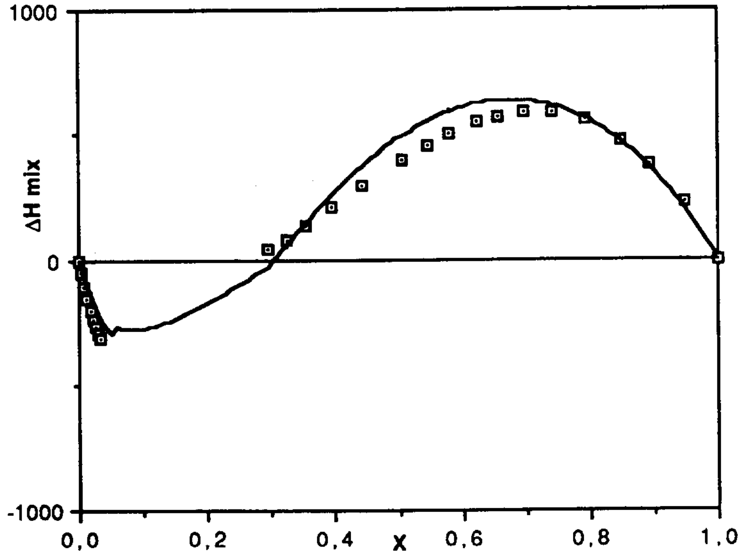


Fig 6. Heat of mixing of water/2-butanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

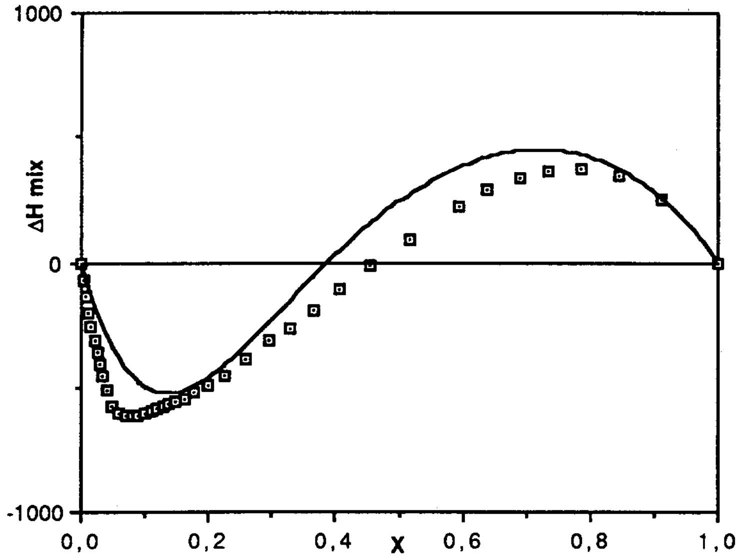


Fig. 7. Heat of mixing of water/*tert*-butanol mixtures (J mol^{-1}) vs. mole fraction of alcohol. The curve is obtained using Eq. (9).

Theoretical approach

Ab initio calculations were performed on all the measured alcohols, their dimers and 1 : 1 complexes with water. Two complexes can be found as water or the alcohol molecule may act as a proton donor and lead to H-bond formation.

The computations were performed at the SCF level of precision using the GAUSSIAN 86 series of programs [11]. The 6-31G valence split basis set [12] was used throughout the theoretical study. The structures of the molecules, dimers and complexes were fully optimised, relaxing any symmetry constraint. The quality of the obtained structure was checked by performing a second-order analytical derivation of the potential hypersurface. This further allows the computation of the normal modes of vibration and their related frequencies. The knowledge of the structure and vibrational frequencies can provide some thermodynamic information through the use of the well-known statistical relations. A detailed analysis of these results will be published elsewhere, but, as an example, some structures are shown in Fig. 8 and the related total energies are given in Table 1.

