

A model for the excess properties of 1-alkanol+ alkane mixtures containing chemical and physical terms

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Abstract - The excess properties of 1-C_mH_{2m+1}OH + C_nH_{2n+2} mixtures are described for 2 ≤ m ≤ 12 and 4 ≤ n ≤ 16 using a model with chemical and physical terms. The model is a development of earlier attempts by Stokes et al., Kohler et al., and Gaube et al.. It assumes chain association with a distribution of association constants favouring chains of medium length, the existence of cyclic tetramers, a heat of formation of a hydrogen bond of -25 kJ mol⁻¹ (except for smaller values of dimer and trimer), and a volume change of formation of -5 cm³ mol⁻¹. The physical terms contain a configurational contribution calculated after Donohue and Prausnitz, and a residual term calculated with Kehiaian's model of group surface interactions. The model reproduces the excess properties g^E, h^E, c_p^E and v^E of numerous systems almost within experimental accuracy, and may thus serve for interpolation between different numbers of m and n. The principal correctness of the chemical terms is corroborated by a n.m.r. investigation on ethanol + cyclohexane and the temperature dependence of v^E of ethanol + hexane.

INTRODUCTION

Alcohols are considered to be associated substances. That means that there exist specific, i.e. strongly orientated, interactions which are appreciably stronger than the general dispersive interactions and which lead to the formation of groups of molecules. These groups stick together for times which are orders of magnitudes longer than the vibration period of a molecule in the liquid quasilattice (ref. 1). This formation of molecular groups, called species, is best to describe by a chemical equilibrium. However, such a description is only necessary when the alcohol is diluted. In pure or concentrated state the effect of association can be formally incorporated into a cohesive energy of somewhat larger value and somewhat different temperature dependence (ref. 2). It is for the consideration of the whole density range of pure alcohols or the whole concentration range of mixtures that the introduction of chemical equilibria is needed.

The accounting for different species by chemical equilibria brings the problem with it how to combine this with the effects of the weaker but more general interactions which are present also in non-reacting mixtures. For short, how to combine chemical with physical terms. Numerous simplifications have been tried, either by neglecting the physical terms as in the treatment of ideal associated mixtures, or by assuming that chemical and physical terms can just be added. The latter assumption means that in the thermodynamic association constant (if written for a dimerization, a₁ and a₂ being the activities of monomer and dimer, resp.)

$$K = a_2/a_1^2 = x_2/x_1^2 \cdot f_2/f_1^2 \quad (1)$$

the activity coefficients f_i are different from unity, but the ratio f₂/f₁² is equal to unity. From investigations on association equilibria in pure liquids and in dilute solutions of different solvents we know that these simplifications are not justified.

The principles of a thermodynamically consistent treatment have been formulated by Kehiaian (refs. 3, 15), and Kohler (ref. 4) has treated various actual mixtures, where one component exists in different species. It could be shown that the physical terms (i.e. the ratio of activity coefficients in eq. 1) exert an appreciable shift on the mole fraction ratio over the concentration interval, in the case of the acetic acid + carbon tetrachloride mixture over three orders of magnitudes. But the physical terms were still much simplified by using only a Porter ansatz for them. This is probably not permissible

for 1-alkanols, where large chain-like species occur so that differences of sizes and contact numbers have to be taken into account.

It will be tried in the following to develop a thermodynamically consistent treatment for alcohol mixtures by incorporating all features which are thought to be essential. The aim is not a simple tool for technical applications, but a physically realistic description which can be applied for interpolating and extrapolating the thermodynamic properties of $1-C_mH_{2m+1}OH + C_nH_{2n+2}$ mixtures for a variety of carbon numbers m and n .

CHEMICAL TERMS

The chemical equilibria between the various alcoholic species should show the following features:

(1) The dimerization should be disfavoured in comparison to the addition of a monomeric unit to an already existing chain. This follows from various investigations in solutions as well as in the gaseous state (refs. 5-9).

(2) The possibility should be provided for the formation of cyclic associates (refs. 10 - 13).

(3) Quantum mechanical calculations (ref. 14) show that the energy of each hydrogen bond increases with increasing length of the chain, until a plateau value is reached for longer chains. On the other hand, it can be expected that longer chains are entropically disfavoured. Therefore, the addition of a monomeric unit to an already existing chain will be most likely when the chain has medium length.

The assumptions on the basis of these considerations are:

The equilibrium constant K_i for the reaction



follows a distribution given by:

$$K_i = \frac{a_i}{a_{i-1} a_1} = K/[1 + \left(\frac{i-4}{i-1.2}\right)^2] \quad (2)$$

where a_i is the activity of the i -mer. This distribution peaks at the tetramer, and decreases slowly for higher i -mers, as can be seen from Table 1.

Table 1. The thermodynamic quantities for the formation of hydrogen bonds between the $(i-1)$ mer and the i mer in ethanol (298.15 K).

i	K_i	$-g_i^\circ/\text{J mol}^{-1}$	$-h_i^\circ/\text{J mol}^{-1}$	$-s_i^\circ/\text{J mol}^{-1}\text{K}^{-1}$
2	5.516	4233	18000	46.2
3	30.57	8478	23700	51.1
4	40.0	9145	25000	53.2
5	37.41	8979	25000	53.7
6	34.08	8748	25000	54.5
7	31.56	8557	25000	55.1
8	29.72	8408	25000	55.6
9	28.35	8291	25000	56.0
4→c	3.0	2723	25000	74.7

Cyclic species can be expected to occur as tetramers or slightly larger i -mers. This is because dimers and trimers are energetically disfavoured for their angular hydrogen bonds, and larger cyclic species are entropically disfavoured (ref. 12). Therefore, it is believed that cyclic tetramers are the dominating cyclic species and that the neglect of cyclic pentamers, and, if existing, cyclic hexamers will not lead to significant errors. The constant for the cyclisation of the tetramers

$$K_c = a_c/a_4 \quad (3)$$

is also written in terms of activities.

