

Excess enthalpies of binary mixtures of 2-ethoxyethanol with four hydrocarbons at 298.15, 308.15, and 318.15 K An experimental and theoretical study

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Abstract

New experimental data are reported for the thermodynamic investigation of the intermolecular and intra-molecular hydrogen bonding in 2-ethoxyethanol + hydrocarbons. The excess enthalpies of the mixtures of 2-ethoxyethanol + *n*-hexane, or cyclohexane, or benzene, or *n*-octane at three temperatures (298.15, 308.15, and 318.15 K) were measured. The data are correlated with the statistical thermodynamic model non-random hydrogen bonding (NRHB) which accounts for both types of hydrogen bonds and was recently developed by the authors. A single set of hydrogen bonding parameters is used for all the alkoxyethanol systems and for the recently calculated thermodynamic properties. The results showed a satisfactory agreement between experimental and calculated data and the contributions of all different types of molecular interactions were calculated. The intra-molecular hydrogen bonding contribution to the heats of mixing is exothermic and significant. The calorimetric measurements are combined with dielectric ones and the derived Kirkwood factor is used to interpret the physicochemical behaviour of our systems.

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Keywords: 2-Ethoxyethanol; Excess enthalpies; Hydrogen bonding; Statistical thermodynamics; NRHB model

1. Introduction

The thermodynamic properties of highly non-ideal mixtures of associated or hydrogen-bonded fluids and their correlation/analysis are not only of key interest in the development and testing of statistical thermodynamic models capable of correlating the macroscopic properties of the fluid systems, but also of importance for the rational design of industrial chemical processes involving such systems. Hydrogen bonding may be one of the most important interactions in these systems and intra-molecular hydrogen bonding may also be an important contribution to the overall hydrogen bonding.

2-Ethoxyethanol (widely known by its trade name, cellosolve) is a common solvent in laboratory practice and in the chemical industry and is able to form two types of hydrogen bonds, inter- and intra-molecular ones. This capacity keeps attracting the interest of many researchers for the theoretical and experimental study of miscellaneous properties of systems

of cellosolve. The excess molar enthalpies of aqueous solution of 2-ethoxyethanol were measured by Tamura et al. [1] and Davis et al. [2]. Other systems of 2-ethoxyethanol include binaries with various carboxylates [3,4], with di-*n*-butylether [5], and with 1,4-dioxane or 1,2-dimethoxyethane or various hydrocarbons [6,7]. More recently, Lee and Lee [8] have introduced intra-molecular association explicitly in their correlations of vapor–liquid equilibria of pure alkoxyalkanols and their mixtures with inert substances.

In our previous works we provided new experimental spectroscopic data on 2-methoxyethanol and 2-ethoxyethanol + *n*-hexane systems in very dilute mixtures [9], and high pressure vapor–liquid equilibrium (VLE) data of the binary mixture of CO₂ + 2-ethoxyethanol at three temperatures [10], and discussed the extent of the two competing types of hydrogen bonds as well as the validity of equations-of-state models, such as the LFHB (lattice-fluid hydrogen bonding) [11] and the NRHB (non-random hydrogen bonding) [15] models.

In the present work, we report measurements of the excess enthalpies of 2-ethoxyethanol with four hydrocarbons, two normal (*n*-hexane and *n*-octane), one cyclic (cyclohexane), and one aromatic (benzene), at three temperatures: 298.15, 308.15, and

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318.15 K. The NRHB model with the known hydrogen bonding parameters [9] and the scaling constants [10] was used to correlate/predict the heats of mixing of the studied systems. The calculated heats of mixing are compared with the experimental ones and the contributions from the different molecular interactions to the heats of mixing are shown and discussed. The same parameters were used for all external conditions and for calculating the effect of temperature on the heats of mixing and the experimental data corroborated the calculations.

We, also, measured the relative permittivities, ϵ , the refractive indices, n_D , and the densities, ρ , of the binary of 2-ethoxyethanol with *n*-hexane at 298.15 K. From these values, the Kirkwood correlation factors, g , over the full composition range were derived. This factor is correlated with our present calorimetric findings and the previous spectroscopic ones [9] and the combined results shed light on the nature of the molecular interactions of 2-ethoxyethanol.

2. Experimental

2.1. Description of the apparatus

Excess enthalpies were measured with a flow mixing unit consisting of the calorimeter, the mixing cell, and auxiliary devices. A schematic view of the calorimetric system is shown in Fig. 1. The *calorimeter* is a commercial Setaram (France), model C80, differential heat-flux apparatus based on the Calvet principle. Two identical wells used for inserting the two mixing cells, one empty (the reference) and one for the flow mixing process (the sample) are located in the calorimetric block. In the outer surface of the wells (interior of the block) there are thermopiles consisting of copper/constantan thermocouples in order to transfer the heat between the cells and the block very fast. The desired temperature of the block is adjusted by a Setaram PID controller being constant within 0.05 °C.

The *mixing cells* are made of a stainless steel tube (outer diameter 1/16 of inch = 1.6 mm, inner diameter 1.0 mm) tightly

coiled in about 32 loops inside a metallic cylinder (inner diameter 14.5 mm, total height 70 mm, height of the coils 55 mm) which fits into the well in the calorimeter block. The length of the coiled tube in thermal contact with the inner wall of the cylinder is about 146 cm. They were designed and constructed in our laboratory.

The *auxiliary devices* are the pumps, the preheater and the temperature controller of the preheater, the heating tape of the tubes before entering the block of the calorimeter and its temperature regulator, the water circulation bath and the computer for collecting the signal. The fluids are delivered from two high pressure piston pumps manufactured by ECOM, model HPP 5001, with operating range from 0.1 to 9.9 mL min⁻¹ (normal mode) or 0.01–0.99 mL min⁻¹ (micro mode), maximum pressure 50 MPa, and barrel volume 400 mL, and accuracy of the selected flow rate $\pm 0.5\%$ at constant pressure. The temperature of the fluids is further regulated during their passage through the preheater which is placed into the unit of the C80 and before the mixing cell. The accuracy of the preheater control was within ± 0.03 K.

The densities, ρ , of the binary of 2-ethoxyethanol with *n*-hexane were measured with an Anton-Paar 60/602 vibrating tube densitometer, which was thermostatted by a Haake F3 digital thermostat with a temperature stability better than ± 0.01 K. The relative permittivities, ϵ , were measured with a Dipolmeter, model WDW DM-01, of Wissenschaftlich Technische Werkstätten GmbH, using MFI-1 and MFL-2 cells. The refractive indices, n_D , were measured with an Abbe refractometer of Zeiss Jena, model G, using sodium light (D). The dipolmeter and the refractometer were thermostatted with a thermoregulator by Techne, model TU-16A, having a ± 0.005 K temperature stability.