From these data, it is possible to calculate the changes in energy corresponding to several processes. One is the formation of an H-bond (ΔE_{I}):

$$\mathrm{ROH} + \mathrm{XOH} \rightarrow \mathrm{ROH}\cdot\mathrm{XOH} \qquad (5)$$

Table 1
Total energies (u) at the RHF 6-31G level

	ROH	ROH→W	W→ROH	$(\mathrm{ROH})_2$
Water	− 75.98535	–	–	−151.98322
Methanol	−114.98817	−190.98541	−109.98658	−229.98877
Ethanol	−154.01323	−230.01030	−230.01188	−308.03886
1-Propanol	−193.03200	−269.02907	−269.03061	−386.07637
2-Propanol	−193.03756	−269.03457	−269.03659	−386.08766
1-Butanol	−232.05032	−308.04737	−308.04898	−464.11308
2-Butanol	−232.05568	−308.05260	−308.05484	−464.12403
t-Butanol	−232.06054	−308.05733	−308.05970	−464.13350

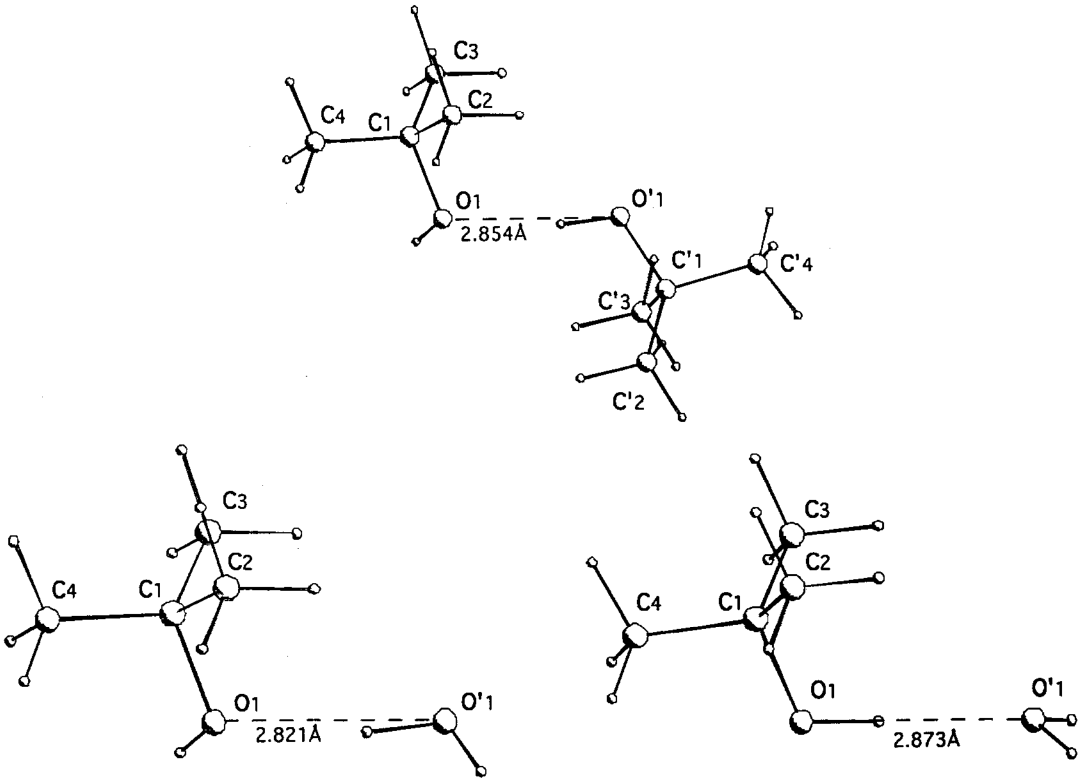


Fig. 8. Structure of *tert*-butanol complexes obtained by ab initio calculations.

When X differs from R, two cases have to be considered depending on the molecule which acts as the proton donor. ΔE_I will therefore be different for the interactions ROH → W and W → ROH. Another energy difference (ΔE_{II}) can be calculated characterising the dismutation process:

$$(ROH)_2 + (H_2O)_2 \rightarrow 2ROH \cdot H_2O \qquad (6)$$

Here, three possibilities exist:

(i) the formed complexes are both of the type ROH → W;

(ii) the complexes are both of the type W → ROH;

(iii) the two types of complexes are present, giving rise to a mixed situation.

These results are shown in Table 2.