For the enthalpy of formation of a hydrogen bond a value near 25 kJ is used frequently (refs. 10, 13). Again, the hydrogen bond of a dimer is thought to have a lower enthalpy of formation (refs. 10, 15), and in order to make the sequence smooth, a slightly lower value than 25 kJ is attached to the formation of the second hydrogen bond in the trimer. The result of these assumptions for the example of ethanol, where we have set $K = 40$, $K_c = 3$, is presented in Table 1.

For the higher 1-alkanols, $m \geq 3$, the equilibrium constants are set to $K = 30$, $K_c = 4.2$, but the enthalpies of formation remain unchanged. Therefore, the entropies of formation become more negative.

For the reaction volume in forming a hydrogen bond a value of $-5 \text{ cm}^3 \text{ mol}^{-1}$ was used throughout (ref. 16).

PHYSICAL TERMS

As i-mers of appreciable size might be formed, it was thought necessary to consider size differences explicitly. Thus the activity coefficients of species i are written

$$\ln f_i = \ln f_{i,\text{conf}} + \ln f_{i,\text{res}} \quad (4)$$

where the first term on the r.h.s. (the configurational term) takes size differences into account and the second (residual) term is due to differences in interaction energies.

For the configurational term the approximation of Donohue and Prausnitz (ref. 17) has been used, which is thought to be superior to the usual Flory-Huggins expression. Gaube et al. (ref. 18) have shown that in 1-alkanol + alkane mixtures an exponent p would be appropriate with $0.9 \geq p \geq 0.7$. Thus, assuming $v_i = i \cdot v_1$, and denoting the alkane by s (solvent),

$$\ln f_{i,\text{conf}} = \ln(iP/D) - iP/D + 1 \quad (5)$$

where

$$D = \sum_1^{\text{chain}} x_i i^p + x_c 4^p + x_s (v_s/v_1)^{p^*} \quad (6)$$

For $p = 1$ the Flory-Huggins expression is recovered. As will be seen in the following, p -values between 0.85 and 0.87 have been used.

For the second term, it proved to be essential to take into account explicitly the differences in contact numbers of molecular groups. Otherwise the change in the composition dependence from hexane systems to hexadecane systems could not be reproduced. Therefore, the residual term has been modelled according to Kehiaian's model of group surface interactions (refs. 19 - 20), used in the zeroth approximation. When from Kehiaian's expression for g^E the logarithm of activity coefficient is derived by standard thermodynamic formulae (ref. 21), the result is for an alcoholic i -mer

$$\begin{aligned} RT \ln f_{i,\text{res}} = & \frac{q_i}{\sum_1 x_i q_i + x_c q_c + x_s q_s} \left\{ \sum_j q_j x_j g_{ij} + q_c x_c g_{ic} + q_s x_s g_{is} \right\} - \\ & - \frac{q_i}{(\sum_1 x_i q_i + x_c q_c + x_s q_s)^2} \left\{ \sum_{i,j>i} q_i x_i q_j x_j g_{ij} + \sum q_i x_i q_c x_c g_{ic} \right. \\ & \left. + \sum q_i x_i q_s x_s g_{is} + q_s x_s q_c x_c g_{sc} \right\} \end{aligned} \quad (7)$$

Here the q_i are relative surface areas of the molecules. The following values have been used for the groups: $q_{\text{CH}_3} = 0.875$, $q_{\text{CH}_2} = 0.75$, $q_{\text{OH}} = 0.8$. The last value is used for both free and bonded OH.

Thus, when m and n denote the number of carbon atoms in the alcohol or alkane, resp.,

$$q_i = 1 \cdot 0.875 + (m-1) \cdot 0.75 + 0.8 \quad (8a)$$

$$q_c = 4 \cdot 0.875 + (m-1) \cdot 0.75 + 0.8 \quad (8b)$$

$$q_s = 2 \cdot 0.875 + 0.75(n-2) \quad (8c)$$

The interaction constants g_{ij} , g_{ic} , g_{is} , g_{cs} of eq. (7) are formed as sum of group interactions

$$g_{ij} = -1/2 \sum_s \sum_t (a_{si} - a_{sj})(a_{ti} - a_{tj}) g_{st} \quad (9)$$

where the a_{si} are the surface fractions of groups s on the molecule i . Denoting methyl/methylene by m , free OH by f , and bonded OH by b , we have:

$$\begin{aligned} a_{f1} = 0.8/q_i, \quad a_{b1} = a_{f1}(i-1)/i, \quad a_{m1} = 1 - a_{f1} \\ a_{bc} = a_{f1}, \quad a_{mc} = 1 - a_{f1} \\ a_{ms} = 1 \end{aligned} \quad (10)$$

Eq. (9) contains the specific group interaction parameters, g_{st} , which are to be adjusted. In alcohol + alkane mixtures, three different parameters have to be taken into account:

g_{mf} for the interaction between methyl/methylene and free OH,
 g_{mb} for the interaction between methyl/methylene and bonded OH,
 g_{fb} for the interaction between free and bonded OH.

