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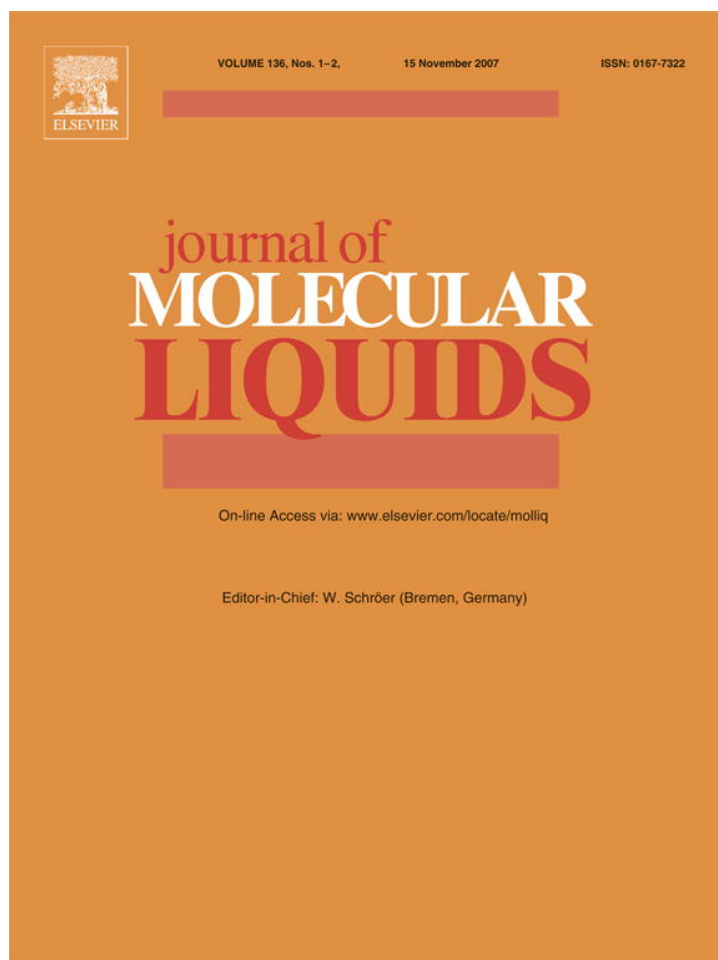


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Experimental and theoretical study of thermodynamic excess properties of associating liquid alkanol+4-picoline mixtures based on quantum mechanical ab initio calculations

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Received 22 January 2006; accepted 2 February 2007

Available online 2 March 2007

Abstract

Experimental data of the molar enthalpy of mixing H_m^E of 6 alkanol+4-picoline systems obtained by flow calorimetric measurements have been compared with statistical–mechanical calculations based on the ERAS-model. The original version of the model has been extended by accounting for results obtained by quantum mechanical ab initio calculations of energetic and structural properties of about 50 molecular clusters, each containing up to 4 molecules associated by hydrogen bonding. The essential results obtained from these calculations are cooperative effects concerning the hydrogen bonding energies of linearly associated alkanol clusters and the quantitative specification of particularly stabilized cyclic alkanol tetrameric clusters. Furthermore, results for the structure and energy of cross-associating clusters containing alkanols and 4-picoline molecules have revealed that the cross-associating energy of the alkanol+4-picoline hydrogen bonding exceeds the self associating energy of alkanol molecules also leading to an additional cooperative energetic effect when more than two molecules are involved. These quantum mechanical results have directly been incorporated as molecular parameters into the extended ERAS-model without increasing the number of freely adjustable parameters compared to previous versions of the model. An excellent description of the thermodynamic mixture properties has been achieved. The molar excess enthalpy H_m^E is negative for all 1-alkanol+4-picoline mixtures while isomeric 2-alkanol+4-picoline mixtures show positive H_m^E values quantitatively described by the theory. An explanation of this effect is given on the basis of the ab initio results.

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Keywords: Quantum mechanical ab initio calculations; Molecular thermodynamics; Molecular clusters; Hydrogen bonding; Liquid mixtures

1. Introduction

The liquid structure of strongly associated systems such as alkanols and mixtures of alkanols with amines or pyridine derivatives is dominated by hydrogen bonding of the type $\text{OH}\cdots\text{O}$ and $\text{OH}\cdots\text{N}$. This fact has been known for decades from a qualitative point of view but only recent information obtained from infrared spectroscopic and ^1H -NMR-data combined with quantum mechanical ab initio or DFT (density functional theory) calculations have provided a more detailed insight into the relationship between spectroscopic data and the structural and energetic properties of molecular clusters formed by hydrogen bonding between the associating molecules [1,2]. It is obvious that thermodynamic properties of associating liquid systems will

be dominated by the structure and energetics of molecular clusters which are responsible for the strong deviation from what is called an ideal behavior of liquid mixtures. However, statistical thermodynamics accounting for the large variety of clusters present in these systems is complicated and has necessarily to be restricted to the essential features of the molecular clusters. Without having more detailed information of the molecular nature of these clusters any statistical thermodynamic model will contain a high degree of arbitrariness concerning the intermolecular parameters such as association constants and association enthalpies which are needed for describing macroscopic thermodynamic properties like vapor pressure of mixtures, activity coefficients, heat of mixing, volumes of mixing and others.

Statistical mechanical models such as the ERAS (extended real associated solution)-model which is based on a realistic molecular picture of the dense liquid state of associating molecules have suffered so far from the deficiency of molecular information such

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as the relationship of statistical weight of open linearly associated species compared to cyclic ones or hydrogen bonding energies responsible for the stability and structure of such clustering species including possible cooperative effects. The flexible nature of the ERAS-model allows to account for these molecular information. However, the increasing number of model parameters has prevented a reasonable application of the extended ERAS-model for describing thermodynamic and spectroscopic properties as long as these parameters can freely be adjusted to experimental data. This situation has changed since a couple of years due to the availability of reliable quantum mechanical calculation procedures treating larger molecular clusters.

Recently we have presented an extensive study of thermodynamic, IR and ^1H -NMR spectroscopic properties of butanol+hexane and butanol+cyclohexane mixtures using an extended version of the ERAS-model, which contains quantitative information obtained from quantum mechanical calculations of butanol clusters in hexane and cyclohexane [2]. It has been shown that the simultaneous description of thermodynamic and spectroscopic properties of these mixtures could be achieved providing a more detailed insight into the molecular structure and energetics of these mixtures. Very recently also heats of dilution of alcohol+pyridine systems have been studied and interpreted on the basis of the ERAS-model using the first results of ab initio calculations of alcohol+pyridine dimers [3]. In this work we extend the ERAS-model to liquid mixtures containing self associating alkanol molecules and a tertiary amine or a pyridine derivative where also cross-association species between different type of molecules occurs. Ab initio and density functional theory (DFT) calculations obtained for about 50 clusters containing alkanol as well as 4-picoline molecules have provided structural and energetic parameters which have been incorporated into the ERAS-model. The results obtained with the model allow to describe the excess enthalpy of 6 alkanol+4-picoline mixtures as function of composition in quantitative agreement with the experiment and the observed experimental results can be interpreted on a reliable molecular basis.

