

Thermodynamics of Alkoxyethanol + Alkane Mixtures

By Doukeni Missopolinou, Katerina Ioannou, Ioannis Prinos and Costas Panayiotou*

Department of Chemical Engineering, University of Thessaloniki, 540 06 Thessaloniki, Greece

(Received May 30, 2001; accepted in revised form July 5, 2001)

Alkoxyethanol / Spectroscopy / Statistical Mechanics / Hydrogen Bonding / LFHB Model

New spectroscopic data are reported for the intermolecular and intramolecular hydrogen bonding in 2-methoxyethanol+*n*-hexane and in 2-ethoxyethanol+*n*-hexane mixtures. The solutions were studied at 30, 40, and 50 °C and at concentrations where either only intramolecular association is observed or where, both, intermolecular and intramolecular associations are present. The data are treated with a new statistical thermodynamic model, which accounts for both types of hydrogen bonds. The energy and entropy change upon formation of the above hydrogen bonds were calculated and were used subsequently for the calculation of heats of mixing of alkoxyethanol+hydrocarbon mixtures. These calculations show that the intramolecular hydrogen bonding contribution to the heats of mixing is exothermic and significant.

1. Introduction

Hydrogen bonding is one of the most important interactions in systems of synthetic molecules as well as in systems of biomolecules. The hydrogen bonding may be intermolecular or intramolecular. The two types of hydrogen bonds are shown in Fig. 1. Much effort has been devoted to the study of intermolecular hydrogen bonding. However, intramolecular hydrogen bonding is often an important contribution to the overall hydrogen bonding in fluid systems, especially in biological systems. Of interest is the case of very dilute systems in inert solvents where intermolecular hydrogen bonding is absent and the only hydrogen bonds observed are the intramolecular ones.

The objective of this work is twofold: First, to provide with new experimental spectroscopic information on two representative alkoxyethanol +

* Corresponding author. E-mail: cpanayio@mailhost.ccf.auth.gr

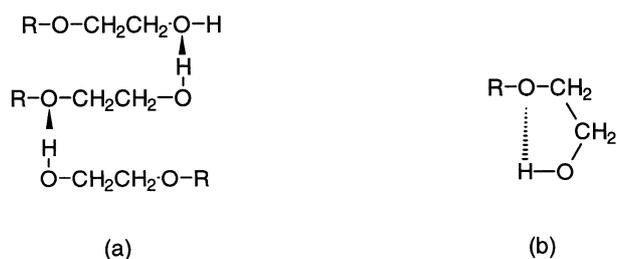


Fig. 1. (a) Intermolecular, (b) intramolecular hydrogen bonds.

alkane systems at conditions where we can extract information on the extent of the two competing types of intermolecular and intramolecular hydrogen bonding. Second, to combine this information with relevant calorimetric information and treat it with a recently developed statistical thermodynamic model of intramolecular hydrogen bonding [1].

2. Materials and methods

The materials used are shown in Table 1. *n*-Hexane was used as received. 2-Methoxyethanol and 2-ethoxyethanol were dried with 4 Å molecular sieves prior to use. Six solutions were prepared for each alkoxyethanol, three very dilute (only intramolecular association present) and three dilute (intermolecular and intramolecular associations present). The solutions were prepared by successive dilutions of an initial concentrated solution. The studied solutions are shown in Table 2.

The solution was placed in a cylindrical microcell possessing two NaCl windows separated by teflon spacers. The microcell was placed in a Graseby–Specac thermostated cell. This cell was placed in the sample compartment of the BIO-RAD, model FTS 45A, FTIR spectrophotometer continuously purged by dry air provided by a model 74 Balston compressor.

The reference spectrum for the pure solvent (*n*-hexane) was obtained at each studied temperature as the average of 128 consecutive scans at 2 cm⁻¹

Table 1. Materials used.