2.2. Materials

The materials used along with their characteristics are summarized in Table 1. 2-Ethoxyethanol was dried over 4 Å

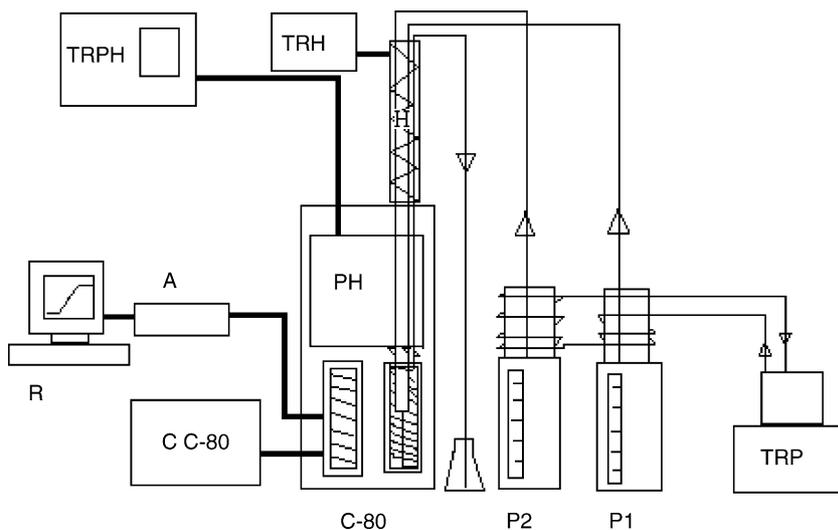


Fig. 1. Schematic diagram of the experimental set up: C-80, calorimeter with the mixing cells; C, C-80, controller of the calorimeter; P1, and P2, pumps; TRP, temperature regulator of the pumps; PH, preheater; TRPH, and TRH, temperature regulator of the preheater and the heating line; A, analogue to digital converter; R, digital recording.

Table 1
Materials used

Substance	Producer	Purity (%)	MW (g mol ⁻¹)	ρ (g ml ⁻¹) 25 °C
2-Ethoxyethanol	Aldrich	>99	90.123	0.92510
<i>n</i> -Hexane	Merck	>99	86.178	0.65489
Cyclohexane	Merck	>99.8	84.162	0.77388
Benzene	Merck	>99.7	78.114	0.87367
<i>n</i> -Octane	Riedel-de Haën	>99	114.230	0.69851
Ethanol	Riedel-de Haën	>99.8	46.069	0.78519

molecular sieves prior to use. The four hydrocarbons were used as received. The chemicals used in the calorimeter were degassed by placing in an ultrasonic bath before filling the pumps.

2.3. Experimental procedure

We first determined the electric constant of the calorimeter (the proportionality ratio between the heat and the output signal) applying the Joule effect. The calibration was performed at each experimental temperature with different values of electric output from 10 and 100 mW. The electrical calibration constant varied with temperature from 30 to 31 $\mu\text{V mW}^{-1}$ and did not depend on the electric input to the heater. Also, we measured the volumetric flow of the pumps by weighing the mass of different liquids delivered by the pumps through the mixing cells at fixed time intervals.

Secondly, we checked the performance of our set up and mixing cell and the efficiency of the electrical calibration constant by measuring the heat of mixing of various mixtures at these three temperatures and comparing the measured values to literature data. The test systems were the binaries of 2-ethoxyethanol with cyclohexane and *n*-octane at 298.2 K [7] and the binaries of benzene with ethanol and propanol at 308.2 and 318.2 K [12].

Having verified the accuracy of our experimental setup, we finally measured the excess enthalpies of the binaries of 2-ethoxyethanol with four hydrocarbons at three temperatures: 298.15, 308.15, and 318.15 K.

The flow rates of the two pumps were varying from 0.10 to 0.40 mL min⁻¹ while the temperature of the liquids in the pumps was kept at 298.2 K in order to have constant and fully controlled volumetric flow. The total flow rate of the liquids was kept constant before, during, and after the mixing process along the whole day, while the flow rates of the individual compounds changed according to the desired mole fraction. The actual mole fraction of the flow mixtures was obtained from the volumetric flows, the pure components densities at 298.2 K, and the molar mass of the compounds.

In a typical run, the procedure steps are as following: before starting the daily experiment, we let enough time for the calorimetric system to come to thermal equilibration. We record the base line of the system without any flow. Being this constant, we start one pump delivering the major compound. After achieving base line stability, we switch on the second pump and decrease the flow rate of the first one in order to have the first mixing solution. As soon as the mixing effect completes, the signal reaches a plateau and the value of the plateau minus the base line sig-

nal is the final value of the signal in mV. The excess enthalpies are obtained from this signal divided by the electric constant in $\mu\text{V mW}^{-1}$ and by the molar flow in mol min⁻¹. This procedure leaves an uncertainty to the determined H^E which is estimated to be less than $\pm 1\%$.

3. Experimental results

The results for the test systems are given in Table 2 and compared with the literature in Figs. 2 and 3. From these diagrams

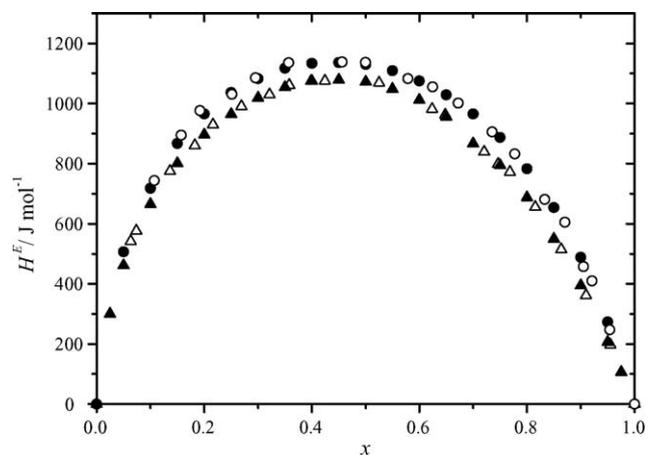


Fig. 2. Comparison of the excess enthalpies, H^E , at $T = 298.15$ K: for x 2-ethoxyethanol + $(1-x)$ cyclohexane: ours, (Δ); Ref. [7], (\blacktriangle); for x 2-ethoxyethanol + $(1-x)$ *n*-octane: ours, (\circ); Ref. [7], (\bullet).

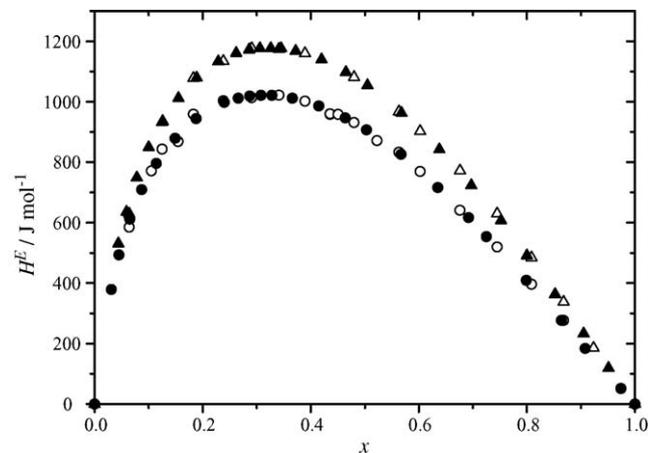


Fig. 3. Comparison of the excess enthalpies, H^E , for x ethanol + $(1-x)$ benzene at $T = 308.15$ K; ours, (\circ); Ref. [12], (\bullet) at $T = 318.15$ K; ours, (Δ); Ref. [12], (\blacktriangle).