2. Calorimetric measurements

Molar excess enthalpies H_m^E of the 6 alkanol+4-picoline mixtures (methanol+4-picoline, ethanol+4-picoline, propan-1-ol+4-picoline, butan-1-ol+4-picoline, propan-2-ol+4-picoline, and butan-2-ol+4-picoline) have been measured at 298.15 K covering the whole range of concentration. The results have been obtained by using a precision flow calorimeter (Thermal Activity Monitor 2277, Thermometrics). The molar flow rates of the two components \dot{n}_A and \dot{n}_B delivered by two precision HPLC-pumps and the continuous heating or cooling rate \dot{Q} measured in the mixing chamber of the calorimetric unit are related to the molar excess enthalpy by

$$H_m^E = - \frac{\dot{Q}}{\dot{n}_A + \dot{n}_B} \quad (1)$$

with the corresponding mole fraction

$$x_A = \frac{\dot{n}_A}{\dot{n}_A + \dot{n}_B} \quad (2)$$

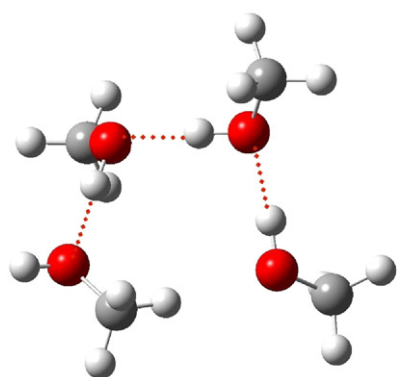
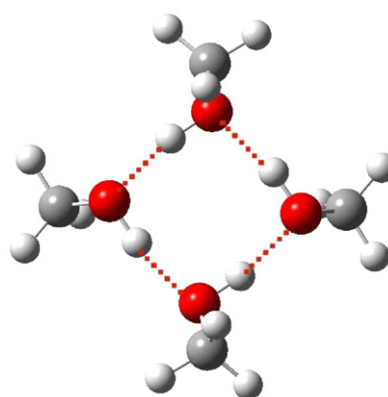
Numerical results of H_m^E as function of the mole fraction x_A of the alkanol are listed in Table 1 and are presented graphically in Figs. 6–11. The chemicals have purities higher than 99% and have been degassed before using them. The accuracy of the experimental results is estimated to be $\pm 1.5\%$ of the H_m^E -value.

3. Ab initio and DFT calculations of cluster properties

Using the Gaussian03 program package [4] quantum mechanical calculations of hydrogen bonding energies were performed for the self association of normal alcohols (methanol, ethanol, propan-1-ol, butan-1-ol) and alcohol isomers (propan-2-ol, butan-2-ol) up to the tetrameric clusters as well as for the association of clusters consisting of the 4-picoline molecule and up to three linearly associated alcohol molecules. The calculated structures

Table 1
Experimental molar excess enthalpies (H_m^E) of alcohols (ROH) in 4-picoline (4P) at $T=298.15$ K

x_A	$H_m^E/\text{J mol}^{-1}$	x_A	$H_m^E/\text{J mol}^{-1}$
(MeOH)+(4P)		(EtOH)+(4P)	
0.0459	−135.0	0.0455	−51.5
0.1074	−305.8	0.1066	−134.6
0.2021	−545.1	0.2044	−232.5
0.3044	−768.8	0.3053	−324.3
0.4026	−951.5	0.4005	−392.9
0.4977	−1048.3	0.5107	−444.0
0.5461	−1064.7	0.5530	−453.5
0.6050	−1053.1	0.5922	−458.3
0.6050	−1063.3	0.6475	−454.2
0.6632	−1021.3	0.7147	−430.9
0.7065	−978.1	0.8067	−360.0
0.8049	−778.6	0.8815	−267.0
0.8845	−524.2	0.9480	−128.0
0.9460	−262.5		
(1PrOH)+(4P)		(1BuOH)+(4P)	
0.0417	−33.9	0.0409	−8.9
0.1060	−84.0	0.1059	−23.3
0.2069	−156.5	0.2024	−55.2
0.3031	−220.3	0.3075	−91.7
0.4071	−274.6	0.4081	−126.4
0.5107	−308.8	0.5159	−156.7
0.5661	−318.1	0.5683	−168.8
0.6421	−318.2	0.6426	−176.9
0.7098	−301.2	0.7057	−175.5
0.8030	−252.3	0.7570	−167.7
0.8852	−173.2	0.8039	−156.4
0.9432	−101.9	0.8857	−114.5
		0.9509	−63.3
(2PrOH)+(4P)		(2BuOH)+(4P)	
0.0407	24.7	0.0407	33.2
0.1038	59.5	0.1055	74.0
0.2031	97.5	0.2018	121.6
0.3053	121.4	0.3067	149.5
0.4014	129.1	0.4072	159.0
0.5048	129.0	0.5149	154.0
0.6046	119.3	0.6053	138.6
0.7049	99.8	0.7049	112.9
0.8024	74.2	0.8033	75.7
0.8828	41.9		
0.9419	15.7		


Fig. 1. Linearly associated (MeOH)₄ cluster (*cis*-conformer).

Fig. 3. Cyclic associated (MeOH)₄ cluster.

were optimized at the B3LYP/6-31++G(d,p) level. They represent real energetic minimum structures on the potential energy surface since no imaginary frequencies were observed.

Molecular clusters consisting of up to 4 alcohol molecules have been studied using the described computational technique. Also cyclic trimers and cyclic tetramers have been accounted for. In addition mixed clusters containing one 4-picoline molecule and up to 3 linearly associated alcohol molecules have been considered. Complete geometric structures and the total cluster formation energy at 298.15 K with respect to the isolated single molecules have been calculated for all together 50 molecular clusters. In some cases structural conformers with almost identical formation energies have been found. As example Figs. 1–3 show different conformers of linearly associated methanol clusters with 4 methanol molecules and the cyclic tetramer. The first linear conformer is a *cis*-conformer (Fig. 1), the second one is *trans*-conformer (Fig. 2). Figs. 4 (*cis*) and 5 (*trans*) show the corresponding structure of the cross-associated (1BuOH)₃(4P) and (EtOH)₃(4P) respectively.

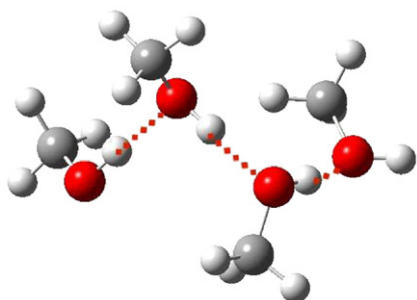
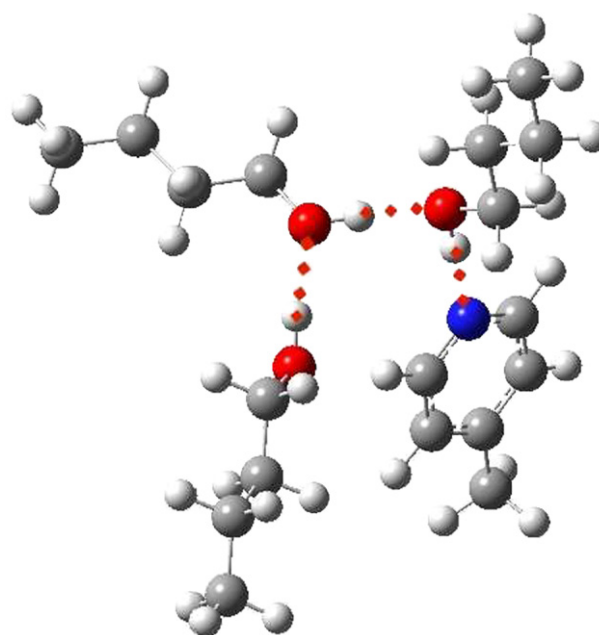
The total interaction energies of the alcohol clusters $\Delta E(A_n)$ and alcohol+4-picoline clusters $\Delta E(A_nP)$ were first calculated using the B3LYP/6-31++G(d,p) method. The supermolecule approach was applied