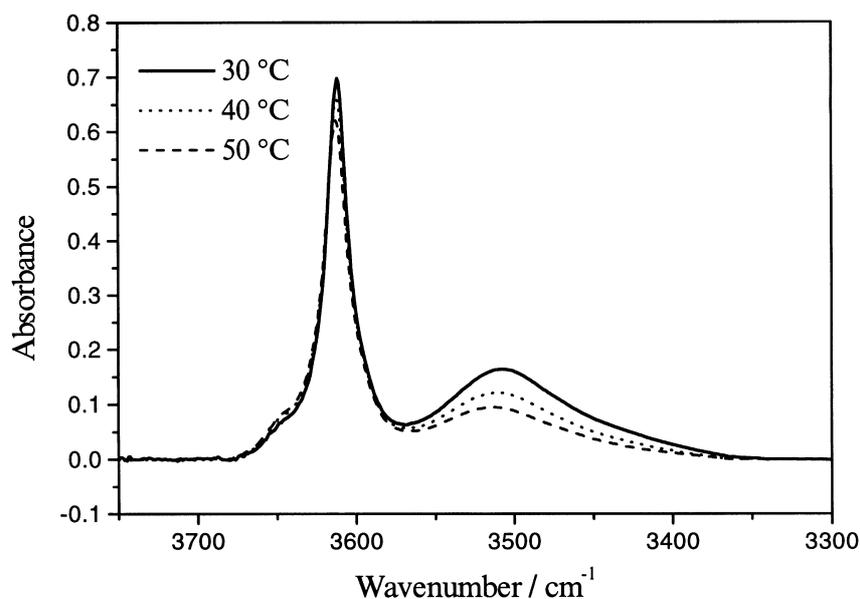
Substance	Producer	Purity	MW	$\rho/g\text{ ml}^{-1}$
2-methoxyethanol	Aldrich	> 99.3%	76.096	0.965
2-ethoxyethanol	Aldrich	> 99%	90.123	0.930
<i>n</i> -hexane	Riedel-de Haën	> 99%	86.178	0.660

Table 2. The studied solutions.

Alkoxyethanol	Solvent	Conc./mol l ⁻¹	Temp./°C	Type of HB
2-methoxyethanol	<i>n</i> -C ₆ H ₁₄	0.0056–0.008	30, 40, 50	Intra-molecular
2-methoxyethanol	<i>n</i> -C ₆ H ₁₄	0.036–0.084	30, 40, 50	Intra-, Inter-molecular
2-ethoxyethanol	<i>n</i> -C ₆ H ₁₄	0.0064, 0.008	30, 40, 50	Intra-molecular
2-ethoxyethanol	<i>n</i> -C ₆ H ₁₄	0.036–0.084	30, 40, 50	Intra-, Inter-molecular

resolution. The average spectrum of each solution was obtained with the same number of scans and resolution. After the appropriate subtractions, the net spectrum was manipulated with the commercial software packages Grams Converter of Galactic and Origin of Microcal. An example of obtained FTIR spectra is shown in Fig. 2.

Only two OH stretch peaks are observed at very low alkoxyethanol concentrations: one at 3646–3648 cm⁻¹ due to free or non-hydrogen bonded –OH and one at 3612 cm⁻¹ due to intramolecularly hydrogen bonded –OH. At higher alkoxyethanol concentrations, peaks in the range of 3100–3600 cm⁻¹

**Fig. 2.** The FTIR spectra of a solution of 0.06 M 2-methoxyethanol in *n*-hexane at three temperatures.

are observed due to intermolecularly hydrogen bonded –OH groups. The extinction coefficients for the free and intramolecularly hydrogen bonded –OH groups were obtained from Beer's law and from the spectra of very dilute solutions. The corresponding coefficient for the intermolecularly hydrogen bonded –OH groups required an additional spectrum from a more concentrated solution. The Lorentz equation was used for the spectra deconvolution and the evaluation of the separate peak areas. Having the separate peak areas and the corresponding extinction coefficients one may calculate in the classical manner the concentration of the corresponding hydrogen bonds. Thus, the number (the concentration) of intramolecular hydrogen bonds C_{intra} (mol l^{-1}) is given by $C_{\text{intra}} = \frac{A_{\text{intra}}}{\alpha_{\text{intra}} l}$, where, A_{intra} is the peak area (cm^{-1}), α_{intra} the extinction coefficient ($1 \text{ mol}^{-1} \text{ cm}^{-2}$) and l the path (cell) length (cm). The new experimental data are reported in Tables 3, 4. These data will subsequently be treated with the theoretical model presented in the next section. x_1 in Tables 3 and 4 is the mole fraction of the alcoxyethanol.

Table 3. Mole fractions of intramolecularly (x_{Intra}), and intermolecularly (x_{Inter}) hydrogen bonded –OH groups and the total mole fraction (x_{total}) of hydrogen bonded –OH groups for various concentrations of 2-methoxyethanol.