Table 2
Ab initio calculated energies (kJ mol^{-1}) of association (ΔE_I) and dismutation (ΔE_{II})

	ΔE_I			ΔE_{II}		
	ROH → W	W → ROH	$(ROH)_2$	ROH → W	W → ROH	Mixed
Water	–	–	−32.80	–	–	–
Methanol	−31.20	−34.27	−32.66	3.06	−3.08	−0.01
Ethanol	−30.74	−34.88	−32.56	3.89	−4.40	−0.51
1-Propanol	−30.74	−34.77	−32.46	3.78	−4.27	−0.49
2-Propanol	−30.57	−35.88	−32.90	4.57	−6.06	−1.49
1-Butanol	−30.68	−34.91	−32.65	4.10	−4.36	−0.26
2-Butanol	−30.34	−36.23	−33.25	5.38	−6.40	−1.02
t-Butanol	−29.99	−36.22	−32.58	5.40	−7.05	−1.65

It is well known that theoretical reaction energies contain some imperfections due to approximations inherent in the theoretical approach. These are essentially the basis set limitation leading to the basis set superposition error and the lack of electron correlation. Nevertheless, from the energetic point of view, these errors cancel out if some care is taken in the definition of a reference reaction. This is the case when the number and nature of the bonds between the reactants and products is conserved. As process II (Eq. (6)) satisfies these requirements, including H-bonds, the corresponding energy may be considered with some confidence. However, from a geometrical point of view, the structures obtained are known to be accurate enough to lie within the experimental error.

Table 2 shows a remarkable constancy in the energy of formation of homodimers from water to *tert*-butanol. In heterodimers, the interaction is always stronger when water acts as a proton donor. In this case, a systematic increase of the absolute value is observed when going from the primary alcohols to secondary or tertiary ones. The reverse effect occurs for the complexes where water acts as proton acceptor.

The most interesting data with respect to the aim of this work are those of the last column. They show a systematic stabilisation when homodimers dismutate into mixed heterodimers. Although these results do not concern associates of more than two molecules, they suggest that the formation of mixed water/alcohol H-bonded chains starting from homogeneous chains is an exothermic process. *This makes the rule of geometric mean no longer valid in such systems.* A last important point is the influence of the isomer structure: the exothermic effect in ΔE_{II} is systematically larger for secondary and tertiary compounds. One therefore expects that the formation of mixed chains of these compounds with water will still be favoured compared to the primary compounds.

Discussion

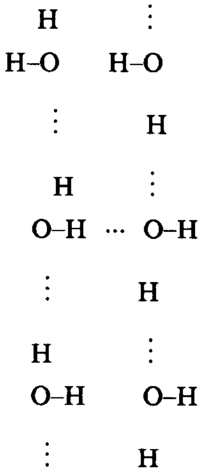
Usually, one tries to express excess enthalpies of mixing by means of a function such as:

$$\Delta H^{\mathrm{e}} = X_{\mathrm{W}} X_{\mathrm{A}} F(X_{\mathrm{W}}, X_{\mathrm{A}}) \tag{7}$$

because this function passes through the origin at mole fractions equal to zero and one.

The derived experimental function $F(X_{\mathrm{W}}, X_{\mathrm{A}})$ is represented in Fig. 9. For all the alcohols, these functions show much more systematic behaviour than the direct ΔH^{e} curves. Above $X_{\mathrm{A}} = 0.2$, F displays only a very limited change, although the average value in this range depends on the nature of the alcohol. Below $X_{\mathrm{A}} = 0.2$ a sharp decrease in F is observed towards pure water. This means that in this region a formal polynomial development of F involves a dominating term of a high power for X_{W} and that the phenomenon implies a large number of water molecules. An initial idea of the molecularity of the phenomenon may be obtained by analysis in this region of the logarithmic behaviour of F against X_{W}. One finds a value of 5.7 ± 1.4 for this slope.

A molecularity of six can be expected on the basis of the reinforcement by the alcohol of the weak chain in water as noted in the Introduction. In order to define a weak chain in water, six molecules are required because a strong chain involves at least three molecules.