Table 2
Excess enthalpies for the test systems at 298.15, 308.15, and 318.15 K

x	H^E (J mol ⁻¹)	x	H^E (J mol ⁻¹)
<i>x</i> 2-Ethoxyethanol + (1 - <i>x</i>) cyclohexane ($T=298.15$ K)			
0.0634	541.5	0.5249	1069.0
0.0738	576.3	0.6237	981.4
0.1363	775.2	0.6481	962.2
0.1825	860.9	0.7205	839.1
0.2164	929.7	0.7464	798.6
0.2692	990.2	0.7682	772.2
0.3213	1029.6	0.8155	655.3
0.3582	1060.9	0.8635	514.3
0.3986	1074.6	0.9095	361.4
0.4242	1075.4	0.9550	197.5
<i>x</i> 2-Ethoxyethanol + (1 - <i>x</i>) <i>n</i> -octane ($T=298.15$ K)			
0.1071	738.2	0.6247	1055.6
0.1572	882.2	0.6723	997.5
0.1921	976.5	0.7350	905.9
0.2514	1031.2	0.7771	829.3
0.2956	1085.3	0.8331	680.9
0.3568	1135.8	0.8704	602.8
0.4563	1138.3	0.9049	457.4
0.4997	1136.8	0.9209	409.7
0.5787	1082.6	0.9539	247.2
<i>x</i> Ethanol + (1 - <i>x</i>) benzene ($T=308.15$ K)			
0.0640	585.2	0.4357	960.4
0.1049	771.4	0.4506	958.1
0.1248	843.6	0.4799	931.6
0.1542	868.2	0.5224	871.7
0.1828	959.1	0.5631	833.2
0.2381	1003.1	0.6023	769.3
0.2908	1013.8	0.6761	640.8
0.3413	1021.8	0.7447	519.7
0.3895	1001.9	0.8084	396.0
0.4357	958.2	0.8678	277.1
<i>x</i> Ethanol + (1 - <i>x</i>) benzene ($T=318.15$ K)			
0.0640	628.5	0.5631	967.4
0.1248	932.7	0.6023	902.5
0.1828	1077.9	0.6761	771.9
0.2381	1134.6	0.7447	629.6
0.2908	1176.6	0.8084	484.1
0.3413	1174.2	0.8678	337.7
0.3895	1160.3	0.9233	185.2
0.4799	1080.9		

it can be seen that our results agree within $\pm 1\%$ with those obtained by different research groups.

The new experimental data for the four binaries at three temperatures are reported in Tables 3–6 and in Figs. 4–7. In Fig. 8 one can see the effect on the excess enthalpy of the type of the hydrocarbon (normal, cyclic, or aromatic) as well as of the number of the carbon atoms in the molecule.

For each of the systems in Tables 3–6, the experimental excess molar enthalpies were fitted with three smoothing functions: the Redlich-Kister type, the Myers-Scott type [7] and the Mrazek-van Ness type [12]. The best fitting was obtained with the Mrazek-van Ness type Eq. (1), the parameters of which are shown in Table 7.

$$H^E = RTx(1-x) \left[A_2x + A_1(1-x) - \frac{B_2B_1x(1-x)}{B_2x + B_1(1-x) + (C_2x + C_1(1-x))x(1-x)} \right] \quad (1)$$

Table 3
Excess enthalpies for the binary *x* 2-ethoxyethanol + (1 - *x*) *n*-hexane

x	H^E (J mol ⁻¹)	x	H^E (J mol ⁻¹)
$T=298.15$ K			
0.0757	607.8	0.6463	944.3
0.1124	723.6	0.6924	873.4
0.1484	805.4	0.7591	797.6
0.2184	933.3	0.8021	708.4
0.2858	1019.8	0.8438	603.0
0.4439	1061.3	0.9044	413.9
0.5989	1005.3	0.9434	267.1
$T=308.15$ K			
0.0802	672.2	0.5322	1170.6
0.1190	800.3	0.5989	1120.7
0.1571	902.2	0.6408	1071.0
0.2309	1034.4	0.6924	1002.5
0.3018	1112.4	0.7591	852.4
0.3626	1184.3	0.8021	772.3
0.4031	1197.4	0.8438	646.0
0.4428	1201.4	0.9044	451.4
0.4996	1186.4	0.9434	297.4
$T=318.15$ K			
0.0757	660.3	0.5500	1219.6
0.1124	804.8	0.5989	1166.2
0.1484	919.7	0.6463	1117.3
0.2184	1071.5	0.6924	1038.5
0.2858	1173.3	0.7591	915.6
0.3508	1231.7	0.8021	791.3
0.4134	1255.9	0.8438	683.5
0.4477	1254.4	0.9044	462.4
0.4738	1253.9	0.9434	303.4
0.4996	1242.9		

Table 4
Excess enthalpies for the binary *x* 2-ethoxyethanol + (1 - *x*) cyclohexane

x	H^E (J mol ⁻¹)	x	H^E (J mol ⁻¹)
$T=308.15$ K			
0.0830	699.6	0.5274	1167.1
0.1363	910.8	0.6237	1074.6
0.1914	1004.5	0.6492	1037.3
0.2173	1040.5	0.7205	919.3
0.2692	1107.4	0.7682	819.3
0.3213	1137.5	0.7700	819.9
0.3986	1186.8	0.8155	716.8
0.4011	1194.1	0.8865	484.4
0.4242	1195.7		
$T=318.15$ K			
0.0634	666.4	0.5523	1287.5
0.1259	938.5	0.6237	1201.9
0.1876	1118.9	0.6481	1155.0
0.2164	1195.6	0.7205	1023.3
0.2692	1258.8	0.7464	959.6
0.3213	1309.7	0.7682	895.8
0.3680	1325.4	0.8155	758.2
0.3986	1331.0	0.8635	605.9
0.4242	1335.5	0.9095	435.7
0.4521	1337.4	0.9550	244.0
0.5249	1306.7		