$C/\text{mol l}^{-1}$	x_1	x_{Intra}	x_{Inter}	x_{total}
$T = 30^\circ\text{C}$				
0.0056	0.0007	0.0005	0	0.0005
0.0064	0.0008	0.0006	0	0.0006
0.0080	0.0011	0.0010	0	0.0010
0.0360	0.0047	0.0040	0.0005	0.0045
0.0600	0.0078	0.0064	0.0012	0.0076
0.0840	0.0110	0.0082	0.0026	0.0108
$T = 40^\circ\text{C}$				
0.0056	0.0007	0.0005	0	0.0005
0.0064	0.0008	0.0006	0	0.0006
0.0080	0.0011	0.0010	0	0.0010
0.0360	0.0047	0.0042	0.0002	0.0044
0.0600	0.0078	0.0068	0.0006	0.0074
0.0840	0.0110	0.0090	0.0016	0.0106
$T = 50^\circ\text{C}$				
0.0056	0.0007	0.0005	0	0.0005
0.0064	0.0008	0.0006	0	0.0006
0.0080	0.0011	0.0010	0	0.0010
0.0360	0.0047	0.0041	0.0002	0.0043
0.0600	0.0078	0.0069	0.0004	0.0073
0.0840	0.0110	0.0093	0.0010	0.0103

Table 4. Mole fractions of intramolecularly (x_{Intra}), and intermolecularly (x_{Inter}) hydrogen bonded $-\text{OH}$ groups and the total mole fraction (x_{total}) of hydrogen bonded $-\text{OH}$ groups for various concentrations of 2-ethoxyethanol.

$C/\text{mol l}^{-1}$	x_1	x_{Intra}	x_{Inter}	x_{total}
$T = 30\text{ }^\circ\text{C}$				
0.0064	0.0008	0.0007	0	0.0007
0.0080	0.0011	0.0010	0	0.0010
0.0360	0.0047	0.0044	0.0002	0.0046
0.0600	0.0078	0.0068	0.0009	0.0077
0.0840	0.0110	0.0088	0.0021	0.0109
$T = 40\text{ }^\circ\text{C}$				
0.0064	0.0008	0.0006	0	0.0006
0.0080	0.0011	0.0010	0	0.0010
0.0360	0.0047	0.0044	0.0000	0.0044
0.0600	0.0078	0.0070	0.0006	0.0076
0.0840	0.0110	0.0092	0.0015	0.0107
$T = 50\text{ }^\circ\text{C}$				
0.0064	0.0008	0.0006	0	0.0006
0.0080	0.0011	0.0010	0	0.0010
0.0360	0.0047	0.0043	0.0000	0.0043
0.0600	0.0078	0.0070	0.0002	0.0072
0.0840	0.0110	0.0094	0.0010	0.0104

3. The theoretical model

In this section we will present the necessary formalism for studying fluid systems with both intermolecular and intramolecular hydrogen bonds. For simplicity, we will confine ourselves to the case of molecules with one donor group (such as $-\text{OH}$) and w equivalent proton acceptor sites (such as ether oxygen $-\text{O}-$) per molecule. This type of system (polyethoxyalcohols) is of key importance in the study of non-ionic surfactants. The formalism can easily be extended to more complex cases. The presentation in this paragraph will heavily be based on our previous work [1–3], where the details of the original Lattice–Fluid/Hydrogen–Bonding (LFHB) model is presented.

As in the LFHB model, the full partition function Q of our system in the N, P, T ensemble in its maximum-term approximation is factorized into a physical term, Q_P , a chemical or hydrogen-bonding term, Q_H , and the classical exponential volumetric term, or

$$Q = Q_P Q_H \exp(-PV/kT) \quad (1)$$

where, V is the total volume of the system. We will focus attention on the chemical factor. According to the LFHB model, this term may, in general, be

written as

$$Q_H = \left(\frac{\tilde{\rho}}{rN} \right)^{N_H} \Omega \exp \left(- \frac{\sum N_{ij} G_{ij}^0}{kT} \right) \quad (2)$$

where N is the total number of molecules in the system, N_{ij} is the number of hydrogen bonds of type $i - j$ characterized by a free energy change G_{ij}^0 and $N_H = \sum N_{ij}$ is the total number of intermolecular hydrogen bonds. rN in Eq. (2) is the total number of segments in the system ($rN = \sum r_i N_i$). The reduced density $\tilde{\rho}$ or the reduced volume \tilde{v} ($= 1/\tilde{\rho} = \rho^*/\rho$) is calculated from the LFHB equation of state [2]:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) + \tilde{\rho} \left(1 - \frac{1}{\tilde{r}} \right) \right] = 0 \quad (3)$$

where,

$$\frac{1}{\tilde{r}} = \frac{1}{r} - \frac{N_H}{rN} \quad (4)$$

while $\tilde{T} = T/T^*$ and $\tilde{P} = P/P^*$ are the reduced temperature and pressure of the system. ρ^* , T^* ($= \varepsilon^*/R$), and P^* ($= \varepsilon^*/v^*$) are the characteristic Lattice-Fluid [4] (LF) scaling constants of the system.