The parameters of the physical terms, g_{mf} , g_{mb} , g_{fb} , p and p_a were first adjusted for the mixture ethanol + hexane. The values chosen were (energies in J mol⁻¹, temperature in K and pressure in MPa)

$$g_{mf} = 10000, \quad g_{mb} = 800, \quad g_{fb} = -6500, \quad p = p_a = 0.85$$

For the sake of calculating h^E and v^E , temperature and pressure derivatives of the g 's have to be given also:

$$\begin{aligned} \text{d}g_{mf} &= -13, & \text{d}g_{mb} &= 0, & \text{d}g_{fb} &= +4 \\ \text{d}p g_{mf} &= 35, & \text{d}p g_{mb} &= 0.6, & \text{d}p g_{fb} &= -6 \end{aligned}$$

In principle, these interaction parameters should apply for all alkanol + alkane mixtures. With this assumption, the empty circles in the Figs. 7-12 are calculated. It is seen that a finer adjustment is necessary for alkanol + alkane mixtures with different m and n . This finer adjustment was brought about by changing somewhat g_{mf} and its derivatives, g_{mb} and its derivatives, and p (crosses in Figs. 7-12). The interpretation for these changes will be given in the discussion. The only change of p was made between ethanol ($p = 0.85$) and pentanol ($p = 0.87$), where p varied linearly with m . For $m \geq 5$, p remained 0.87. The parameter g_{mf} and its derivatives changed only with n , as given in Table 2. The parameter g_{mb} and its derivatives are shown as function of n and m in Table 3.

Table 2. The variations of g_{mf} and its derivatives with n (carbon no. of alkane).

n	4	5	6	7	8	9	10-16
g_{mf}	7750	8875	10000	11125	12250	13375	14500
$\text{d}T g_{mf}$	+14	+0.5	-13	-26.5	-40	-53.5	-67
$\text{d}p g_{mf}$	28.5	31.75	35	38.33	41.67	45	48-($n-10$)

Table 3. The variations of g_{mb} and its derivatives with n (carbon no. of alkane) and m (carbon no. of 1-alkanol). The first entry is g_{mb} , the second $\text{d}T g_{mb}$, and the third $\text{d}p g_{mb}$. For intermediate values of n and m , the variation is linear.

$m \backslash n$	4	6	10	16
2	680	800	1040	1400
	6	0	-4	-8.2
		0.6	0.6	0.6
4	-120	266.67	1040	1400
	25.2	10	-2	-34
		-6.5	-0.6	28.5
5	520	0	1040	1400
	35.25	15	1	-29.5
		-12	-1.2	
6	-1020	-333.33	1040	1400
	45	23.33	5	-25
		-18.5	-1.8	
8	-2020	-1000	1040	1400
	62.5	40	22	-16
		-3.8	-7.133	
10	-3020	-2333.33	1040	1400
	80	56.67	30	-7
		-62	-12.467	
12	-4020	-2333.33	1040	1400
	97.5	73.33	38	2
		-92	-17.8	

METHOD OF CALCULATION

The problem is to find the set of mole fractions of species $x_1, x_2, \dots, x_1 \dots, x_c, x_a$ which satisfies all

$$K = \frac{a_1}{a_1 - 1a_1} = \frac{x_1 f_1}{x_1 - 1f_1 - 1x_1 f_1} \quad \text{and} \quad K_c = \frac{x_c f_c}{x_c f_c}.$$

As the activity coefficients are relatively complicated functions of the mole fractions (eq. 5 and 7), an elaborate iteration procedure is necessary for each set of parameters. For a quick solution several interconnected variables were adjusted simultaneously by a modified Newton method (ref. 22).

Denoting the formal mole fractions of alkanol and solvent by X_a and X_s , and the corresponding activity coefficients by Γ_a and Γ_s , the excess Gibbs energy is

$$g^E = RT(X_a \ln \Gamma_a + X_s \ln \Gamma_s) \quad (11)$$

with

$$X_a = (\sum i x_i + 4 x_c) / (\sum i x_i + 4 x_c + x_s) \quad (12)$$

and

$$X_a \Gamma_a = x_1 f_1 / (x_1 f_1)^{\circ} \quad (13)$$

$$X_s \Gamma_s = x_s f_s, \quad (14)$$

the superscript \circ denoting the limit $X_a \rightarrow 1$.

Another scheme for calculating g^E has been described previously (refs. 4, 23), and was used as a check for the correctness of the calculation. The programming was done independently at Bochum and Darmstadt in order to be sure that no errors slipped in.

The excess Gibbs energy was calculated at five temperatures around 298.15 K and five pressures around 0.1 MPa. The five points were fitted by polynomials of second degree in $1/T$ or $\ln p$, resp.. From these, values of h^E , c_p^E and v^E were derived.