Table 5
Excess enthalpies for the binary x 2-ethoxyethanol + $(1-x)$ n -octane

x	H^E (J mol ⁻¹)	x	H^E (J mol ⁻¹)
$T=308.15$ K			
0.0654	648.0	0.6247	1240.8
0.1274	915.1	0.6723	1139.5
0.1934	1098.1	0.6754	1149.1
0.2171	1141.3	0.6893	1126.0
0.2626	1210.2	0.7351	1043.9
0.3223	1280.3	0.7690	955.2
0.3568	1304.6	0.8062	870.3
0.3997	1310.7	0.8332	790.8
0.4542	1320.0	0.8535	711.5
0.4997	1323.3	0.9210	471.7
0.5711	1284.9	0.9539	286.3
$T=318.15$ K			
0.1071	1039.4	0.6247	1370.4
0.1722	1192.1	0.6893	1256.2
0.2257	1309.0	0.7351	1147.3
0.3223	1435.7	0.7690	1066.3
0.3568	1475.2	0.7966	984.3
0.3997	1492.8	0.8062	949.7
0.4542	1486.3	0.8535	790.0
0.4997	1486.3	0.9300	462.2
0.5552	1445.2	0.9696	216.6
0.5711	1425.0		

In Table 7 is also shown the standard deviation $\sigma_d = [\sum(H_{\text{calc}}^E - H_{\text{exp}}^E)^2 / (n - p)]^{1/2}$, where, n is the number of experimental values and p is the number of parameters.

As observed, the H^E values of all studied mixtures are positive over the whole concentration range and increase with increasing temperature. The shapes of the curves for the binaries of 2-ethoxyethanol with n -hexane, cyclohexane, and n -octane are similar, while the shape and the maximum value of H^E for the binary with benzene is quite different but in agreement with Ref. [7] as is shown in Fig. 7. These shapes are the outcome of the interplay of various factors, such as the breakage

Table 6
Excess enthalpies for the binary x 2-ethoxyethanol + $(1-x)$ benzene

x	H^E (J mol ⁻¹)	x	H^E (J mol ⁻¹)
$T=308.15$ K			
0.0263	223.7	0.3551	584.3
0.0693	421.8	0.4042	554.7
0.0792	446.9	0.4786	491.2
0.1159	528.2	0.5503	424.3
0.1327	559.2	0.6047	368.1
0.1630	592.0	0.6669	303.3
0.1866	614.0	0.7336	232.6
0.2104	623.6	0.7859	179.9
0.2411	630.3	0.8653	106.5
0.2961	622.6	0.9188	64.7
$T=318.15$ K			
0.0307	249.5	0.4786	553.5
0.0615	406.9	0.5539	475.0
0.1237	581.9	0.6047	419.6
0.1866	639.2	0.6559	361.3
0.2502	671.9	0.7336	270.2
0.3065	662.2	0.7859	218.1
0.3551	645.4	0.8653	130.2
0.4042	616.3	0.9188	79.5

of hydrogen bonds, the occurrence of σ - π hydroxyl-aromatic ring interactions and even the endothermic breakage of liquid-crystal-like structures (orientation order of alkane mixtures [16]).

4. The non-random hydrogen bonding (NRHB) model

In this section we will briefly present the essentials of an equation-of-state model, which will be used for correlating our experimental data. The details of the model can be found in our previous publications [11,14,15]. It is based on the lattice-fluid rationale [11,17], on the quasi-chemical approach [14,18], it incorporates a number of molecular features that augment its capacity, and is referred to as NRHB (non-random hydrogen bonding) model [15].

Table 7
The coefficients of Eq. (1) and standard deviations

T (K)	A_1	A_2	B_1	B_2	C_1	C_2	σ_d J mol ⁻¹
2-Ethoxyethanol + n -hexane							
298.15	17.1848	2.1741	17.755	1485.229	255.2	344.22	2.8
308.15	6.5070	2.3760	9.005	66.406	36.18	125.56	1.9
318.15	6.6856	2.2418	7.094	91.268	37.37	70.87	1.2
2-Ethoxyethanol + cyclohexane							
298.15	7.3375	1.8735	6.4161	139.215	17.54	20.8	1.7
308.15	5.3399	2.1869	7.0774	24.153	1.59	51.5	2.1
318.15	6.8428	2.0565	5.7745	72.348	11.18	16.6	2.1
2-Ethoxyethanol + n -octane							
298.15	5.0967	2.5328	7.298	29.986	24.36	46.59	2.7
308.15	5.9410	2.8916	10.543	37.576	36.90	107.42	2.1
318.15	13.7069	2.9412	16.169	328.308	88.79	280.05	1.7
2-Ethoxyethanol + benzene							
308.15	4.5321	0.2542	3.473	56.387	5.24	-8.40	0.7
318.15	3.8909	0.4038	3.715	24.229	2.19	20.26	1.0

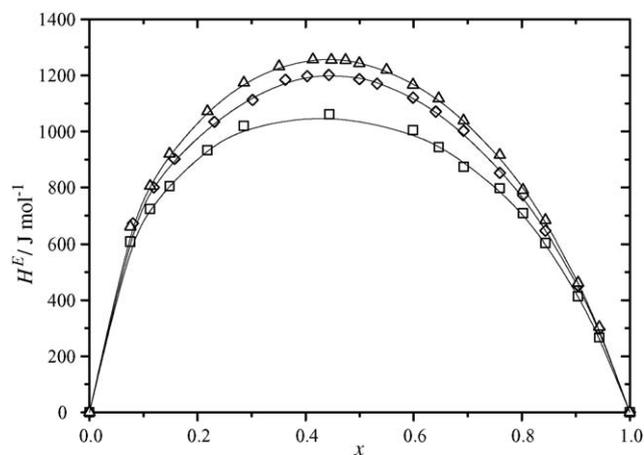


Fig. 4. Excess molar enthalpies, H^E , of the binary x 2-ethoxyethanol + $(1-x)$ n -hexane at $T=298.15$ K, (\square); 308.15 K, (\diamond); 318.15 , (\triangle); (—), Eq. (1) (parameters in Table 7).

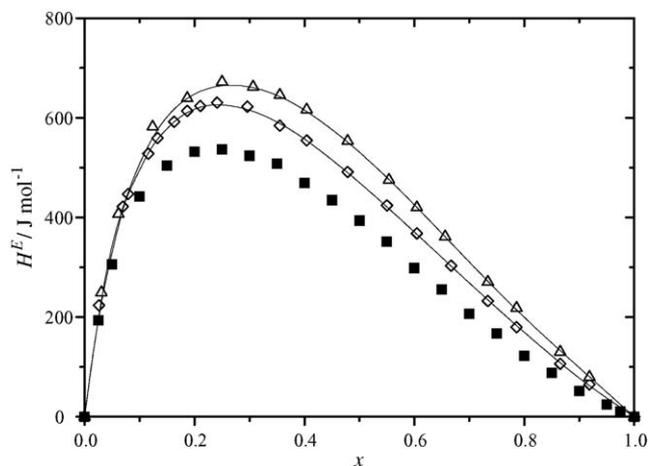


Fig. 7. Excess molar enthalpies, H^E , of the binary x 2-ethoxyethanol + $(1-x)$ benzene; reference at $T=298.15$ K [7], (\blacksquare); ours at 308.15 K, (\diamond); at 318.15 K, (\triangle); (—), Eq. (1) with parameters in Table 7.