The preexponential factor Ω in Eq. (2) is the number of different ways of distributing the hydrogen bonds in the system without requiring that donor and acceptor groups be neighbors. This requirement of donor/acceptor proximity is taken into account by the first term in the rhs of the above Eq. (2). The statistical derivation of Ω was done in our previous work [1] for the system of N_1 polyalkoxy alkanol (PAA) molecules and N_2 molecules of an inert solvent ($N = N_1 + N_2$). If w is the number of ether oxygen sites in PAA, the number of proton donors of type 1 ($-\text{OH}$) is N_1 , of proton acceptors of type 1 ($-\text{OH}$) is N_1 , and of proton acceptors of type 2 ($-\text{O}-$) is wN_1 . Let there be N_{11} hydrogen bonds $\text{OH}---\text{OH}$, N_{12} intermolecular bonds $\text{OH}---\text{O}-$, and B intramolecular bonds $\text{OH}---\text{O}-$ in the system. The number of free proton donors is

$$N_{10} = N_1 - N_{11} - N_{12} - B \quad (5)$$

With these definitions, Ω is given by the following equation¹:

$$\Omega = \frac{x^B (N_1!)^2 (wN_1 - B)!}{B! N_{11}! N_{12}! N_{10}! (N_1 - N_{11})! (wN_1 - B - N_{12})!} \quad (6)$$

In our case, there are three types of hydrogen bonds: N_{11} 1-1 bonds with free energy of bond formation G_{11}^0 , N_{12} 1-2 intermolecular bonds with free energy of bond formation G_{12}^0 , and B 1-2 intramolecular bonds with free energy of bond formation G_B^0 . The free energy of the $i - j$ bond formation can be

resolved as following:

$$G_{ij}^0 = E_{ij}^0 + PV_{ij}^0 - TS_{ij}^0 \quad (7)$$

E_{ij}^0 , V_{ij}^0 , S_{ij}^0 been the energy, volume, and entropy change of $i - j$ bond formation respectively.

Thus, the hydrogen bonding term Q_H of the partition function in Eq. (2) can then be written as following:

$$Q_H = \left(\frac{\tilde{\rho}}{rN} \right)^{N_{11}+N_{12}} c^B \frac{w^B (N_1!)^2 (wN_1 - B)!}{B!N_{11}!N_{12}!N_{10}! (N_1 - N_{11})! (wN_1 - B - N_{12})!} \times \exp \left(- \frac{N_{11}G_{11}^0 + N_{12}G_{12}^0 + N_B G_B^0}{kT} \right) \quad (8)$$

The hydrogen-bonding part of the free energy of the system is obtained from the equation

$$G_H = -kT \ln Q_H \quad (9)$$

By minimizing this equation with respect to the unknowns N_{11} , N_{12} , and B we obtain the following coupled equations:

$$\frac{B (wN_1 - B)}{(wN_1 - B - N_{12}) N_{10} w} = c \exp \left(- \frac{G_B^0}{kT} \right) = K_B \quad (10)$$

$$\frac{N_{11}}{(N_1 - N_{11}) N_{10}} = \frac{\tilde{\rho}}{rN} \exp \left(- \frac{G_{11}^0}{kT} \right) = \frac{K_{11}}{N} \quad (11)$$

$$\frac{N_{12}}{(wN_1 - B - N_{12}) N_{10}} = \frac{\tilde{\rho}}{rN} \exp \left(- \frac{G_{12}^0}{kT} \right) = \frac{K_{12}}{N} \quad (12)$$

The coupled Eqs. (10)–(12) must be solved simultaneously by an appropriate iteration scheme. After some algebra the above three equations lead to the following equations

$$N_{12} = \frac{K_{12}}{K_B N w} B (wN_1 - B) \quad (13)$$

$$N_{11} = \frac{K_{11}}{K_B N w + B (K_{11} - K_{12})} B N_1 \quad (14)$$

$$B = \frac{(NwK_B - K_{12}B)}{N} \times \left[N_1 - B - B \frac{K_{12}}{wK_B} \frac{wN_1 - B}{N} - N_1 \frac{K_{11}B}{wNK_B + B(K_{11} - K_{12})} \right] \quad (15)$$

The last equation contains only the unknown B and it can be solved numerically by successive substitutions. The solution for B can then be replaced in Eqs. (13) and (14) in order to obtain N_{12} and N_{11} respectively.

In the limiting case of highly dilute systems, we have $N_{11} = N_{12} = 0$ and, consequently, (10) becomes

$$\begin{aligned} \frac{B}{(N_1 - B)w} &= K_B && \text{or} \\ \frac{B}{N_1} &= \frac{K_B}{1 + wK_B} && \text{(very dilute system)} \end{aligned} \quad (16)$$

This is a useful equation, which can be used for determining K_B from experimental (such as spectroscopic) information on the degree of hydrogen bonding B/N_1 .