Suppose the vertical chains are strong. When ROH is inserted in the weak horizontal chain, the water

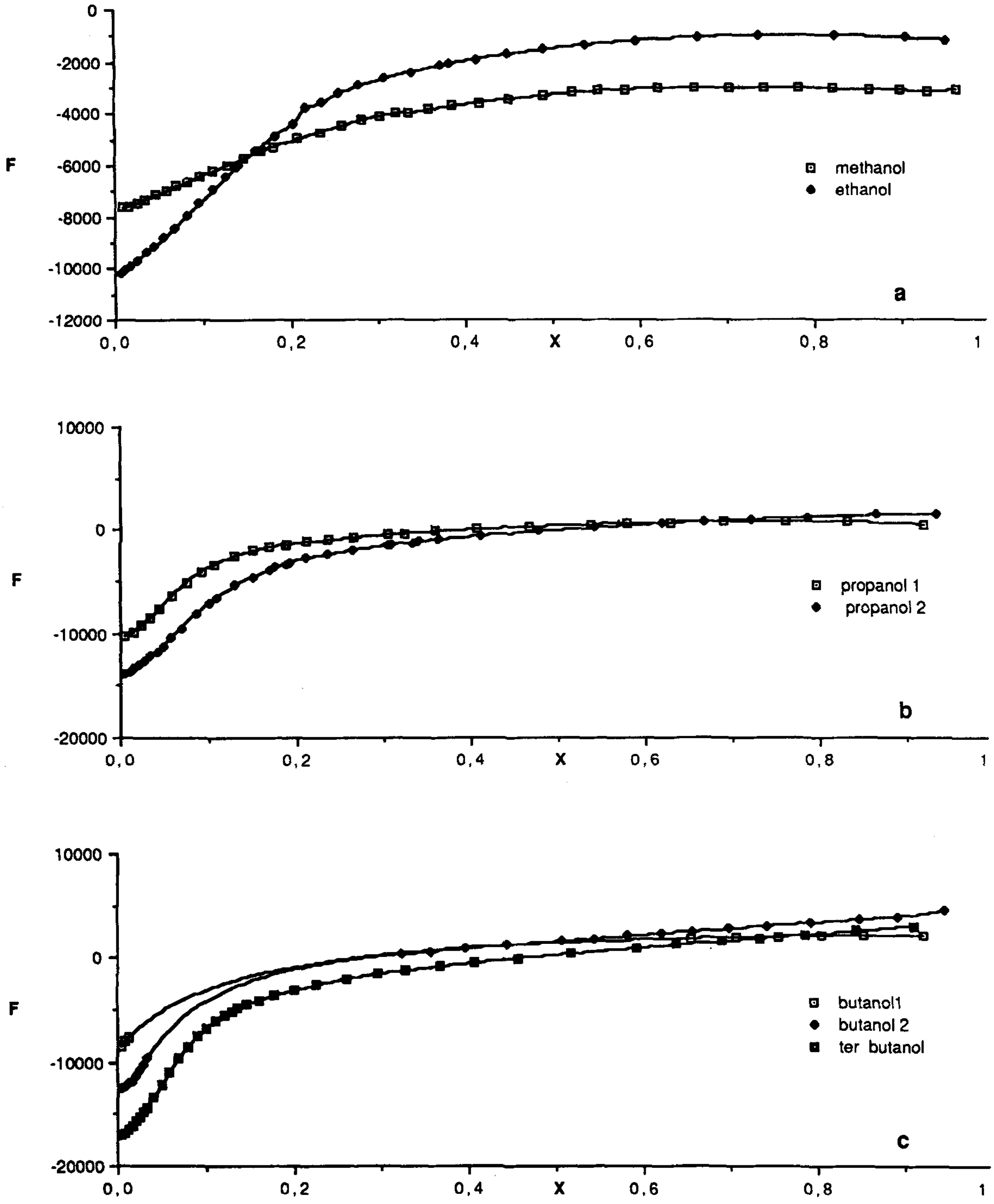


Fig. 9. $F(X)$ function obtained for the water/alcohol mixtures vs. mole fraction of alcohol.