$$\Delta E(A_n) = E(A_n) - nE(A_1) \quad (3)$$

$$\Delta E(A_nP) = E(A_nP) - nE(A_1) - E(P) \quad (4)$$

Since the density functional method is known to have problems with accounting correctly for the effect of the dispersion

interactions, we also made energy calculations using the MP2 perturbation method based on the geometric structures obtained at the B3LYP/6-31++G(d,p) level. The 6-31++G(d,p) and cc-pVTZ basis sets were applied using the MP2 level. Corrections for the basis set super position error (BSSE) and differences in the zero point energies (ZPE) were applied at both theoretical levels. These corrections have been calculated by using the method of Boys and Bernardi [5] and the harmonic approximation (ZPE), respectively. Since the MP2/cc-pVTZ method is considered as the most reliable one, results obtained by this method are presented in Table 2, additive results obtained by the B3LYP/6-31++G(d,p) and the MP2/6-31++G(d,p) method are given in the supplementary material. Values of $\Delta E(0 \text{ K})$, the electronic cluster bonding energies at 0 K according to Eqs. (3) and (4), are shown without correction (1st column), with the BSSE correction (2nd column), and with BSSE and ZPE correction (3rd column). The ZPE correction contains the zero point energies of all harmonic normal frequencies existing in the corresponding cluster and the separated molecules of which the


Fig. 2. Linearly associated (MeOH)₄ cluster (*trans*-conformer).

Fig. 4. Cross associated (1BuOH)_{3,linear}+(4P) cluster (*cis*-conformer).

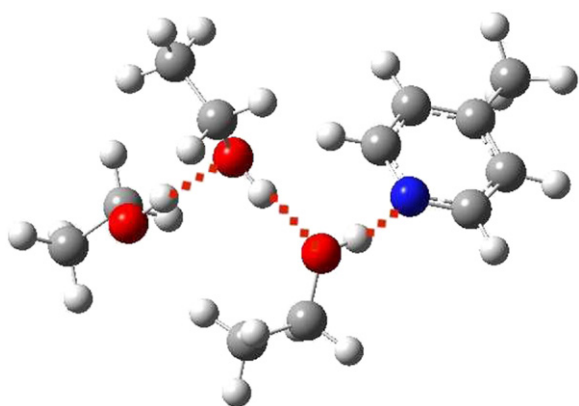


Fig. 5. Cross associated (EtOH)_{3,linear}+(4P) cluster (*trans*-conformer).

cluster consist. The last column contains the total formation enthalpy Δh of the clusters at 298 K obtained from the $\Delta E(0\text{ K})$ values in the 3rd column plus the thermal contribution arising from translational, rotational and vibrational contributions according to the usual formulas of statistical thermodynamics. It has to be pointed out that enthalpy values are identical to the corresponding values of the internal energy since the $p\Delta v$ is negligible in the condensed liquid state. The complete numerical data material of normal frequencies and geometric parameters of the clusters is also available in the supplementary material.

It is obvious from the results in Table 2 that the BSSE corrections are particularly important in the MP2 calculations, since it is well known that this method is highly sensitive to this kind of error [6]. The corrections for the ZPE's were taken from the B3LYP calculations.

Inspection of Table 2 shows that different conformers of linearly associated tetramers have to be considered. In case of methanol results of the linear *cis*-conformer (see Fig. 1) and linear *trans*-conformer (see Fig. 2) are presented. Obviously the *cis*-conformer is the more stable conformer. In case of all other linear tetramers only the most stable *cis*-conformer is presented with exception of (1PrOH)_{4,linear,trans} and (2BuOH)_{3,linear,trans}(4P).

The stepwise association enthalpies step $\Delta_R h$ for building up the clusters at 298 K have been calculated according to the following definitions

$$\Delta_R h(A_2) = \Delta h(A_2), \quad (5)$$

$$\Delta_R h(A_{n,\text{linear}}) = \Delta h(A_{n,\text{linear}}) - \Delta h(A_{n-1,\text{linear}}) \quad (n > 2) \quad (6)$$

$$\Delta_R h(A_{n,\text{cyclic}}) = \Delta h(A_{n,\text{cyclic}}) - \Delta h(A_{n,\text{linear}}) \quad (n = 3 \text{ or } 4) \quad (7)$$

$$\Delta_R h(A_n P) = \Delta h(A_n P) - \Delta h(A_{n-1} P) \quad (n \geq 1) \quad (8)$$

where $\Delta h(A_2)$, $\Delta h(A_{n,\text{linear}})$, $\Delta h(A_{n,\text{cyclic}})$, $\Delta h(A_n P)$ are the values given in the last column of Table 2. Results of the step association enthalpies based on the results of Table 2 are presented in Table 3.

From Table 3 the cooperative effect of linearly associating alcohol clusters can be clearly recognized. Values of the H-bonding enthalpy $\Delta_R h$ for linearly associated alcohols is ca.

double as large for trimers and tetramers as for dimers. The observed increase of the $\Delta_R h$ in cyclic tetramers compared to cyclic trimers is not surprising due to the less favorable steric situation in cyclic trimers. Comparison of linear and cyclic

Table 2

Calculated total cluster bonding energies using the MP2/cc-pVTZ method according to Eqs. (3) and (4)