With the aid of classical thermodynamics we may use Eq. (1) for obtaining equations for all basic thermodynamic quantities for, both, pure components and mixture. For example, the equation for the heat of mixing of the binary system is [2]:

$$\begin{aligned} H^E &= x_1 r_1 \tilde{\rho}_1 \varepsilon_1^* + x_2 r_2 \tilde{\rho}_2 \varepsilon_2^* - r \tilde{\rho} \varepsilon^* + N_{11} E_{11}^0 + N_{12} E_{12}^0 + B E_B^0 \\ &\quad - x_1 (N_{11}^0 E_{11}^0 + N_{12}^0 E_{12}^0 + B^0 E_B^0) \end{aligned} \quad (17)$$

where

$$\varepsilon^* = \phi_1 \varepsilon_1^* + \phi_2 \varepsilon_2^* - \phi_1 \phi_2 X_{12} \quad (18)$$

$$\phi_1 = \frac{r_1 N_1}{rN} = \frac{x_1 r_1}{r} = 1 - \phi_2 \quad (19)$$

$$X_{12} = \frac{\varepsilon_1^* + \varepsilon_2^* - 2\sqrt{\varepsilon_{12}^*}}{RT} \quad (20)$$

$$\varepsilon_{12} = \xi_{12} \sqrt{\varepsilon_{11} \varepsilon_{22}} \quad (21)$$

The dimensionless parameter ξ_{12} is expected to have values close to unity (equal to one in Berthelot's rule).

4. Application of the model

In order to apply the Model to the experimental data reported in Tables 3, 4 we need on the one hand the LF scaling constants T^* , P^* , ρ^* for the pure components and on the other hand the hydrogen bonding constants E^0 , S^0 , V^0 for each of the three types of hydrogen bonds. For simplicity, we neglect the volume changes upon hydrogen bond formation or, we set $V^0 = 0$. It is assumed here that the same set of E^0 and S^0 is valid for both alkoxyethanols. It is expected that the presence of the electron – drawing ether oxygen in the alkoxyethanol molecules will strengthen the O–H---OH interaction relative to the corresponding interaction in alkanols as is shown in Fig. 3. Thus, we expect E_{11}^0 to have more negative values than $-25\ 100\ \text{J mol}^{-1}$, which corresponds to alkanols [2]. The entropy change S_{11}^0 , however, is not expected to be significantly

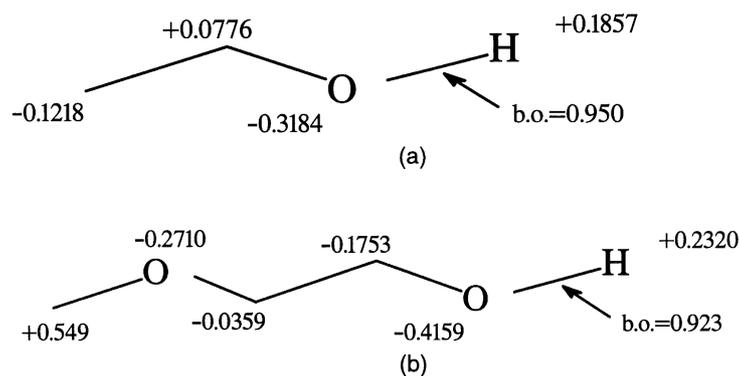


Fig. 3. Semi-empirical quantum mechanical calculation of point charge distribution and bond order, for: (a) ethanol and (b) 2-methoxyethanol, by the Mopac suite, using PM3 Hamiltonian [5].

different from that of alkanols. Thus, it is set equal to $-26.5 \text{ J K}^{-1} \text{ mol}^{-1}$ as before [2].

Unfortunately, we have no means to evaluate the above parameters from first principles and in an unequivocal manner. The best we can do is to use as much experimental information as possible on as many thermodynamic properties as possible and estimate the parameters from a least squares fit of calculated to experimental data. Thus, besides the spectroscopic data of this work, we have used experimental information on vapor pressures, heats of vaporization, and densities of pure alkoxyethanols [6] as well as heat of mixing data [7] on alkoxyethanol + alkane mixtures. This procedure has generated the scaling constants and hydrogen bonding parameters reported in Table 5^{TS4}. All calculations reported hereafter are done with these parameters. Two hy-

Table 5. LF scaling constants and hydrogen bonding parameters.