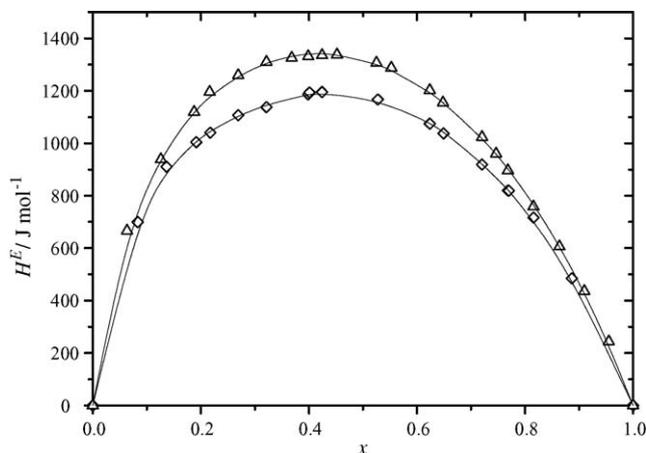


Fig. 5. Excess molar enthalpies, H^E , of the binary x 2-ethoxyethanol + $(1-x)$ cyclohexane at $T=308.15$ K, (\diamond); 318.15 , (\triangle); (—), Eq. (1) with parameters in Table 7.

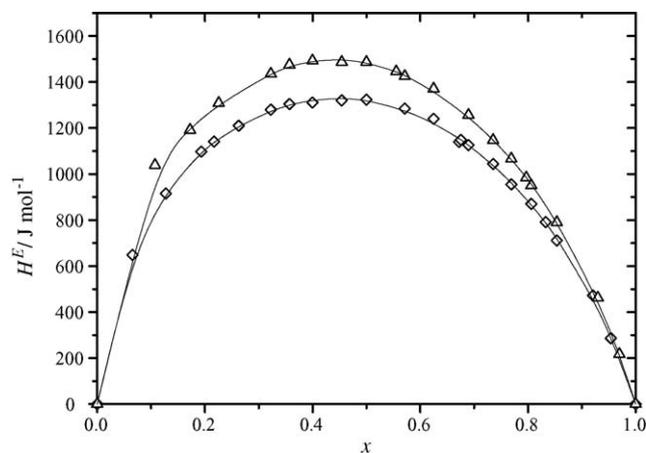


Fig. 6. Excess molar enthalpies, H^E , of the binary x 2-ethoxyethanol + $(1-x)$ n -octane at $T=308.15$ K, (\diamond); 318.15 , (\triangle); (—), Eq. (1) with parameters in Table 7.

4.1. The formalism of the model

Let us consider a system of N molecules consisting of N_1 molecules of an associating component (2-ethoxyethanol, in our case) and N_2 molecules of an inert solvent ($N=N_1+N_2$) at a temperature T , total volume V , and an external pressure P , which are assumed to be arranged on a quasi-lattice of coordination number z and of N_r sites, N_0 of which are empty. Each molecule of type i is assumed to be divided in r_i segments of segmental volumes v_i^* . The total number N_r of lattice sites is given by

$$N_r = rN + N_0 \quad (2)$$

The average interaction energy per molecular segment is given by

$$\varepsilon_i^* = \frac{z}{2} \varepsilon_i \quad (3)$$

where ε_i is the interaction energy per segment – segment contact.

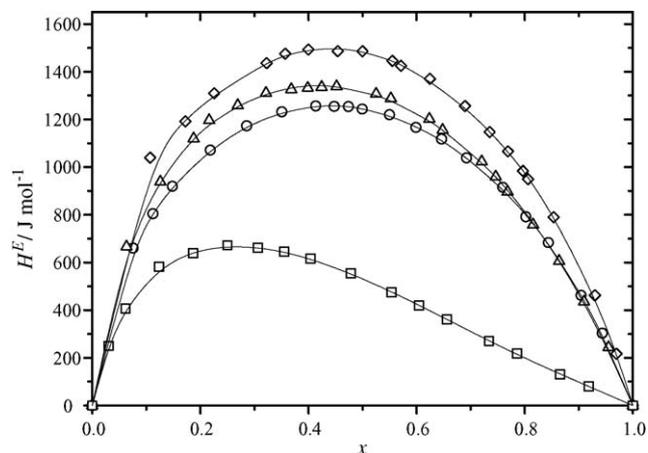


Fig. 8. Excess molar enthalpies, H^E , at $T=318.15$ K of the binaries: x 2-ethoxyethanol + $(1-x)$ benzene, (\square); + $(1-x)$ n -hexane, (\circ); + $(1-x)$ cyclohexane, (\triangle); + $(1-x)$ n -octane, (\diamond); (—), Eq. (1) with parameters in Table 7.

Each molecule i has $zq_i = zs_i r_i$ external intermolecular contacts, where s_i is the average number of contacts per segment – a surface-to-volume ratio characteristic of the molecule.

The average segmental interaction energy for a binary mixture is given by

$$\varepsilon^* = P^* v^* = RT^* = \theta_1^2 \varepsilon_1^* + \theta_2^2 \varepsilon_2^* + 2\theta_1 \theta_2 \varepsilon_{12}^* \quad (4)$$

where a Berthelot-type combining rule is adopted for the cross term

$$\varepsilon_{12}^* = \xi_{12} \sqrt{\varepsilon_1^* \varepsilon_2^*} \quad (5)$$

The average segmental volume is given by

$$v^* = \varphi_1^2 v_1^* + 2\varphi_1 \varphi_2 v_{12}^* + \varphi_2^2 v_2^* \quad (6)$$

where

$$v_{12}^* = \zeta_{12} \left(\frac{v_1^{*1/3} + v_2^{*1/3}}{2} \right)^3 \quad (7)$$

The dimensionless parameters ξ_{12} and ζ_{12} are adjustable binary parameters with values close to unity.

The site or volume fractions φ_i , and the surface fractions θ_i are defined as follows:

$$\varphi_i = \frac{r_i N_i}{\sum_k r_k N_k} = \frac{r_i N_i}{rN} = \frac{x_i r_i}{r} \quad (8)$$

and

$$\theta_i = \frac{q_i N_i}{\sum_k q_k N_k} = \frac{q_i N_i}{qN} = \frac{\varphi_i s_i}{\sum_k \varphi_k s_k} = \frac{\varphi_i s_i}{s} \quad (9)$$

x_i being the mole fraction of component i in the mixture.