Cluster	$\Delta E(0\text{ K})/\text{kJ mol}^{-1}$ uncorrected	$\Delta E(0\text{ K})/\text{kJ mol}^{-1}$ corrected with BSSE	$\Delta E(0\text{ K})/\text{kJ mol}^{-1}$ corrected with BSSE and ZPE	$\Delta h(298\text{ K})/\text{kJ mol}^{-1}$ corrected with BSSE and ZPE
(MeOH) ₂	−28.4	−20.8	−15.0	−11.4
(MeOH) _{3,linear}	−71.7	−53.1	−40.5	−34.3
(MeOH) _{3,cyclic}	−85.4	−64.6	−49.5	−44.8
(MeOH) _{4,linear,cis}	−116.5	−88.0	−68.6	−59.8
(MeOH) _{4,linear,trans}	−108.9	−81.4	−63.5	−51.1
(MeOH) _{4,cyclic}	−148.3	−114.8	−92.1	−85.5
(MeOH) (4P)	−35.4	−27.9	−23.1	−19.0
(MeOH) ₂ (4P)	−84.0	−64.8	−53.1	−46.4
(MeOH) _{3,linear}	−131.6	−102.0	−84.1	−74.4
(4P) _{cis}				
(EtOH) ₂	−31.4	−22.2	−16.7	−12.8
(EtOH) _{3,linear}	−73.6	−54.1	−42.6	−35.1
(EtOH) _{3,cyclic}	−86.3	−65.2	−51.9	−45.7
(EtOH) _{4,linear,cis}	−122.0	−92.0	−87.4	−63.8
(EtOH) _{4,cyclic}	−151.1	−117.5	−96.3	−87.9
(EtOH) (4P)	−35.5	−28.0	−23.4	−19.0
(EtOH) ₂ (4P)	−85.3	−65.8	−55.0	−47.4
(EtOH) _{3,linear}	−127.2	−96.8	−80.6	−69.0
(4P) _{trans}				
(1PrOH) ₂	−31.7	−22.6	−17.2	−13.1
(1PrOH) _{3,linear}	−73.2	−53.6	−43.1	−34.9
(1PrOH) _{3,cyclic}	−88.3	−67.3	−54.6	−47.9
(1PrOH) _{4,linear,trans}	−120.3	−88.4	−73.2	−60.6
(1PrOH) _{4,cyclic}	−157.0	−124.5	−104.5	−95.7
(1PrOH) (4P)	−35.6	−28.2	−23.9	−19.3
(1PrOH) ₂ (4P)	−85.7	−66.5	−56.3	−48.2
(1BuOH) ₂	−32.0	−22.8	−18.2	−13.8
(1BuOH) _{3,linear}	−78.1	−58.1	−47.2	−39.2
(1BuOH) _{3,cyclic}	−89.2	−68.4	−55.8	−49.0
(1BuOH) _{4,linear,cis}	−123.7	−94.7	−78.8	−66.5
(1BuOH) _{4,cyclic}	−154.8	−119.6	−100.8	−90.6
(1BuOH) (4P)	−35.6	−28.1	−24.0	−19.3
(1BuOH) ₂ (4P)	−86.0	−66.7	−57.1	−48.7
(1BuOH) _{3,linear}	−136.6	−106.2	−90.8	−78.8
(4P) _{cis}				
(2PrOH) ₂	−33.2	−24.2	−19.0	−14.7
(2PrOH) _{3,linear}	−80.0	−59.9	−49.2	−41.0
(2PrOH) _{3,cyclic}	−93.5	−71.3	−58.8	−51.3
(2PrOH) _{4,linear,cis}	−127.1	−96.8	−82.3	−69.2
(2PrOH) _{4,cyclic}	−161.3	−125.2	−104.9	−95.2
(2PrOH) (4P)	−37.5	−29.9	−25.6	−21.0
(2PrOH) ₂ (4P)	−90.6	−68.3	−58.2	−49.8
(2PrOH) _{3,linear}	−144.2	−107.8	−92.4	−80.1
(4P) _{cis}				
(2BuOH) ₂	−33.5	−23.6	−19.1	−14.4
(2BuOH) _{3,linear}	−86.9	−68.1	−59.7	−50.9
(2BuOH) _{3,cyclic}	−101.7	−80.7	−70.1	−62.4
(2BuOH) _{4,linear,cis}	−138.3	−106.8	−93.1	−80.1
(2BuOH) _{4,cyclic}	−167.5	−132.4	−115.1	−104.3
(2BuOH) (4P)	−37.1	−29.7	−25.9	−21.0
(2BuOH) ₂ (4P)	−97.2	−77.8	−68.8	−60.2
(2BuOH) _{3,linear}	−143.6	−112.6	−98.9	−85.9
(4P) _{trans}				

Table 3
Calculated step association enthalpies $\Delta_R h$, kJ mol⁻¹

Step reaction according to Eqs. (5)–(8)	$\Delta_R h(\text{MP2/cc-pVTZ})$
(MeOH) + (MeOH) → (MeOH) ₂	-11.4
(MeOH) ₂ + (MeOH) → (MeOH) _{3,linear}	-22.8
(MeOH) _{3,linear} → (MeOH) _{3,cyclic}	-10.6
(MeOH) _{3,linear} + (MeOH) → (MeOH) _{4,linear,cis}	-25.6
(MeOH) _{3,linear} + (MeOH) → (MeOH) _{4,linear,trans}	-20.5
(MeOH) _{4,linear,cis} → (MeOH) _{4,cyclic}	-25.7
(MeOH) + (4P) → (MeOH)(4P)	-19.0
(MeOH)(4P) + (MeOH) → (MeOH) ₂ (4P)	-27.4
(MeOH) ₂ (4P) + (MeOH) → (MeOH) _{3,linear} (4P) _{cis}	-28.0
(EtOH) + (EtOH) → (EtOH) ₂	-12.8
(EtOH) ₂ + (EtOH) → (EtOH) _{3,linear}	-22.3
(EtOH) _{3,linear} → (EtOH) _{3,cyclic}	-10.6
(EtOH) _{3,linear} + (EtOH) → (EtOH) _{4,linear,cis}	-28.7
(EtOH) _{4,linear,cis} → (EtOH) _{4,cyclic}	-24.1
(EtOH) + (4P) → (EtOH)(4P)	-19.0
(EtOH)(4P) + (EtOH) → (EtOH) ₂ (4P)	-28.3
(EtOH) ₂ (4P) + (EtOH) → (EtOH) _{3,linear} (4P) _{trans}	-21.7
(1PrOH) + (1PrOH) → (1PrOH) ₂	-13.1
(1PrOH) ₂ + (1PrOH) → (1PrOH) _{3,linear}	-21.8
(1PrOH) _{3,linear} → (1PrOH) _{3,cyclic}	-12.9
(1PrOH) _{3,linear} + (1PrOH) → (1PrOH) _{4,linear,trans}	-25.7
(1PrOH) _{4,linear,cis} → (1PrOH) _{4,cyclic}	-24.3 ^c
(1PrOH) + (4P) → (1PrOH)(4P)	-19.3
(1PrOH)(4P) + (1PrOH) → (1PrOH) ₂ (4P)	-28.9
(1BuOH) + (1BuOH) → (1BuOH) ₂	-13.8
(1BuOH) ₂ + (1BuOH) → (1BuOH) _{3,linear}	-25.4
(1BuOH) _{3,linear} → (1BuOH) _{3,cyclic}	-9.8
(1BuOH) _{3,linear} + (1BuOH) → (1BuOH) _{4,linear,cis}	-27.4
(1BuOH) _{4,linear,cis} → (1BuOH) _{4,cyclic}	-24.1
(1BuOH) + (4P) → (1BuOH)(4P)	-19.3
(1BuOH)(4P) + (1BuOH) → (1BuOH) ₂ (4P)	-29.4
(1BuOH) ₂ (4P) + (1BuOH) → (1BuOH) _{3,linear} (4P) _{cis}	-30.1
(2PrOH) + (2PrOH) → (2PrOH) ₂	-14.7
(2PrOH) ₂ + (2PrOH) → (2PrOH) _{3,linear}	-26.2
(2PrOH) _{3,linear} → (2PrOH) _{3,cyclic}	-10.4
(2PrOH) _{3,linear} + (2PrOH) → (2PrOH) _{4,linear,cis}	-28.3
(2PrOH) _{4,linear,cis} → (2PrOH) _{4,cyclic}	-26.0
(2PrOH) + (4P) → (2PrOH)(4P)	-21.0
(2PrOH)(4P) + (2PrOH) → (2PrOH) ₂ (4P)	-28.8
(2PrOH) ₂ (4P) + (2PrOH) → (2PrOH) _{3,linear} (4P) _{cis}	-30.3
(2BuOH) + (2BuOH) → (2BuOH) ₂	-14.4
(2BuOH) ₂ + (2BuOH) → (2BuOH) _{3,linear}	-36.5
(2BuOH) _{3,linear} → (2BuOH) _{3,cyclic}	-11.5
(2BuOH) _{3,linear} + (2BuOH) → (2BuOH) _{4,linear,cis}	-29.2
(2BuOH) _{4,linear,cis} → (2BuOH) _{4,cyclic}	-24.2
(2BuOH) + (4P) → (2BuOH)(4P)	-21.0
(2BuOH)(4P) + (2BuOH) → (2BuOH) ₂ (4P)	-39.1
(2BuOH) ₂ (4P) + (2BuOH) → (2BuOH) _{3,linear} (4P) _{trans}	-28.8 ^a

^a Averaged in the homologous series.

trimers indicate that linear trimers are better stabilized while the comparison of linear and cyclic tetramers reveals a certain stabilization of the cyclic species. Of course the total formation energy of cyclic species is always higher than for linear ones due to the higher number of hydrogen bonds.