RESULTS

Figs. 1-6 present the comparison of calculated and experimental data of g^E and h^E , reduced by the product of mole fractions, of the key systems ethanol + hexane, ethanol + hexadecane, and 1-pentanol + hexane. Figs. 7-12 show the comparison for g^E , h^E , and c_p^E at fixed compositions for $C_2H_5OH + C_2H_{2n+2}$ as function of n and for $1-C_mH_{2m+1}OH + C_6H_{14}$ as function of m . Because of lack of experimental data, some experimental points for $C_mH_{2m+1}OH$ -systems were also included for pentane and/or heptane. In order to show how the model works for systems with higher n and m numbers, Fig. 13 shows h^E and Fig. 14 v^E at fixed compositions for $C_mH_{2m+1}OH + C_{10}H_{22}$. Similarly, Fig. 15 presents h^E (at fixed compositions) for $C_{12}H_{25}OH + C_nH_{2n+2}$, and Fig. 16 displays v^E for $C_{10}H_{21}OH + C_nH_{2n+2}$. For c_p^E , we show the composition dependence for the mixture $C_6H_{13}OH + C_{10}H_{22}$ in Fig. 17. As we will show v^E of the mixture $C_2H_5OH + C_6H_{14}$ in the discussion, we omit here the presentations for smaller numbers of m and n .

DISCUSSION

As the present model is able to reproduce the excess properties of $1-C_mH_{2m+1}OH + C_nH_{2n+2}$ for many systems within the bounds of $2 \leq m \leq 12$ and $4 \leq n \leq 16$ almost within experimental accuracy, it might serve as a method for interpolation for different m and n . We have not yet tried methanol systems, because of various indications that methanol behaves differently to the other alkanols. Therefore, we have reserved methanol mixtures for future work.

Now the numerical values of the parameters should be discussed. Starting with the chemical terms, it is obvious that our association constants are much smaller than most of the other authors. Furthermore, the change in our constants between ethanol and propanol is smaller, and from propanol on all constants are equal. The influence of the physical terms on the ratio of the mole fractions is very big, e.g. we have for ethanol + hexane (298.15 K)

$$\frac{x_4}{x_1 x_3} = K_4 \frac{f_1 f_3}{f_4}$$

equal to 92.67 for $X_a = 0.01$ and equal to 5.78 for $X_a = 1$. Similarly, we have there

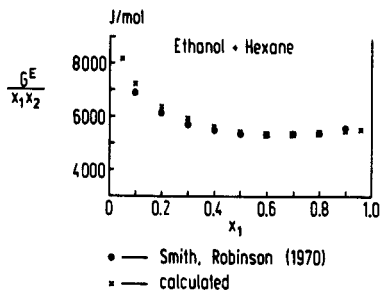


Fig. 1. The excess Gibbs energy, reduced by the product of mole fractions, of ethanol (1) + hexane at 298.15 K. ● experimental (ref. 24), x model calculation.

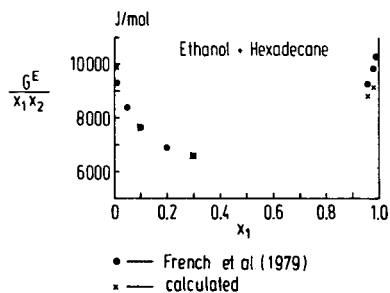


Fig. 3. Same as Fig. 1, but for ethanol(1) + hexadecane. Experimental data: ref. 28.

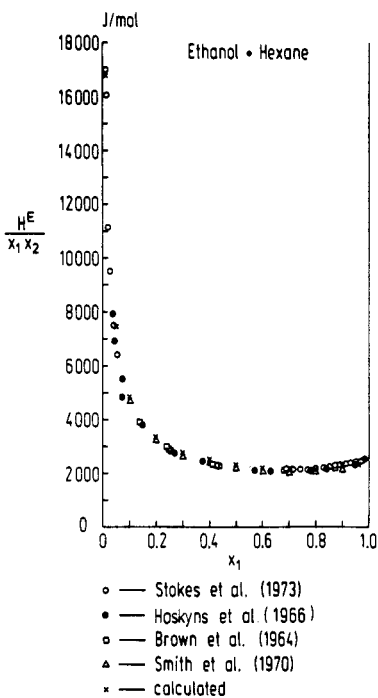


Fig. 2. Same as Fig. 1, but for the excess enthalpy. Experimental data: refs. 24-27.

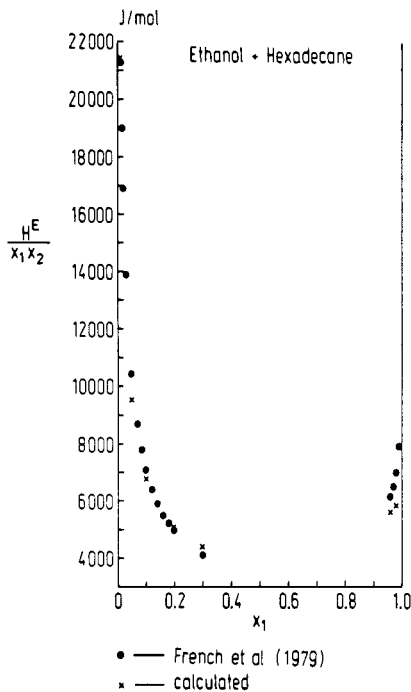


Fig. 4. Same as Fig. 3, but for the excess enthalpy. Experimental data: ref. 28.

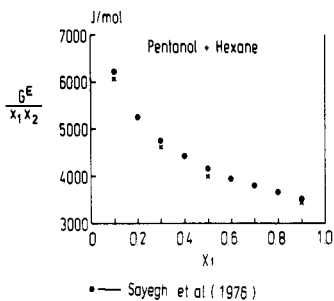


Fig. 5. Same as Fig. 1, but for 1-pentanol (1) + hexane. Experimental data: ref. 29.