Table 3
Regression coefficients of ΔH^e following Eq. (9) (kJ mol^{-1})

	$C_{6/1}$	$C_{1/1}$	$C_{1/2}$
Methanol	− 5.1	−3.4	0.5
Ethanol	−10.6	−1.2	0.1
1-Propanol	− 6.3	0.7	0.4
2-Propanol	−10.4	−0.2	1.9
1-Butanol	− 9.1	1.1	1.0
2-Butanol	− 8.7	0.1	4.2
t-Butanol	− 8.4	−1.1	4.6

molecule at the left forms two strong bonds because all the bonds formed by the alcohol are strong. As 94% of the water molecules in water form weak chains, the proportion will depend on X_W^6.

For the primary alcohols, experimental F functions above $X_A = 0.2$ present a remarkable plateau. For this series, one can thus envisage to a first approximation a two term function:

$$\Delta H^e = C_{6/1} X_W^6 W_A + C_{1/1} X_W X_A \tag{8}$$

For the branched alcohols, a small positive slope is observed which can be accounted for by an additional $X_W X_A^2$ term. Thus:

$$\Delta H^e = C_{6/1} X_W^6 W_A + C_{1/1} X_W X_A + C_{1/2} X_W X_A^2 \tag{9}$$

The coefficients of this equation were fitted by a multifactor regression analysis procedure. Curves calculated with these coefficients are reproduced in Figs. 1–7. The corresponding coefficients are listed in Table 3.

It is evident that Eq. (9) correctly describes the general behaviour of alcohol/water mixtures. For methanol and ethanol, where the non-specific effects are clearly less important, the agreement is astonishing (especially for ethanol where the inflection of the curve is perfectly reproduced).

For higher alcohols, the overall behaviour is satisfactory and the passage from exothermicity to endothermicity is correctly predicted. However, the intervention of non-specific forces is more roughly approximated. In particular, the higher endothermicity at lower X_A values may be related to dipole-dipole induced forces which are not taken into account and are more important for the alkyl residues of the alcohol in water than in their own phase.

We shall now discuss the various coefficients of the correlation. The $C_{6/1}$ coefficients have important negative values which exhibit differences which do not seem to present any systematic correlation with the molecular weight or the structure of the alcohols. Their mean value is -8.3 ± 2 kJ mol^{-1}. According to the ideas discussed above, this may be interpreted as resulting from the reinforcement of the weak H-bond in liquid water where one alcohol molecule is inserted in the weak chain. The H-bond formed by the inserted alcohol molecule will of course preserve the strength it had in its own phase. This effect is restricted to the first insertion of an alcohol molecule. The enforcement is estimated to have a mean value of 8.3 kJ mol^{-1}. In this sense, the dissolution of alcohol in water is always markedly exothermic. As a consequence, we may say that the energy difference between strong and weak H-bonds is close to 8.3 kJ mol^{-1} and, if one neglects the entropic effects due to the enhancement of vibrational motions, one expects between the insertion constants in both chains a factor of:

$$\frac{K_1}{K_2} \approx \exp\left(\frac{8300}{RT}\right) \approx 28$$

This is the order of magnitude of previous estimations of such a ratio (see introduction in ref. 7 for a value of 33).

The coefficient $C_{1/1}$ is negative for some alcohols and positive for others. This demonstrates that this term has a hybrid origin. Dispersion and dipole-dipole interactions lead to a positive heat of mixing (Scatchard-Hildebrand), whereas the previous theoretical study shows that the contrary effect is expected for H-bonding. One can therefore divide the $C_{1/1}$ term into two contributions:

$$C_{1/1} = C'_{1/1}\,(\text{H-bond}) + C''_{1/1}\,(\text{non-specific}) \qquad (10)$$

The latter term is positive, the former negative.

If we consider the sequence of primary alcohols, this coefficient exhibits a systematic increase. For this series $C_{1/1}$ may be related to the number of carbon atoms n_C by