Qualitatively the energetic results for alkan-2-ols are similar to those of alkan-1-ols. However, it is interesting to see that the H-bonding enthalpies are shifted to more negative values for alkan-2-ol clusters. They are energetically better stabilized than alkanol-1-ol clusters.

We now discuss the results of cross association for alkanols (ROH) with 4-picoline (4P). Comparison of dimers (ROH)₂ with dimers (ROH)(4P) shows that the hydrogen bonding O–H···N is stronger than the O–H···O bond (see Table 3). The stabilization enthalpy defined as ($\Delta_R h(A_1P) - \Delta_R h(A_2)$) is -7.6 kJ mol⁻¹ for methanol, -5.1 kJ mol⁻¹ for ethanol, -6.1 kJ mol⁻¹ for propan-1-ol, -4.4 kJ mol⁻¹ for butan-1-ol, -6.3 kJ mol⁻¹ for propan-2-ol, and -6.6 kJ mol⁻¹ for butan-2-ol. This confirms theoretical results obtained previously for alkanol+pyridine dimers and alkanol+triethylamine (TMA) dimers where the O–H···N bonding of (MeOH)(TMA) is even more stabilized by -13 kJ/mol compared to the corresponding bonding in (MeOH)₂ dimers [7].

4. Statistical thermodynamic calculations using the ERAS-model

The “Extended Real Association Solution” model (ERAS-model) [7–13] exhibits a statistical–mechanical procedure for treating complex flexible molecules of different sizes in the dense liquid state. It is based on Flory’s free volume theory of mixtures consisting of chainlike molecules. It turned out to be most suitable to describe properties of molecular mixtures with strongly associating components of any chain length such as alcohols. The most simple version of the model accounts for molecular clusters linearly associated by hydrogen bonding. In more recent versions of the model different kinds of association steps have been considered according to the following scheme [1–3]



Furthermore cyclic species have been introduced e.g.



The corresponding association constants are generally given by

$$K_i = \frac{c_{A_i}}{c_{A_{i-1}} c_{A_1}} \frac{1}{V_A^*} = C \exp \left[-\frac{\Delta h_i}{RT} \right] \quad (13)$$

where V_A^* is the hard core molar volume of the monomer species. Δh_i is the association enthalpy and C is a constant which is independent on i as long as linearly associated multimers are considered. With other words, the association entropy $\Delta s_i = R \ln C$ is found to be independent on the chain length in the frame of the model. However, the value of Δs_i cannot be fixed, it depends on the coordination number of the virtual space lattice on which Flory’s theory is based. The same holds for the ERAS-model. Eq. (13) has already been derived long time ago by P. Flory [14,15] and has become a cornerstone in the association theory provided by the ERAS-model [1–3,8–13]. Most recently the model has proved to

predict simultaneously excess properties of butanol+alkane mixtures like excess enthalpies, IR-spectroscopic data of the monomer alkanol concentration, and the H-NMR chemical shift of the alcoholic OH-groups over the whole range of concentration using only 3 adjustable parameters [2]. The basis of this procedure was the incorporation of quantum mechanical results of the stability of linearly and ringlike associated molecular clusters of alkanol molecules. It turned out that a co-operative effect of the energetic stability of linearly associated alcohol clusters could be accounted for by distinguishing between the association constant for the first step (K_2) and the following steps (K_A) connected by the relationship

$$K_A = K_2 \exp \left[-\frac{\Delta h_A - \Delta h_2}{RT} \right] \quad (14)$$

where Δh_2 and Δh_A are association enthalpies of the first and all the following linear association steps respectively obtained from the quantum mechanical ab initio calculations. In addition cyclic species of 4 or 5 alcohol molecules have a particularly preferred stability according to the ab initio calculation results.

This has been accounted for by introducing a cyclization constant K_{C4} :

$$K_{C4} = \frac{C_{4,cyclic}}{C_{4,linear}} \quad (15)$$

Cyclization of trimers has been neglected due to their low stabilization energy.

In this work we follow this successful concept by extending the ERAS-model to mixtures of a series of alkanol (A)+4-pyridine (B) mixtures where the following additional cross association steps have to be considered



The ab initio results presented in the previous section suggest that association enthalpies of steps in Eqs. (17)–(19) have similar values and therefore values of K_{AAB} are assumed to be constant, i.e. independent on the chain length i . According to the basic assumption made by Flory's theory of chemical equilibria occurring in dense fluid mixtures with linearly associated molecules of different sizes [14] it holds

$$K_{AAB} = K_{AB} \exp \left[-\frac{\Delta h_{AAB} - \Delta h_{AB}}{RT} \right] \quad (20)$$

while K_{AB} itself is related to K_2 by

$$K_{AB} = K_2 \exp \left[-\frac{\Delta h_{AB} - \Delta h_2}{RT} \right] \quad (21)$$

On this basis the new extended version of the ERAS-model can be developed. The first step is the determination of the volume fractions of monomeric species A and B in the mixture designed as φ_{A1} and φ_{B1} respectively. The original formulas in which no cyclic species have been considered and also no distinction between K_2 and K_A as well as between K_{AB} and K_{AAB} has been made [10,13] are now modified in the following way

$$\Phi_A = \frac{\varphi_{A1}}{(1 - K_A \varphi_{A1})^2} (1 - 2K_A \varphi_{A1} + 2K_2 \varphi_{A1} + K_A^2 \varphi_{A1}^2 - K_A K_2 \varphi_{A1}^2 + 4K_A^2 K_2 K_{C4} \varphi_{A1}^3 - 8K_A^3 K_2 K_{C4} \varphi_{A1}^4 + 4K_A^4 K_2 K_{C4} \varphi_{A1}^5) + \frac{V_A^*}{V_B^*} K_{AB} \frac{\varphi_{A1} \varphi_{B1}}{(1 - K_{AAB} \varphi_{A1})^2}, \quad (22)$$

where Φ_A is the given hard core volume fraction of the alcohol molecule

$$\Phi_A = \frac{x_A V_A^*}{x_A V_A^* + x_B V_B^*} = 1 - \Phi_B \quad (23)$$

with x_A , x_B , V_A^* , V_B^* being the mole fractions of A and B and the hard core volumes of A and B respectively.