The full partition function Q of our system in the N, P, T ensemble is factorized into a combinatorial term for the random distribution of the empty sites, Ω_R , according to the generalized expression of Staverman [19], a correction factor for the actual non-random distribution of the empty sites, Ω_{NR} , according to Guggenheim's quasi-chemical theory [18] and the classical exponential enthalpic term [15]

$$Q(N, P, T) = \Omega_R \Omega_{NR} \exp\left(-\frac{E + PV}{RT}\right) \quad (10)$$

The Gibbs free energy of the system is obtained from the partition function as follows:

$$G = -RT \ln Q \quad (11)$$

By minimizing this equation with respect to the reduced density, defined as $\tilde{\rho} = \rho/\rho^* = \rho v_{sp}^* = 1/\tilde{v} = V^*/V$, we obtain the equation of state (EoS):

$$\tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) - \tilde{\rho} \left(\sum_i \varphi_i \frac{l_i}{r_i} - \nu_H \right) - \frac{z}{2} \ln \left(1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right) + \frac{z}{2} \ln \Gamma_{00} \right] = 0 \quad (12)$$

where \tilde{P} and \tilde{T} are the reduced pressure ($\tilde{P} = P/P^*$) and temperature ($\tilde{T} = T/T^*$) of the system.

The rest of the symbols in the EoS are defined as follows: the Staverman [19] parameter l_i

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad (13)$$

ν_H is the average number of hydrogen bonds per segment (defined below) and the Γ 's are factors for the non-random distribution of empty sites around an empty site (Γ_{00}), for the distribution of molecular segments around a central molecular segment (Γ_{rr}), and for the distribution of a molecular segment around an empty site (Γ_{r0}). These non-randomness factors are obtained through Guggenheim's quasi-chemical condition [18,14] and are given by

$$\Theta_0 \Gamma_{00} + \Theta_r \Gamma_{r0} = 1, \quad \Theta_r \Gamma_{rr} + \Theta_0 \Gamma_{r0} = 1 \quad (14)$$

and

$$\Gamma_{r0} = \frac{2}{1 + [1 - 4\Theta_0 \Theta_r (1 - A)]^{1/2}} \quad (15)$$

where A is given by the equation

$$A = \frac{4\Gamma_{rr}\Gamma_{00}}{\Gamma_{r0}^2} = \exp\left(\frac{2\varepsilon^*/z}{RT}\right) \quad (16)$$

and

$$\Theta_r = 1 - \Theta_0 = \frac{q/r}{q/r + \tilde{v} - 1} \quad (17)$$

Let us now define the number of different hydrogen bonds in which participates the associated component. In the general case of alkoxy-alkanols, if y is the number of ether oxygen acceptor sites, the number of proton donors and acceptors of type 1 (–OH) is N_1 and of proton acceptors of type 2 (–O–) is yN_1 . As previously [9,10], y is assumed to be equal to 2 and the ether oxygen is able to bond both inter- and intra-molecularly. Let there be N_{11} intermolecular hydrogen bonds OH–OH, N_{12} intermolecular bonds OH–O–, and B intra-molecular bonds OH–O– in the system. As a consequence, the total number of free proton donors is

$$N_{10} = N_1 - N_{11} - N_{12} - B \quad (18)$$

The free energy change upon formation of the i – j bond can be resolved into its components as following:

$$G^{\circ}_{ij} = E^{\circ}_{ij} + PV^{\circ}_{ij} - TS^{\circ}_{ij} \quad (19)$$

E°_{ij} , S°_{ij} , V°_{ij} being the energy, volume, and entropy change, respectively, upon formation of the i – j bond.

From free energy minimization with respect to the unknowns N_{11} , N_{12} , and B , we obtain the following coupled equations:

$$\frac{B(yN_1 - B)}{(yN_1 - B - N_{12})N_{10}y} = c \exp\left(-\frac{G^{\circ}_B}{kT}\right) = K_B \quad (20)$$

$$\frac{N_{11}}{(N_1 - N_{11})N_{10}} = \frac{\tilde{\rho}}{rN} \exp\left(-\frac{G^{\circ}_{11}}{kT}\right) = \frac{K_{11}}{N} \quad (21)$$

$$\frac{N_{12}}{(yN_1 - B - N_{12})N_{10}} = \frac{\tilde{\rho}}{rN} \exp\left(-\frac{G^{\circ}_{12}}{kT}\right) = \frac{K_{12}}{N} \quad (22)$$

Table 8
Scaling constants for pure fluids [15]

Fluid	$\varepsilon^* = RT^*$ (J mol ⁻¹)	$v^* = \varepsilon^* P^{*-1}$ (cm ³ mol ⁻¹)	$v_{sp}^* = \rho^{*-1}$ (cm ³ g ⁻¹)	$s = q/r$
2-Ethoxyethanol	4837.4	11.731	1.002	0.938
<i>n</i> -Hexane	4557	13.57	1.317	0.857
<i>n</i> -Octane	4870	14.45	1.283	0.844
Cyclohexane	5171	13.040	1.205	0.800
Benzene	5026	9.217	1.075	0.753

The coupled Eqs. (20)–(22) must be solved simultaneously by an appropriate iteration scheme. After some algebra the above three equations lead to the following equations:

$$N_{12} = \frac{K_{12}}{K_B N y} B (y N_1 - B) \quad (23)$$

$$N_{11} = \frac{K_{11}}{K_B N y + B(K_{11} - K_{12})} B N_1 \quad (24)$$

$$B = \frac{(N y K_B - K_{12} B)}{N} \left[N_1 - B - B \frac{K_{12}}{y K_B} \frac{y N_1 - B}{N} - N_1 \frac{K_{11} B}{y N K_B + B(K_{11} - K_{12})} \right] \quad (25)$$

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. (23) and (24) in order to obtain N_{12} and N_{11} , respectively.

Having obtained the numbers of hydrogen bonds in the system, the average number of hydrogen bonds per segment, ν_H , can be calculated by the following form:

$$\nu_H = \frac{N_H}{rN} = \frac{N_{11} + N_{12}}{rN} \quad (26)$$

The equation for the heat of mixing of the binary system, H^E , that takes into account the contribution of the van der Waals interactions as well as the inter- and intra-molecular hydrogen bonds, is

$$H^E = x_1 q_1 \Theta_{r1} \varepsilon_1^* + x_2 q_2 \Theta_{r2} \varepsilon_2^* - q \Theta_r \varepsilon^* + N_{11} E_{11}^\circ + N_{12} E_{12}^\circ + B E_B^\circ - x_1 (N_{11}^\circ E_{11}^\circ + N_{12}^\circ E_{12}^\circ + B^\circ E_B^\circ) \quad (27)$$

It is essential to point out that the NRHB model (as most of the analogous and widely used models of fluids) divides the intermolecular forces into physical or van der Waals and chemical or hydrogen bonding ones. The physical forces encompass the London or dispersion forces and the polar forces. In what follows they will be collectively referred to as van der Waals or dispersive forces. In other words, we will not further discriminate between dispersion and polar interactions.