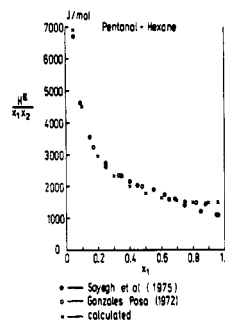


Fig. 6. Same as Fig. 5, but for the excess enthalpy. Experimental data: refs. 30, 31.

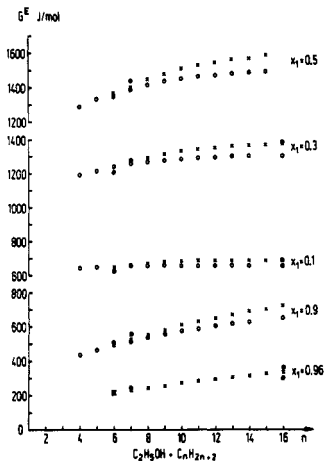


Fig. 7. The excess Gibbs energy (at 298.15 K) at fixed mole fractions, for C_2H_5OH (1) + C_nH_{2n+2} as functions of n . ● experimental (refs. 24,28,32), ○ model calculations with the parameter set of ethanol+hexane, x model calculations with adjusted parameters.

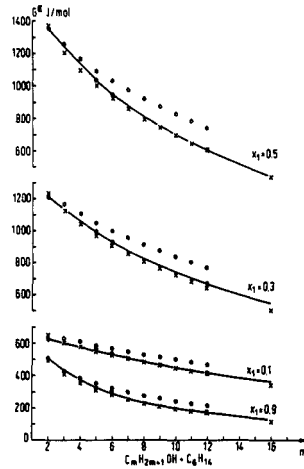


Fig. 10. Same as Fig. 7, but for $1-C_mH_{2m+1}OH + C_6H_{14}$. Curves connect the experimental data (refs. 24,29,41).

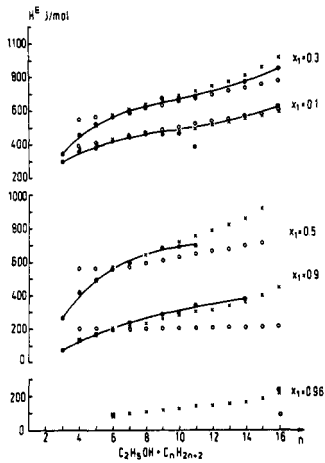


Fig. 8. Same as Fig. 7, but for the excess enthalpy. Curves connect the experimental data (refs. 27,28,32-39).

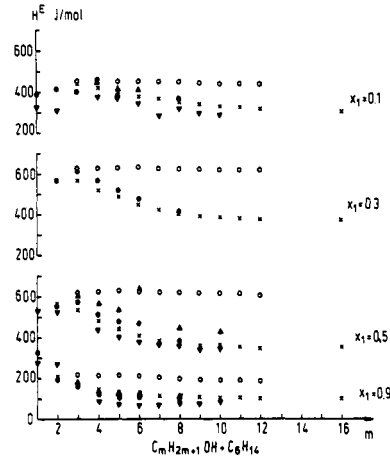


Fig. 11. Same as Fig. 10, but for the excess enthalpy. Experimental points (refs. 27,30,35,37,42-47) are added for pentane (▼) and heptane (▲) mixtures.

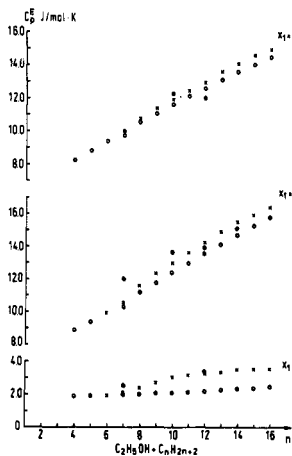


Fig. 9. Same as Fig. 7, but for the excess heat capacity. Experimental data: refs. 32, 39,40.

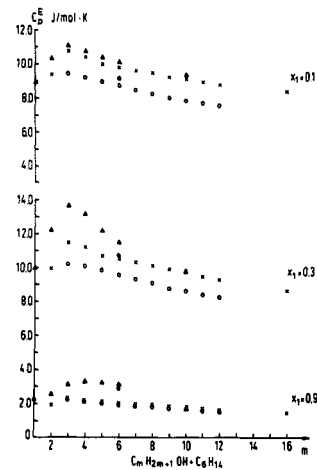


Fig. 12. Same as Fig. 10, but for the excess heat capacity. Experimental points are added for heptane (▲) mixtures (refs. 32,40,48).

$$\frac{x_c}{x_4} = K_c \frac{f_4}{f_c}$$

equal to 13.37 for $X_a = 0.01$ and equal to 2.83 for $X_a = 1$. It is the neglect or inconsistent inclusion of the physical terms, which makes the association constants of most other authors bigger, because the ratio of mole fractions determines the steepness of the $g^E/x_{1,2}$ -curve at high dilution. The limiting value of $(g^E/x_{1,2})_{x \rightarrow 0} = RT \ln \Gamma_a^\infty$ is given by (cf. eq. 13)

$$RT \ln \Gamma_a^\infty = RT \ln f_1^\infty - RT \ln(x_1^\circ f_1^\circ) \quad (15)$$