φ_{A1} and φ_{B1} are related by

$$\Phi_B = \varphi_{B1} \left(1 + \frac{K_{AB} \varphi_{A1}}{1 - K_{ABA} \varphi_{A1}} \right) \quad (24)$$

At a given mole fraction x_A of the binary mixture φ_{A1} and φ_{B1} can be calculated by a numerical procedure from the coupled Eqs. (22) and (24).

Excess properties such as the molar excess enthalpy H_m^E consist of two contributions, a chemical contribution $H_{m,Chem}^E$ arising from the molecular association, and a physical contribution $H_{m,Phys}^E$ arising from the differences of van der Waals segmental intermolecular energies expressed by the parameter X_{AB} . The result for the formula of $H_{m,Chem}^E$ is

$$H_{m,Chem}^E = \left\{ \Delta h_2 K_2 \frac{\varphi_{A1}^2}{1 - K_A \varphi_{A1}} + \Delta h_A K_2 K_A \frac{\varphi_{A1}^3}{(1 - K_A \varphi_{A1})^2} + (\Delta h_2 + 2\Delta h_A + \Delta h_{C4}) K_2 K_A^2 K_{C4} \varphi_{A1}^4 + \Delta h_{AB} \frac{V_A^*}{V_B^*} K_{AB} \frac{\varphi_{A1} \varphi_{B1}}{1 - K_{AAB} \varphi_{A1}} + \Delta h_{AAB} \frac{V_A^*}{V_B^*} K_{AB} K_{AAB} \frac{\varphi_{A1}^2 \varphi_{B1}}{(1 - K_{AAB} \varphi_{A1})^2} \right\} / \left\{ \Phi_A + \frac{V_A^*}{V_B^*} \cdot \Phi_B \right\} - x_A \left\{ \Delta h_2 K_2 \frac{\varphi_{A1}^2}{1 - K_A \varphi_{A1}} + \Delta h_A K_2 K_A \frac{\varphi_{A1}^3}{(1 - K_A \varphi_{A1})^2} + (\Delta h_2 + 2\Delta h_A + \Delta h_{C4}) K_2 K_A^2 K_{C4} \varphi_{A1}^4 \right\} \quad (25)$$

The physical contribution is

$$H_{m,Phys}^E = (V_A^* \cdot x_A + V_B^* \cdot x_B) \times \left(\frac{\Phi_A \cdot P_A^*}{\tilde{v}_A} + \frac{\Phi_B \cdot P_B^*}{\tilde{v}_B} - \frac{P_M^*}{\tilde{v}_M} \right) - \frac{P_M^* V_{m,Chem}^E}{\tilde{v}_M^2} \quad (26)$$

with

$$P_M^* = P_A^* \Phi_A + P_B^* \Phi_B - X_{AB} \Phi_A \Phi_B, \quad (27)$$

Table 4
ERAS-model and quantum-chemical (qc) complex bonding enthalpy values, kJ mol⁻¹

Binary system	Δh_A		Δh_2		Δh_{C4}		Δh_{AB}		Δh_{AAB}	
	ERAS	qc	ERAS	qc	ERAS	qc	ERAS	qc	ERAS	qc
(MeOH)+(4P)	-19.0	-22.8 ^a -20.5 ^b	-14.9	-11.4	-22.4	-25.7	-20.9	-19.0	-27.4	-27.4 ^c -28.0 ^d
(EtOH)+(4P)	-19.5	-22.3 ^a	-16.0	-12.8	-23.8	-24.1	-19.9	-19.0	-28.0	-28.3 ^c
(1PrOH)+(4P)	-19.7	-21.8 ^a	-14.5	-13.1	-24.3	-24.3	-21.4	-19.3	-31.0	-28.9 ^c
(1BuOH)+(4P)	-22.0	-25.4 ^a	-15.9	-13.8	-23.1	-24.1	-20.5	-19.3	-29.9	-29.4 ^c -30.1 ^d
(2PrOH)+(4P)	-23.7	-26.2 ^a	-15.0	-14.7	-28.6	-26.0	-23.1	-21.0	-30.8	-28.8 ^c -30.3 ^d
(2BuOH)+(4P)	-25.8	-29.2 ^b	-16.8	-14.4	-26.0	-24.2	-23.9	-21.0	-30.4	-28.8

^a According to Eq. (6), $n=3$.

^b According to Eq. (6), $n=4$.

^c According to Eq. (8), $n=2$.

^d According to Eq. (8), $n=3$.

P_A^* and P_B^* are the reduced pressures of the pure components A and B obtained in the usual way from p , V , T -data of the pure components [8–13]. The total molar excess enthalpy is then

$$H_m^E = H_{m,Chem}^E + H_{m,Phys}^E \quad (28)$$

The second term in Eq. (26) is a coupled contribution of chemical and physical effects. This term is small compared to the first term and $V_{m,Chem}^E$ has been estimated by

$$V_{m,Chem}^E = \left\{ \Delta v_2 K_2 \frac{\varphi_{A_1}^2}{1-K_A \varphi_{A_1}} + \Delta v_A K_2 K_A \frac{\varphi_{A_1}^3}{(1-K_A \varphi_{A_1})^2} + (\Delta v_2 + 2\Delta v_A + \Delta v_{C4}) K_2 K_A^2 K_{C4} \varphi_{A_1}^4 + \Delta v_{AB} \frac{V_A^*}{V_B^*} K_{AB} \frac{\varphi_{A_1} \varphi_{B_1}}{1-K_{AAB} \varphi_{A_1}} + \Delta v_{AAB} \frac{V_A^*}{V_B^*} K_{AB} K_{AAB} \frac{\varphi_{A_1}^2 \varphi_{B_1}}{(1-K_{AAB} \varphi_{A_1})^2} \right\} / \left\{ \Phi_A + \frac{V_A^*}{V_B^*} \cdot \Phi_B \right\} - x_A \left\{ \Delta v_2 K_2 \frac{\varphi_{A_1}^2}{1-K_A \varphi_{A_1}} + \Delta v_A K_2 K_A \frac{\varphi_{A_1}^3}{(1-K_A \varphi_{A_1})^2} + (\Delta v_2 + 2\Delta v_A + \Delta v_{C4}) K_2 K_A^2 K_{C4} \varphi_{A_1}^4 \right\} \tilde{v}_M \quad (29)$$

All association volumes Δv are negative. Since their values are not exactly known we choose $-5.6 \text{ cm}^3 \text{ mol}^{-1}$ for the Δv_2 , Δv_A , Δv_{C4} , Δv_{AB} , and Δv_{AAB} respectively accounting for the fact that this value is known to describe excess volumes of alkanol+alkane mixtures by the ERAS-model in the most appropriate way [8,11,12].