LF scaling constants			
Fluid	T^*/K	P^*/MPa	$\rho^*/\text{kg m}^{-3}$
2-Methoxyethanol	522	509	1062
2-Ethoxyethanol	514	441	1030
Hydrogen bonding parameters			
Interaction	$E^0/\text{J mol}^{-1}$	$S^0/\text{J K}^{-1} \text{ mol}^{-1}$	$V^0/\text{cm}^3 \text{ mol}^{-1}$
1 – 1 (OH---OH)	-28100	-26.5	0
1 – 2 (OH---O Inter)	-19000	-24.0	0
B (OH---O Intra)	-10470	-16.0	0

^{TS4} Please check renumbering of Table 9.

Editor's or typesetter's annotations (will be removed before the final \LaTeX run)

drogen bonding sites per ether oxygen in alkoxyethanols were assumed in the calculations.

In Figs. 4 and 5 are compared the experimental and calculated vapor pressures and liquid densities along the saturation line, respectively, of 2-methoxyethanol. The ability of the model to describe the degree of hydrogen bonding

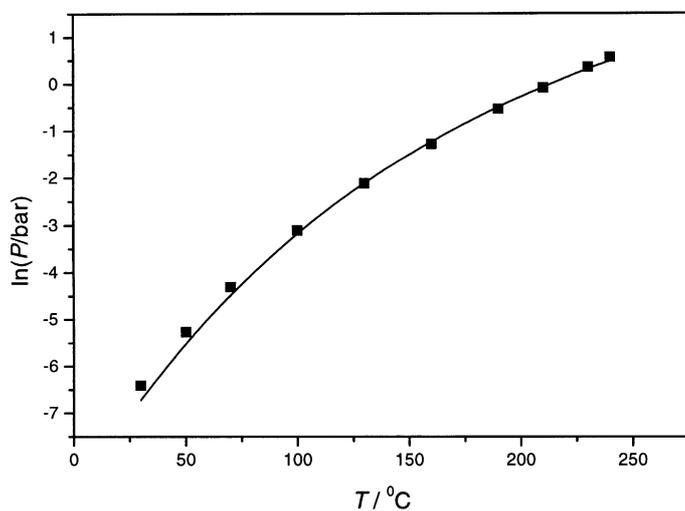


Fig. 4. Experimental [6], ■, and calculated, —, vapor pressures for 2-methoxyethanol.

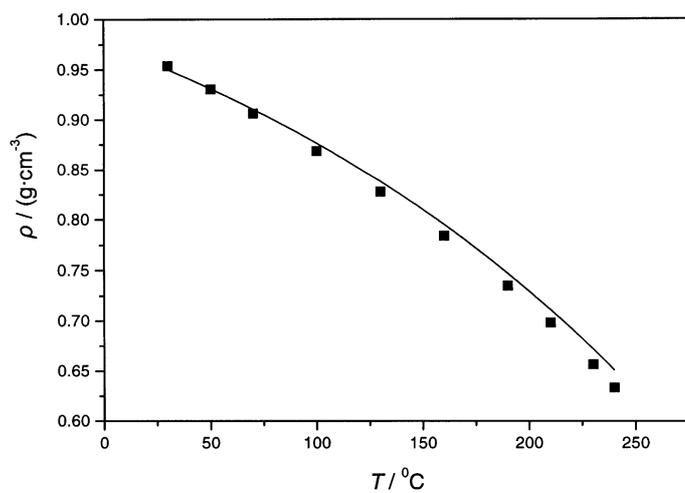


Fig. 5. Experimental [6], ■, and calculated, —, liquid densities along the saturation VLE line for 2-methoxyethanol.

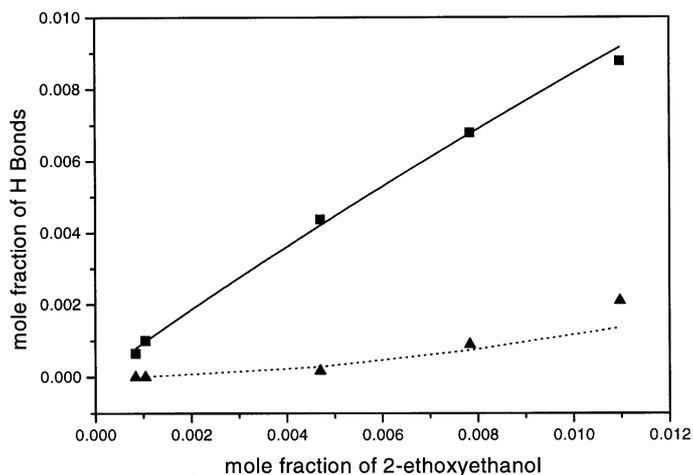


Fig. 6. Experimental, ▲, and calculated, ..., degree of intermolecular and experimental, ■, and calculated, —, degree of intramolecular hydrogen bonding in the mixture: 2-ethoxyethanol + *n*-hexane at 30 °C.