4.2. Application of the model to the experimental data

In order to apply the model to the experimental data reported in Tables 3–6, we need the scaling constants ε^* , v^* , v_{sp}^* , and the geometric constant, s , for the pure components. In addition,

Table 9
Hydrogen bonding parameters [9,10]

Interaction	E° (J mol ⁻¹)	S° (J K ⁻¹ mol ⁻¹)	V° (cm ³ 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

we need the hydrogen bonding constants E° , S° , V° for each of the three types of hydrogen bonds. For simplicity, we neglect the volume changes upon hydrogen bond formation so, we set $V^\circ = 0$.

The characteristic constants of pure substances are already known [15] and are reported in Table 8. The hydrogen bonding parameters are also known [9,10] and are reported in Table 9. All calculations reported in this paper are done with these parameters.

The NRHB model permits the calculation of the separate contributions to the heat of mixing, namely, from non-hydrogen bonding (dispersion and polar) interactions, from intermolecular, as well as from intra-molecular hydrogen bonds. The calculated heats of mixing are compared with the experimental ones in Figs. 9–14.

5. Discussion

The experimental measurements as well as the theoretical calculations indicate that the heats of mixing for the four

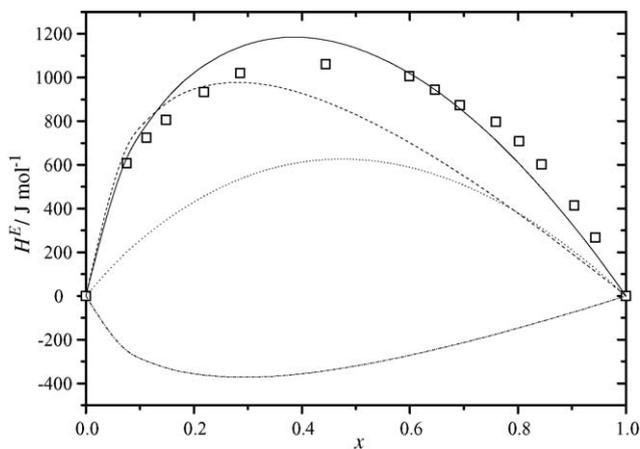


Fig. 9. Experimental, (\square), and calculated, (—), heats of mixing for the system x 2-ethoxyethanol + $(1-x)$ *n*-hexane at 298.15 K. The contributions from intermolecular hydrogen bonds (dash, - - -), dispersive interactions (dot, ···), and intra-molecular hydrogen bonds (dash dot, - · - ·) are shown by separate lines.

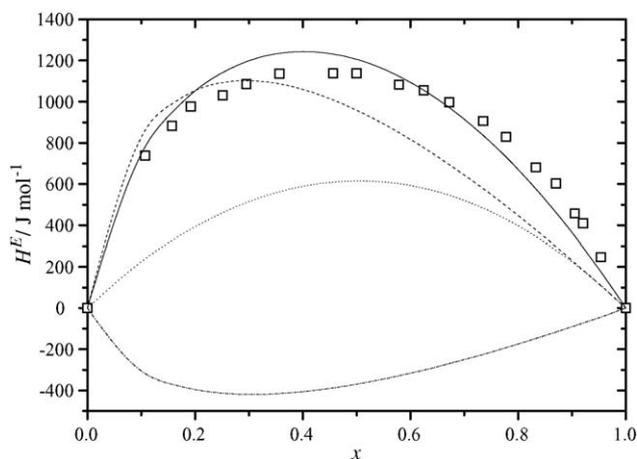


Fig. 10. Experimental, (\square), and calculated, (—), heats of mixing for the system x 2-ethoxyethanol + $(1-x)$ n -octane at 298.15 K. The contributions from intermolecular hydrogen bonds (dash, ---), dispersive interactions (dot, ···), and intra-molecular hydrogen bonds (dash dot, -·-·-) are shown by separate lines.

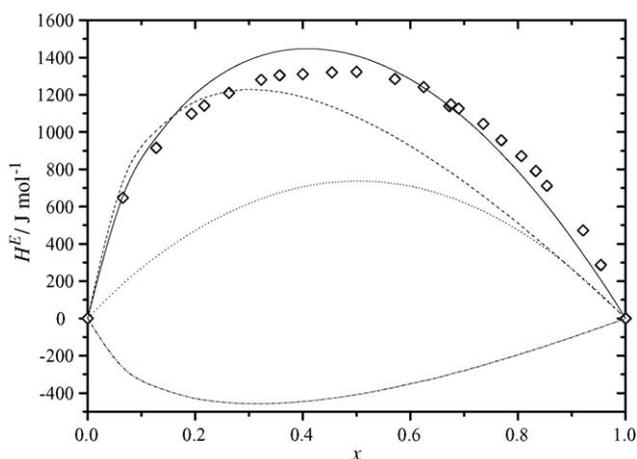


Fig. 11. Experimental, (\diamond), and calculated, (—), heats of mixing for the system x 2-ethoxyethanol + $(1-x)$ n -octane at 308.15 K. The contributions from intermolecular hydrogen bonds (dash, ---), dispersive interactions (dot, ···), and intra-molecular hydrogen bonds (dash dot, -·-·-) are shown by separate lines.

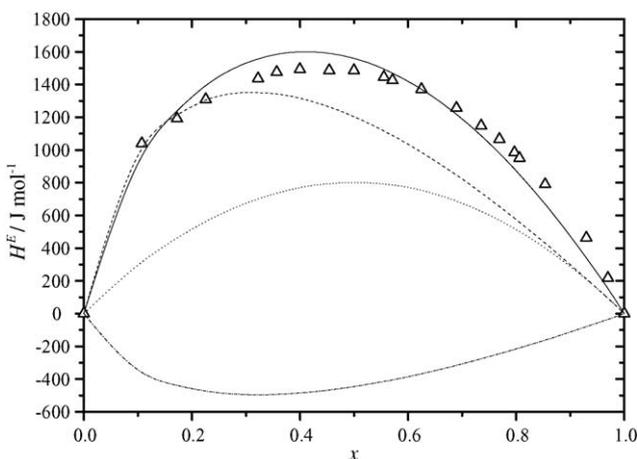


Fig. 12. Experimental, (\triangle), and calculated, (—), heats of mixing for the system x 2-ethoxyethanol + $(1-x)$ n -octane at 318.15 K. The contributions from intermolecular hydrogen bonds (dash, ---), dispersive interactions (dot, ···), and intra-molecular hydrogen bonds (dash dot, -·-·-) are shown by separate lines.