An important question is the source of the different association constants K_A , K_2 , K_{C4} , K_{AB} , K_{AAB} and the corresponding association enthalpies Δh_A , Δh_2 , Δh_{C4} , Δh_{AB} and Δh_{AAB} appearing in Eq. (25). As already mentioned above most of them can essentially be fixed by the results obtained from the ab initio calculations described in the previous section. Δh_2 , Δh_A , Δh_{C4} , Δh_{AB} and Δh_{AAB} have been principally identified with the corresponding values of $\Delta_R h(A_2)$, $\Delta_R h(A_{3,linear})$, $\Delta_R h(A_{4,cyclic})$, $\Delta_R h(A_1P)$, $\Delta_R h(A_2P)$ respectively defined by Eqs. (5)–(8). However, since the DFT-results and the MP2-results provide not exactly the same values and due to the fact, that anharmonic vibrational effects of the calculated normal

frequencies have not been taken into account, the error of ab initio calculated values is estimated to be $\pm(3 \div 4) \text{ kJ/mol}$ and we allow $\Delta_R h$ -values to be variable within this estimated error limit. Association enthalpies used in the ERAS-model for calculations of H_m^E are listed in Table 4 and are compared there with the ab initio calculations of the last column of Table 3 (MP2/cc-pVTZ) which are considered to be the most reliable ab initio results. The quantities which have really been freely adjusted in Eq. (28) to experimental data of H_m^E are K_2 , K_{C4} , K_{AB} and X_{AB} with the restriction of X_{AB} lying between $+15$ and -15 J cm^{-3} . The reason for this restriction is the fact that values of X_{AB} have been found to lie within this range for various binary mixtures of unpolar components such as hydrocarbons [1,2]. Since X_{AB} is also responsible for the van der Waals interactional energy in hydrogen bonded liquid systems such as alkanol+4-picoline mixtures its value should not exceed this range.

5. Results and discussion

The parameters of the extended version of the ERAS-model are listed in the Tables 4–6. K_2 , K_{C4} and K_{AB} have freely been adjusted to the experimental data. The Δh -values have only been varied inside the range $\pm(3 \div 4) \text{ kJ/mol}$ of the theoretical values and X_{AB} has been adjusted within $\pm 15 \text{ J cm}^{-3}$. The

Table 5
Thermodynamic data of pure liquids at 298 K^d

	$\rho^a \text{ g cm}^{-3}$	$\alpha_p^b 10^{-4} \text{ K}^{-1}$	$\kappa_T^c \text{ MPa}^{-1}$	$P^* \text{ cm}^3 \text{ mol}^{-1}$	$V^* \text{ J cm}^{-3}$
Methanol	0.787	11.89	12.48	342.07	33.04
Ethanol	0.785	10.93	11.49	403.14	47.10
Propan-1-ol	0.800	10.20	10.06	424.14	60.90
Butan-1-ol	0.806	9.79	9.42	408.19	75.46
Propan-2-ol	0.781	10.64	11.42	370.33	62.46
4-Picoline	0.950	9.68	6.92	642.42	78.98

^d Values for 2-butanol taken from 1-butanol.

^a Density ρ .

^b Isobaric expansion coefficient α_p .

^c Isothermal compressibility κ_T .

Table 6
ERAS-model parameters of alcohol+4-picoline mixtures at 298 K

Mixture	K_A	K_2	K_{C4}	K_{AB}	K_{AAB}	X_{AB} J cm ⁻³
(MeOH)+(4P) ^a	731.6	196.7	471.0	269.5	388.4	3.1
(EtOH)+(4P)	575.5	142.5	603.5	15.2	398.2	-13.4
(1PrOH)+(4P)	372.2	45.9	791.9	5.7	280.0	-1.2
(1BuOH)+(4P)	250.3	21.6	966.4	4.7	204.1	4.1
(2PrOH)+(4P)	554.0	16.8	242.2	8.7	196.8	3.8
(2BuOH)+(4P)	931.8	24.6	895.7	32.1	445.8	4.0

^a Without accounting Eqs. (20) and (21).

comparison between the experimental data of H_m^E and the theoretical expression of H_m^E (Eq. (28)) is shown in the Figs. 6–11. The model is able to describe the experiments quantitatively, i.e. within the experimental error limit ($\pm 1.5\%$ of the absolute values) over the whole range of mole fraction.

H_m^E -values of mixtures with linear alcohols are negative becoming smaller in their negative values with increasing chain length. H_m^E of the two isomeric alcohols propan-2-ol and butan-2-ol are positive in contrast to the corresponding results of the linear alcohols. The theoretical results (see Table 5) reveal that the reason for this remarkable difference is most probably not the weaker cross association of propan-2-ol and butan-2-ol but the stronger self association of these isomeric alcohols compared to the propan-1-ol and butan-1-ol respectively. Figs. 6–11 indicate also that in case of methanol and propan-1-ol mixtures the chemical contribution of H_m^E is dominating while in the other mixtures also the physical contributions are of considerable importance.

The conclusions drawn from these results have a more realistic basis as in former discussions because now reliable ab initio calculations of hydrogen bonded molecular clusters have been available. Comparison of K_2 , K_A and K_{C4} of methanol given in Table 6 with those used in a previous publication [3] reveal remarkable differences while K_{AB} and all Δh -values are similar. This seems to be surprising because in Ref. [3] the systems studied there (methanol+pyridine and +2,6-dimethylpyridine) are similar to the methanol+4-picoline systems studied in this work. The reason for this discrepancy is the

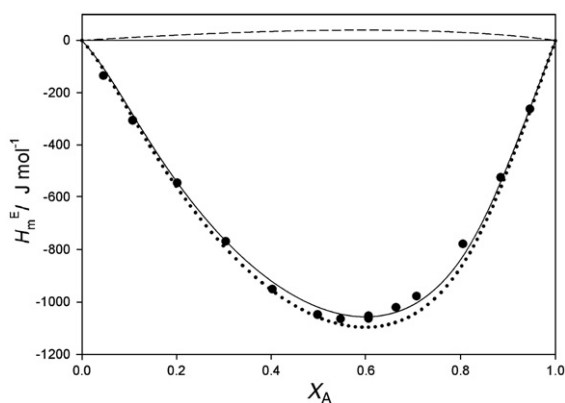


Fig. 6. The molar excess enthalpy H_m^E of the system methanol+4-picoline vs. the mole fraction of alcohol x_A at 298.15 K. ●, experimental results; —, ERAS-model (Eq. (28)); ·····, chemical contribution (Eq. (25)); - - -, physical contribution (Eq. (26)). Parameters: see Table 6.

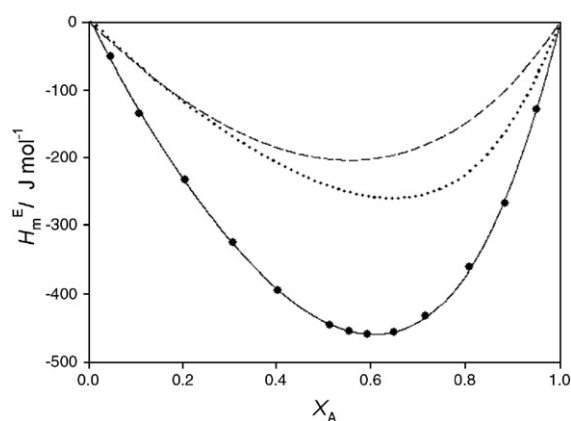


Fig. 7. The molar excess enthalpy H_m^E of the system ethanol+4-picoline vs. the mole fraction of alcohol x_A at 298.15 K. ●, experimental results; —, ERAS-model (Eq. (28)); ·····, chemical contribution (Eq. (25)); - - -, physical contribution (Eq. (26)). Parameters: see Table 6.

different procedure of determining the association constants K_2 , K_A and K_{C4} . In the present work we have adjusted K_2 to the H_m^E -values of the methanol+4-picoline systems and K_A has been calculated from Eq. (14) while in Ref. [3] K_2 , K_A and K_{C4} has been taken from results obtained from methanol+alkane mixtures. This problem reflects the limitations of the ERAS-model itself rather than the uncertainties of the ab initio calculations when applied to such complicated mixtures as alkanol+pyridine derivative systems.