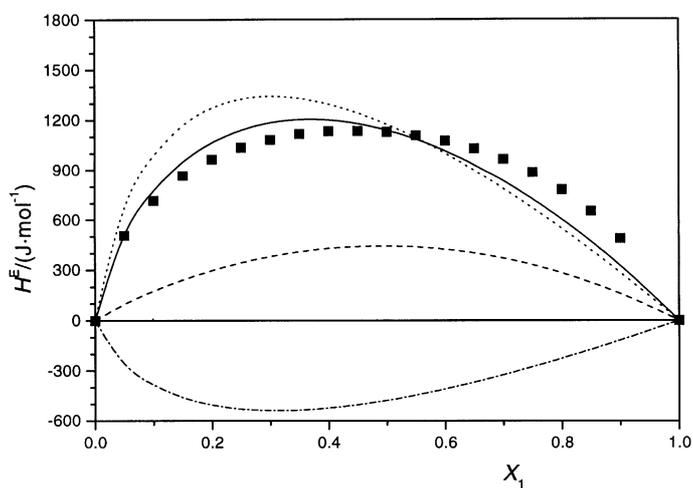


Fig. 7. Experimental [6], ■, and calculated, —, heats of mixing for the system 2-ethoxyethanol(1) + *n*-octane(2) at 25 °C. The contributions from dispersive interactions, ---, intermolecular hydrogen bonds, ..., and intramolecular hydrogen bonds, -·-·-, are shown.

in the mixtures of alkoxyethanols with *n*-hexane can be appreciated from the Fig. 6 where our spectroscopic data are compared with the calculated ones. The number of hydrogen bonds per mol in the system has been calculated with Eqs. (13)–(16).

We have not found in the open literature experimental data on the heats of mixing for the two binary systems examined in this work. However, the parameters reported in Table 5 should, in principle, be valid for all mixtures of alkoxyethanols with inert hydrocarbons. In Fig. 7 the calculated heats of mixing are compared with the experimental ones for the system of 2-ethoxyethanol with *n*-octane at 25 °C. A similar picture is obtained for the mixture of 2-ethoxyethanol with cyclohexane. A number of comments regarding the above experimental data and the calculations are in order.

5. Discussion and conclusions

The experiment as well as the calculations show that a large fraction of the –OH groups of alkoxyethanol molecules in the very dilute mixtures with *n*-hexane are associated via intramolecular hydrogen bonding. This fraction is sensibly higher for 2-methoxyethanol at 30 °C but the difference disappears at 50 °C. In both systems, as the temperature increases, the overall degree of hydrogen bonding diminishes. This trend is also followed by the degree of intermolecular hydrogen bonding. However, the degree of intramolecular hydrogen bonding increases as the temperature is increased. The explanation provided by the model is the following: As the temperature increases there is a drastic decrease of intermolecular hydrogen bonds due to the relatively large entropy change upon formation of these bonds. Upon destruction of intermolecular hydrogen bonds, more –OH are available for intramolecular association. Thus, although the negative entropy change upon formation of this bond tends to reduce the number of hydrogen bonds, the increased population of available –OH groups overruns this trend and finally increases the number of intramolecular hydrogen bonds.

An interesting point comes from Fig. 7. As observed, the contribution of the intramolecular hydrogen bonds to the heats of mixing of the system is by no means negligible. The important point is that its contribution is negative (exothermic) while that of intermolecular hydrogen bonding as well as that of the van der Waals dispersive interactions are positive (endothermic). An explanation of this behavior may come from Fig. 8 where the degree of hydrogen bonding is estimated over the full composition range for a typical system. As observed, there is a positive deviation from linearity for the intramolecular bonding. This excess of intramolecular bonds is responsible for the negative contribution to the heat of mixing since the formation of an intramolecular bond is an exothermic process (negative E_B^0).