For ethanol + hexane, the first term on the r.h.s. which is (cf. eq. 7)

$$RT \ln f_1^\infty = q_1 a_{1f}^2 g_{mf} + RT \ln f_{1,conf}^\infty \quad (16)$$

amounts to 2170 J mol⁻¹, and the second term to 8112 J mol⁻¹. The second term contains f_1° , which is very small on account of the configurational contribution and the negative value of g_{fb} (for ethanol + hexane at 298.15 K, $f_1^\circ = 0.177$). A model which neglects f_1^∞ and f_1° would need a much smaller x_1° for compensation, which again means much larger association constants. The limiting value for $X_a \rightarrow 1$ of $g^E/x_{1,2} = RT \ln \Gamma_a^\infty$ is given by

$$RT \ln \Gamma_a^\infty = RT \ln(x_a/X_a)^\infty + RT \ln f_a^\infty \quad (17)$$

The first term on the r.h.s. is given by

$$\left(\frac{x_a}{X_a}\right)_{x_a \rightarrow 0} = \frac{\sum x_1^0 + 4x_c^0}{\sum x_1^0 + x_c^0} = \frac{\sum x_1^0 + 4x_c^0}{\sum x_1^0} (1 - x_c^0) = \frac{1 - x_c^0}{\phi_{OH}^0} \quad (18)$$

where

$$\phi_{OH} = \frac{\sum x_1}{\sum x_1 + 4x_c} \quad (19)$$

is the fraction of free OH groups, and the superscript ⁰ denotes $X_a=1$. When the dimerization is weaker than the higher association, this fraction is smaller than the mole fraction of monomer, $\phi_{OH}^0 < x_1^0$. The second term on the r.h.s. of eq. (17) varies between relatively narrow bounds. Its first contribution, $RT \ln f_{a,conf}^\infty$ is negative for the smaller solvent molecules (-1473 J mol⁻¹ for hexane in ethanol) and the second contribution, $RT \ln f_{a,res}^\infty$, is mainly influenced by g_{mb} and only a little bit by g_{mf} (its value for hexane in ethanol is 1066 J mol⁻¹). This means that ϕ_{OH}^0 has to be such that the whole spectrum of $RT \ln \Gamma_a^\infty$ -values can be covered, which ranges for ethanol (at 298.15K) from 10600 (hexadecane) over 5800 (hexane) to 4100 (carbon tetrachloride) and 3700 J mol⁻¹ (benzene). Our calculations on ethanol give $x_c^0 = 0.05585$ and $\phi_{OH}^0 = 0.08333$, so that $RT \ln (1-x_c^0)/\phi_{OH}^0$ is 6019 J mol⁻¹, and that for the hexane mixture $(g^E/x_{1,2})_{x \rightarrow 1} = 5612$ J mol⁻¹. It is seen that the ratio of the two limiting values in the ethanol + hexane mixture, 10282/5612, can only be achieved with the physical terms, which contribute very positively on the side $X_a \rightarrow 0$, and only little and negatively on the side $X_a \rightarrow 1$.

The important contribution of the physical terms leads to quite different values for the mole fractions of species in our model compared with that of other authors. Especially for the pure alcohol our values for x_1^0 and ϕ_{OH}^0 are substantially higher than from other models. It would be nice if this could be checked by independent investigations. It is for this reason that we investigated the chemical shift of n.m.r. for the mixture ethanol + cyclohexane, which is thermodynamically almost equivalent to ethanol + hexane. The results of this study, together with a discussion of some literature data on infrared spectroscopy, are given in the appendix. The conclusion is that the n.m.r. data are consistent with our model, but cannot disprove values which are up to 50% smaller. A second study which shows the principal correctness of our model is on the temperature dependence of v^E . This temperature dependence is usually big in alcohol + alkane systems because of the breaking up of associates at higher temperature (refs. 54,56). Fig. 18 shows experimental points for $v^E/x_{1,2}$ at 298.15 K and 313.15 K for ethanol + hexane (ref. 54) in comparison to our calculation, with no adjustment made for 313.15 K. Finally, it should be stressed that the c_p^E -values presented earlier are rather insensitive on the physical terms (the curves and circles are quite near together in Figs. 7-12) and have been calculated without any additional assumption. They are, therefore, an additional evidence for the principal correctness of our chemical terms.

Proceeding now with the discussion of the numerical values of the physical terms, the first point is the value of p and p_a . This is completely in line with the discussion of Gaube et al. (ref. 18) for alkanols and of Donohue and Prausnitz (ref. 17) for hydrocarbons. On the other hand, the excess properties react quite sensitively on a small variation. This can be understood because increasing p leads to more negative values of \ln

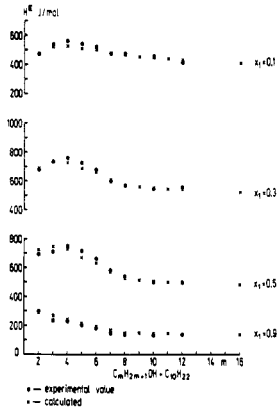


Fig. 13. The excess enthalpy (at 298.15 K) for fixed mole fractions of alkanol, for $1-C_mH_{2m+1}OH + C_{10}H_{22}$ as function of n . ● experimental (refs. 37,49,50), x model calculation.