It must be pointed out again that numerical results obtained for association enthalpies using ab initio methods as given in Table 3 have a restricted value, i.e. their uncertainty is estimated to be not better than $\pm(3 \div 4)$ kJ mol⁻¹ for inherent reasons of the calculation procedure, e.g. the restricted number of basis sets, BSSE correction, harmonic approximation etc. Nevertheless the results are of great value to fix the ERAS parameters such as Δh -values in a reliable way within a narrow range. The quantitative information about the cooperative effect, the stabilization of cyclic tetramers or the fact that OH···N association is stronger than the OH···O association by a certain amount is of essential importance for a reasonable application of the ERAS-

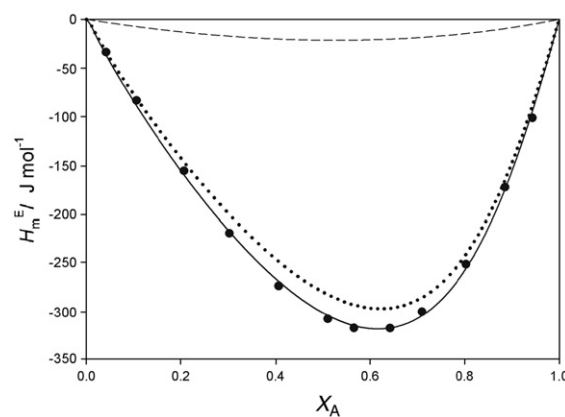


Fig. 8. The molar excess enthalpy H_m^E of the system propan-1-ol+4-picoline vs. the mole fraction of alcohol x_A at 298.15 K. ●, experimental results; —, ERAS-model (Eq. (28)); ·····, chemical contribution (Eq. (25)); - - -, physical contribution (Eq. (26)). Parameters: see Table 6.

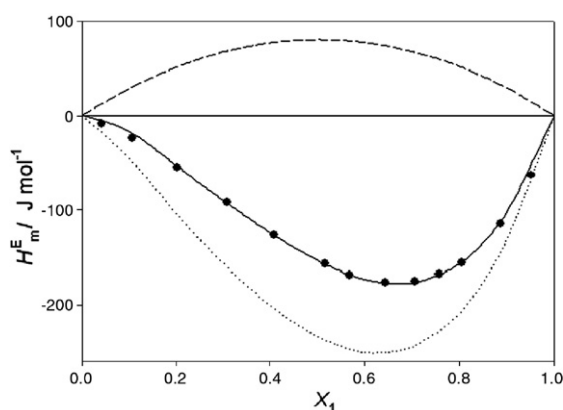


Fig. 9. The molar excess enthalpy H_m^E of the system butan-1-ol+4-picoline vs. the mole fraction of alcohol x_A at 298.15 K. ●, experimental results; —, ERAS-model (Eq. (28)); ·····, chemical contribution (Eq. (25)); - - -, physical contribution (Eq. (26)). Parameters: see Table 6.

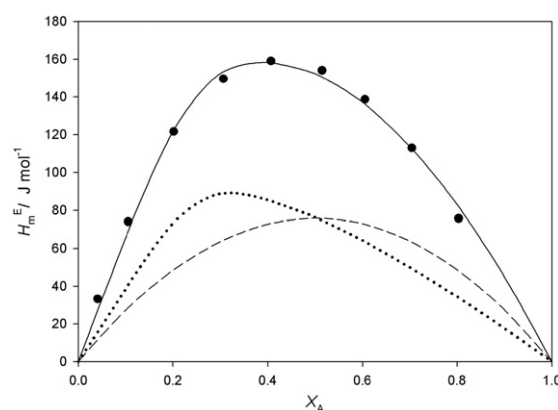


Fig. 11. The molar excess enthalpy H_m^E of the system butan-2-ol+4-picoline vs. the mole fraction of alcohol x_A at 298.15 K. ●, experimental results; —, ERAS-model (Eq. (28)); ·····, chemical contribution (Eq. (25)); - - -, physical contribution (Eq. (26)). Parameters: see Table 6.

model compared to the former situation where such molecular information was not available.

Another question which is worth to be discussed concerns the justification of using ab initio results obtained in the ideal gas phase rather than in the surrounding of a polarizable liquid. We have applied Tomasi's polarized continuum model (PCM) [16–18] and also its extension based on the self consistent isodensity method (SCI-PCM) available in Gaussian03 program package [4]. We have treated all clusters which involve methanol including cross associated clusters with 4-picoline using both methods. While the enthalpy of association for dimers gives -9.5 kJ mol^{-1} using the PCM-model compared to the gas phase value of $-11.4 \text{ kJ mol}^{-1}$, the association enthalpies of further step-wise association give $-12.5 \text{ kJ mol}^{-1}$ and $-10.0 \text{ kJ mol}^{-1}$ compared to $-22.9 \text{ kJ mol}^{-1}$ and $-25.5 \text{ kJ mol}^{-1}$ in the gas phase respectively. The SCI-PCM results approach generally more to the gas phase results. However, since BSSE corrections failed in the PCM-model as well as in the SCI-PCM-model, we have to rely on the ab initio

results presented in this work as the most reliable data available at present.

List of symbols

H_m^E	Molar excess enthalpy
$H_{m,\text{Chem}}^E$	Chemical contribution of molar excess enthalpy
$V_{m,\text{Chem}}^E$	Chemical contribution of molar excess volume
$H_{m,\text{Phys}}^E$	Physical contribution of molar excess enthalpy
\dot{n}_i	Molar flow rate of component i
\dot{Q}	Heating (cooling) rate
x_i	Mole fraction of component i
V_i^*	Hard core volume of i -component monomeric species
φ_i	Volume fraction of monomeric species i in mixture
φ_i^0	Volume fraction of monomeric species in pure substance i
P_i^*	Reduced pressure of pure component i
ΔE	Total interaction cluster energy
Δh_j	Association enthalpy for cluster formation containing j molecules
Δv_j	Association volume for j -cluster bonding
K_j	Association constant for j -cluster bonding
c_j	Concentration of clusters containing j molecules
X_{AB}	Parameter for the description of differences of van der Waals segmental intermolecular energies

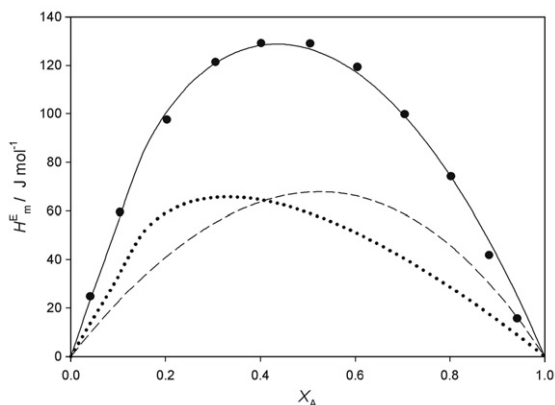


Fig. 10. The molar excess enthalpy H_m^E of the system propan-2-ol+4-picoline vs. the mole fraction of alcohol x_A at 298.15 K. ●, experimental results; —, ERAS-model (Eq. (28)); ·····, chemical contribution (Eq. (25)); - - -, physical contribution (Eq. (26)). Parameters: see Table 6.

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