At low concentrations the degree of intramolecular hydrogen bonding is increasing with increasing mole fraction of the alkoxyethanol much stronger than the degree of intermolecular hydrogen bonding, as shown in Fig. 6. This is due to the fact that in this concentration region the inert solvent does not influence essentially the intramolecular hydrogen bonds while it influences very much

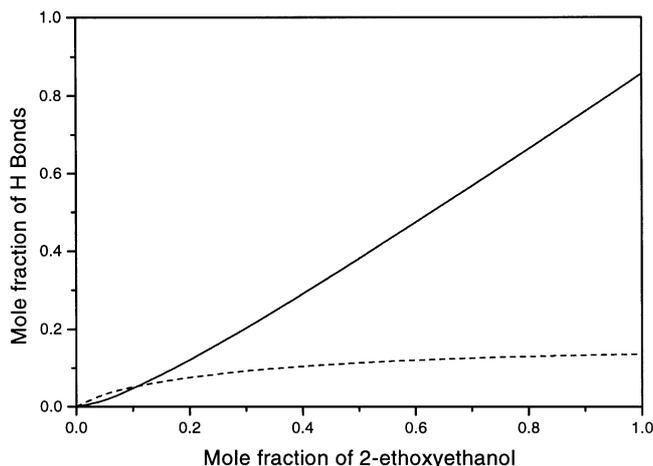


Fig. 8. The calculated degree of intermolecular, —, and intramolecular, ---, hydrogen bonding in the mixture: 2-ethoxyethanol + *n*-octane at 25 °C over the full composition range.

the formation of the intermolecular bonds as the interacting molecules must come close together (proximity condition). Of course, at higher concentrations, the -OH prefer to bond intermolecularly and thus the number of intramolecular hydrogen bonds levels off as shown in Fig. 8.

Before judging the overall performance of the model, it is essential to keep in mind that a single set of hydrogen bonding parameters is used for all alkoxyethanol systems and for all thermodynamic properties. In view of this, the ability of the model to describe the diverse properties of these systems is rather satisfactory.

It is worth pointing out that the above formalism can be integrated to any equation-of-state framework leading to an equation-of-state theory of hydrogen-bonded systems. The formalism can also be extended in a straightforward manner to the case of more complex systems with more than one proton donor group per molecule. However, we must keep in mind that, due to steric and other interactions, the acceptor sites may not be equivalent [8]. This is important when estimating equilibrium constants and hydrogen bonding energies. In the case of polyethoxyalcohol molecules, the strength of the intermolecular $\text{OH} \cdots \text{O}$ bond is expected to be close to the corresponding intramolecular $\text{OH} \cdots \text{O}$ bond only when the two interacting groups are sufficiently far apart [8, 9]. In general, however, we are not justified to neglect the difference in strength between intermolecular and intramolecular hydrogen bonds [10] as is also clear from the present work.

The parameters of Table 5 were used for calculating the effect of temperature on the heats of mixing in alkoxyethanol + hydrocarbon systems.

It was found that the heat of mixing increases as the temperature increases. Preliminary experimental data in our laboratory for the system 2-ethoxyethanol + cyclohexane corroborated these findings.

The findings of this work could be summarized in the following conclusions:

1. The thermodynamic properties of alkoxyethanol + hydrocarbon mixtures are dictated by the interplay of *dispersive forces*, *intermolecular* hydrogen bonding and *intramolecular* hydrogen bonding.
2. The intramolecular hydrogen bonds are the weakest hydrogen bonds in the system. They increase rapidly with concentration at very low alkoxyethanol concentrations and level off at higher concentrations.
3. The self-associations (OH—OH interactions) are the strongest in the system.
4. The contribution of the intermolecular hydrogen bonds to the heat of mixing is endothermic while that of intramolecular bonds is exothermic.
5. The new theoretical model can, at least qualitatively, describe the spectroscopic and calorimetric data for these systems.

References

1. D. Missopolinou and C. Panayiotou, *Fluid Phase Equilib.* **156** (1999) 51.
2. C. Panayiotou and I. C. Sanchez, *J. Phys. Chem.* **95** (1991) 10090.
3. D. Missopolinou and C. Panayiotou, *J. Phys. Chem. A* **102** (1998) 3574.
4. I. C. Sanchez and C. Panayiotou, In *Models for Thermodynamic and Phase Equilibria Calculations*, S. I. Sandler, Ed., Dekker, New York (1994) Chapt. 3.
5. M. F. Schlecht, *Molecular Modeling on the PC*, Wiley, New York (1998).
6. T. E. Daubert and R. P. Danner, Eds., *Data Compilation Tables of Properties of Pure Compounds*, AIChE Symp. Ser. No. 203, American Institute of Chemical Engineers, New York (1985).
7. H. Ohji, A. Oskai, K. Tamura, S. Murakami and H. Ogawa, *J. Chem. Thermodynamics* **30** (1998) 761.
8. M. D. Joesten and L. J. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York (1974) Chapt. 5.
9. S. N. Vinogradov and R. H. Linnel, *Hydrogen Bonding*, Van Nostrand Reinhold Co., New York (1971).
10. D. Missopolinou and C. Panayiotou, *Fluid Phase Equilib.* **110** (1995) 73.