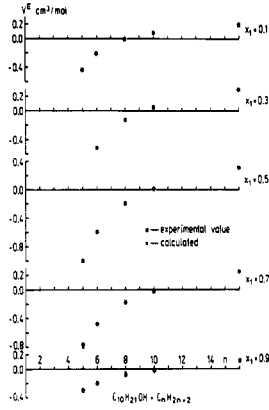


Fig. 16. The excess volume (at 298.15 K) of $C_{10}H_{21}OH + C_nH_{2n+2}$ as function of n . ● experimental (ref. 53), x model calculation.

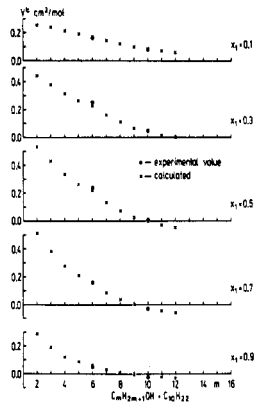


Fig. 14. Same as Fig. 13, but for the excess volume. Experimental data: refs. 51,52.

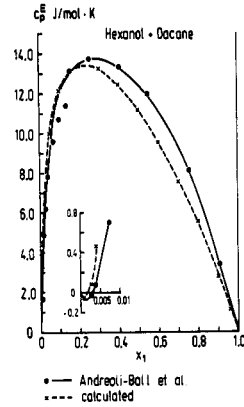


Fig. 17. The excess heat capacity for 1-hexanol (1) + decane. Experimental data: ref. 40.

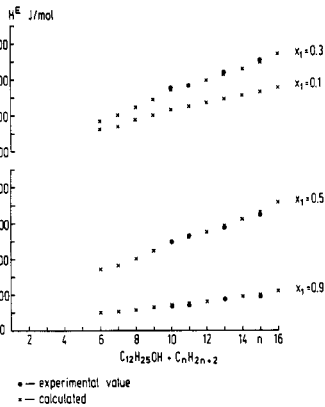


Fig. 15. Same as Fig. 13, but for $C_{12}H_{25}OH + C_nH_{2n+2}$ as function of n . Experimental data: refs. 38,50.

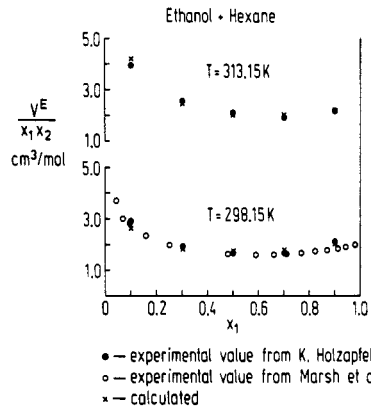
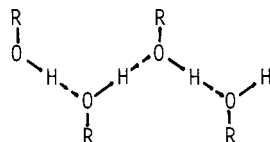


Fig. 18. The excess volume, reduced by the product of mole fractions, of ethanol (1) + hexane, at 298.15 K and 313.15 K. Experimental data: refs. 54,55.

f_1 and to smaller values of the ratio ϕ_{OH}/x_1 , an effect, which corresponds somewhat to a change in the K_i distribution in the sense of decreasing K_i at a smaller rate with i .

Coming now to the values of the interaction parameters g_{mf} , g_{mb} , g_{fb} and their derivatives, so is the general pattern for ethanol + hexane conform to chemical intuition. The parameter g_{mf} corresponds to a strong positive interaction of a very polar molecule with hydrocarbons, g_{mb} to the much weaker interaction of an oxygen bridge (like in dioxane) with hydrocarbon, and the negative value of g_{fb} reflects a tendency of complexation between free OH and an oxygen bridge. The derivatives correspond in sign and in magnitude roughly to what one would expect, i.e. that dr_{get} is between $0.001 g_{et}$ and $0.01 g_{et}$, and that an increase of pressure for 1 MPa is roughly equivalent to a decrease in temperature for 1 K. The change of g_{mf} with n is parallel to the experience with other mixtures of n -alkanes, and is thought to be caused by the fact that the longer hydrocarbon chains order themselves in the liquid state, an order which is broken by the mixing partner (Patterson-effect) (ref. 51). This effect is absent or even reversed when the mixing partner furnishes contact points for the methylene groups (aromatic rings, chlorine and even oxygen atoms, ref. 58), but the alcoholic chains are probably so much shielded by the paraffinic residues R that the



sequences cannot serve as contact points. The explanation for the increase of g_{mf} with n as an order breaking effect is

in line with the rapid decrease of $dr_{g_{mf}}$, which indicates an entropic effect. More difficult is the interpretation for the variation of g_{mb} with m for smaller values of n , which leads to very negative values for large m and small n (cf. Table 3). We believe that this is a packing effect. The big residues R of the alcoholic chains are forced by the hydrogen bond sequences into a packing which is not optimal. Small alkanes as mixing partners can fill some holes and act as "lubricant" between different chains. This interpretation is again supported by the variation of $dr_{g_{mb}}$ which stresses the entropic character. If the alkane molecules become larger ($n \geq 10$), the lubricant effect vanishes. The constancy of g_{mb} with m for larger n might not be so perfect as given by Table 3 when a better determination of the parameters will be possible by new experimental investigations of mixtures for large numbers of m and n . The variation of g_{mb} and its derivatives with n (m small) is again the Patterson effect.