$$C_{1/1} = -4.6 + 1.6n_C\,(\text{kJ mol}^{-1})$$

The value of $-4.6\,\text{kJ mol}^{-1}$ describes the stabilisation of the mixed R-OH $\cdots$ H-OH bonds which is supposed to be the same for the whole series. For the secondary and tertiary alcohols, $C_{1/1}$ is systematically more negative, the differences being of the order of -1 and $-2\,\text{kJ mol}^{-1}$ respectively. This demonstrates, as predicted by the theoretical results, that the reinforcement of the H-bonds for mixing is more important in these cases. It should be noted that for the primary alcohols the non-specific part of the heat of mixing is given to a first approximation (neglecting the $C_{1/2}$ contribution) by $C''_{1/1}X_W X_A$. This equation differs fundamentally from the Scatchard-Hildebrand relation because it contains only the mole fractions and ignores effects due to the difference in molar volumes which should not be negligible in the considered case ($V_{(\text{H}_2\text{O})} = 18\,\text{cm}^3\,\text{mol}^{-1}$ and $V_{(\text{Butanol})} = 92\,\text{cm}^3\,\text{mol}^{-1}$). The reason is that in structured mixtures such as alcohols and water, no random mixing rules the contacts between molecules embedded in long molecular chains.

Finally, the $C_{1/2}$ coefficients are negligible for the normal alcohols. For secondary and tertiary alcohols, they exhibit positive values and, in contrast to $C_{1/1}$, concern only non-specific effects.

Differences in the non-specific cohesive forces are clearly shown in the energies of vaporisation (ΔU^V) given in Table 4. They are compared with the half-vaporisation energies of the dimers obtained from the two alkyl residues. The differences are related to the cohesion of the OH group, (ΔU^M_{OH}). For the primary alcohols, the latter value is close to the energy obtained from the theoretical calculations. However, it must be kept in mind that in the liquid, the OH group in the chains is also bound to the surroundings by non-specific forces. This means that the concurrence of the forces lowers the contribution of the H-bond in the energy of vaporisation. Such effects can be a priori expected.

The differences in ΔU^V between the isomers is essentially a consequence of the differences in the non-specific forces, with a lowering of about $2\,\text{kJ mol}^{-1}$ on going from the primary to the secondary isomer and $4\,\text{kJ mol}^{-1}$ on going from the primary to the tertiary isomer. A similar trend is observed in the $C_{1/2}$ coefficient.

Table 4
Vaporisation energies of alcohols and related dimer alkanes (kJ mol^{-1}) [9]

	ROH ΔU^V	R-R $1/2\Delta U^V$	H-bond ΔU^M_{OH}
Water	41.5	–	–
Methanol	34.9	(1.3)	33.6
Ethanol	39.8	9.3	30.5
1-Propanol	44.7	14.6	30.1
2-Propanol	42.9	13.3	29.6
1-Butanol	49.9	19.5	30.4
2-Butanol	47.2	18.3	28.9
t-Butanol	44.1	16.8	27.3

Comparing the isomers of butanol, one is confronted by the fact that $C_{1/1} + C_{1/2}$ is larger for 2-butanol than for *tert*-butanol. This can only be explained by a competition between the non-specific forces which, on the one hand, increase the endothermicity of the mixture and, on the other hand, increase the reinforcement of the mixed H-bonds, which induces an exothermic effect and favours the tertiary butyl isomer. This competition clearly leads to the sequence observed at $X_A \to 1$ for the various butanol isomers (Figs. 5–7 and 9(c)) putting *tert*-butanol between the primary and secondary isomers.

Conclusions

The most important results of this study are on the one hand, the confirmation of the existence of two kinds of H-bonded chains in water, the weakest of which can become reinforced by the insertion of one alcohol molecule, and on the other hand, the non-applicability of the rule of the geometric mean to the formation of mixed H-bond chains. The study demonstrates the usefulness of the comparison of results obtained from ab initio calculations which lead to the above-mentioned conclusions, with experimental quantities such as heats of vaporisation and mixing. The theoretical method shows an impressive constancy in the energy of dimerisation for the whole series of alcohols and of water. This can be compared with the constancy of the share of H-bonds in the experimental energies of vaporisation of the primary alcohols. However, both figures differ by a constant value. This is the consequence of the fact that other cohesive forces have a concurrent effect which reduces the share of H-bonding in the liquid.

The heat of mixing of an alcohol with water is ruled by the peculiarities of H-bonding as they are predicted by the ab initio calculations, and by the intervention of non-specific forces which are ruled to a first approximation by the geometric mean rule but deviate from the Scatchard-Hildebrand equation because of the non-randomness of the contacts.

Acknowledgement

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