One might summarize the discussion by the statement that the numerical values of all parameters, chemical and physical, appear to be reasonable and consistent. Still it might be possible to achieve an equally good representation of the excess properties of the 1-alkanol + alkane mixtures with slightly different assumptions, e.g., by changing the association model slightly and compensating with the physical terms. But it is believed that the present model is near the true physical situation. It will be tried in the future to corroborate this opinion by applying the model to 1-alkanol systems with other mixing partners than alkanes.

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APPENDIX: NMR INVESTIGATIONS

The chemical shift of the OH proton has been measured in the mixture ethanol + cyclohexane, where about two thirds of cyclohexane were deuterated. The actual spectroscopic measurements were done by H. Duddeck, faculty of chemistry of the Ruhr-University Bochum, by means of a Bruker AM-400 spectrometer (400.1 MHz), with deuterium lock for field stabilisation. For the measurement of FID 32 K data points were used, 16 K after Fourier transformation. Spectral width was 4000 Hz = 10 ppm, digital resolution ± 0.25 Hz. Temperature was room temperature (ca 25°C). Number of scans was usually 16, but for low concentrations of ethanol up to 80. All chemical shifts refer to TMS.

The resulting chemical shifts are shown in Table A1 and Figure A1. The connection between chemical shift δ and fraction of free OH groups ϕ_{OH} depends on the values of the chemical shift assigned to bonded and free OH proton:

$$\delta = \phi_{OH}(\delta_f - \delta_b) + \delta_b \quad (A1)$$

From ϕ_{OH} calculated by our model (cf. eq. 19) the values of $\delta_b = 5.75$ and $\delta_f = -0.19$ were found. With these values the crosses in Fig. A1 were calculated which are in excellent agreement to the experimental points. The question is if other models for ϕ_{OH} could give reasonable agreement also with other values for δ_b and δ_f . Especially, we were interested to check results from infrared spectroscopy. Here we refer to work of three different groups. Sassa and Katayama (ref. 59) have measured in ethanol + cyclohexane up to ethanol mole fractions of 0.2, and Luck (ref. 60) has measured pure ethanol. Van Ness et al. (ref. 61) have measured ethanol + heptane up to ethanol mole fractions of 0.5. The last results, though rather scattering, corroborate our values of ϕ_{OH} . Sassa and Katayama agree with our value of ϕ_{OH} for $X_a = 0.01$, but come to smaller values of ϕ_{OH} for higher ethanol concentrations. If their ϕ_{OH} -values are used in connection with our n.m.r. results, they can be reasonably fitted with $\delta_b = 5.48$ and $\delta_f = -0.04$. There are some systematic trends which could indicate that the ϕ_{OH} -values of Sassa and Katayama are too low for the mole fractions $X_a = 0.15$ and $X_a = 0.20$, but this might still be within the limits of accuracy of our chemical shift. However, when the fit on Sassa and Katayama's values is extrapolated to $X_a = 1$, a value of about $\phi_{OH} = 0.04$ results, about half the value of our model, but still substantially higher than Luck's value of about $\phi_{OH} = 0.03$. Apparently, there are still inherent difficulties in the infrared method which make quantitative comparisons doubtful. So far, we can conclude that the n.m.r. results are consistent with our model but cannot disprove the lower values of ϕ_{OH} of Sassa and Katayama for higher ethanol concentrations. But the value of ϕ_{OH} of Luck for pure ethanol is definitely too low.

An additional remark might be of interest concerning the values of δ_b and δ_f . The difference is 5.94 (or 5.52 with ϕ_{OH} of Sassa and Katayama), which is much higher than the value of about 4.0 fitted to phenol + cyclohexane (ref. 11). Furthermore, the value of δ_f is extremely low. It is not unexpected that the free OH is better shielded in ethanol than in phenol, but the extent is remarkable. On the other hand, the decrease in shielding when the proton is engaged in the hydrogen bond ($\delta_b - \delta_f$) is larger for ethanol than for phenol, which parallels the stronger association in ethanol. Still, δ_b for ethanol (5.75) is smaller than in phenol (7.5).

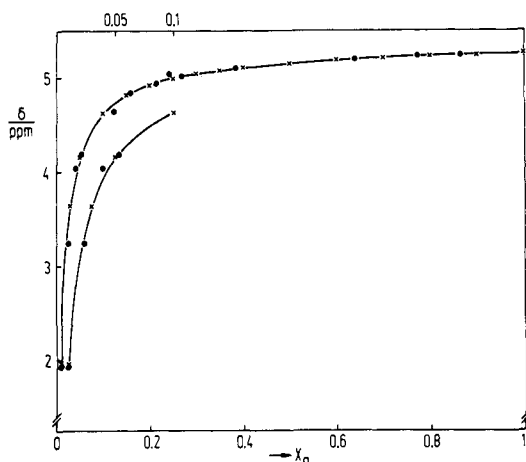


Table A1. The chemical shift of the hydroxyl proton of ethanol in ethanol + cyclohexane mixtures at about 298 K.

X_a	δ /ppm
0.00965	1.937
0.02380	3.243
0.03908	4.040
0.05280	4.185
0.12273	4.628
0.15871	4.835
0.21400	4.938
0.24185	5.034
0.26723	5.010
0.38207	5.096
0.63958	5.201
0.77143	5.233
0.86469	5.247

Fig. A1. The chemical shift of ethanol + cyclohexane (ca. 298.15 K). ● experimental, x model calculation. The low mole fractions of ethanol are plotted also in an enlarged scale (scale on top of figure).