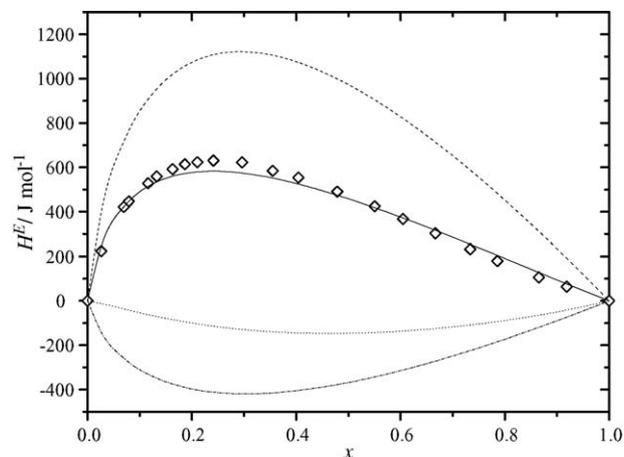


Fig. 13. Experimental, (\diamond), and calculated, (—), heats of mixing for the system x 2-ethoxyethanol + $(1-x)$ benzene at 308.15 K. The contributions from intermolecular hydrogen bonds (dash, ---), dispersive interactions (dot, ···), and intra-molecular hydrogen bonds (dash dot, -·-·-) are shown by separate lines.

binary mixtures studied in this work are positive (endothermic) over the full composition range and at the studied temperature range. In addition, the H^E values of all studied mixtures increase with increasing temperature. This endothermic process was rather expected and could be explained on the basis of the breaking of intermolecular hydrogen bonds upon mixing of 2-ethoxyethanol with the inert solvents and the weakening of the dipole–dipole interactions. The higher H^E values are exhibited by the binary with n -octane. This is attributed to the bigger size of n -octane, resulting in more extensive breaking of the above interactions between the molecules of 2-ethoxyethanol and also to the endothermic breakage of its liquid-crystal-like orientation order of n -alkane mixtures [16].

Interestingly, the behaviour of the binary with benzene is different in two points: the maximum and the shape of the H^E curve. The maximum value is about half the values of the systems with the other three hydrocarbons. The decreased maximum

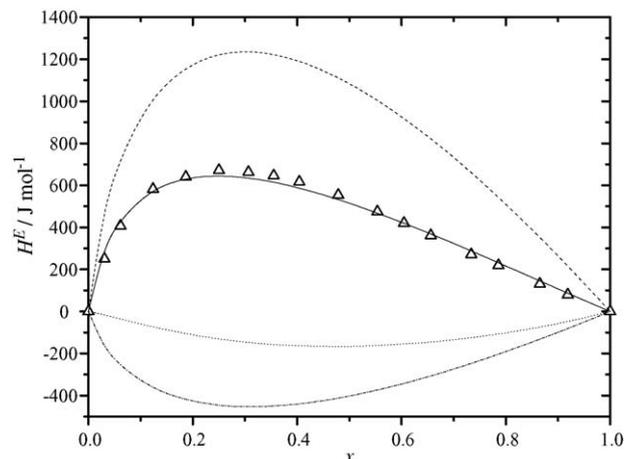


Fig. 14. Experimental, (\triangle), and calculated, (—), heats of mixing for the system x 2-ethoxyethanol + $(1-x)$ benzene at 318.15 K. The contributions from intermolecular hydrogen bonds (dash, ---), dispersive interactions (dot, ···), and intra-molecular hydrogen bonds (dash dot, -·-·-) are shown by separate lines.

value for the benzene system could be explained on the basis of the occurrence of σ – π hydroxyl–aromatic ring interactions (exothermic process). The asymmetric shape of the H^E curve could be explained by the difficulty of breaking the interactions in the 2-ethoxyethanol – rich region: in this region, the low presence of benzene fails to break the interactions of the pure 2-ethoxyethanol, while in the benzene-rich region the breakage of the intermolecular hydrogen bonding is rather extensive. The above results are in agreement with the findings of other researchers [7].

The application of the NRHB model [15] brings up interesting features as shown in Figs. 9–14. The model is able to calculate the separate contribution of each type of intermolecular interactions. As observed, the contribution of the intra-molecular hydrogen bonds to the heats of mixing of the studied systems is by no means negligible. The important point is that its contribution is negative (exothermic). An explanation of this negative contribution comes from our previously published spectroscopic data [9], and from literature [13] which indicated that at low concentration, the degree of intra-molecular hydrogen bonding is increasing with increasing mole fraction of 2-ethoxyethanol much more than the degree of intermolecular hydrogen bonding. The degrees of hydrogen bonding, calculated by our model over the full composition range for a representative binary system of 2-ethoxyethanol with a non-polar solvent, are shown in Fig. 15. As observed, there is a positive deviation from linearity for the intra-molecular hydrogen bonding. This excess of intra-molecular bonds at low mole fraction of 2-ethoxyethanol is responsible for the negative contribution to the heat of mixing since the formation of an intra-molecular bond is an exothermic process (negative E°_B).

It is also known that, at the low concentration region, the inert solvent does not influence essentially the intra-molecular hydrogen bonds, while it causes the destruction of the intermolecular bonds, as the interacting molecules fail to come close together (proximity condition).

At this point of our discussion, it is interesting to add and combine our findings regarding the Kirkwood correlation factor

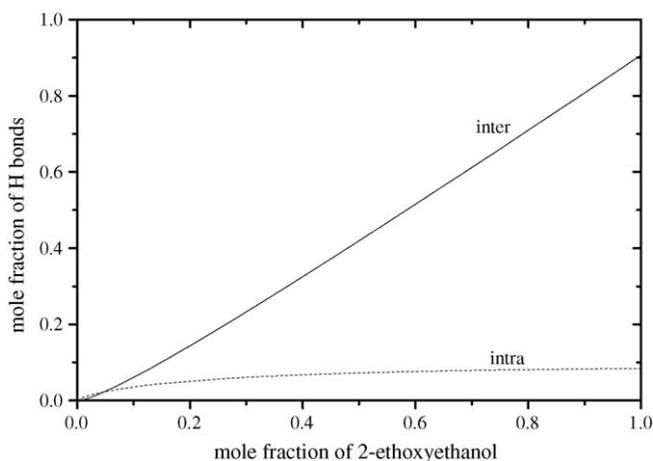


Fig. 15. The calculated degree of intermolecular (—), and intra-molecular (---), hydrogen bonding in the mixture 2-ethoxyethanol + *n*-hexane at 25 °C over the full composition range.

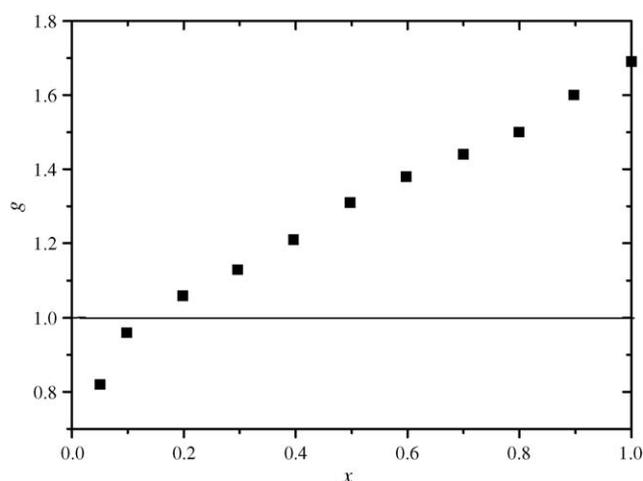


Fig. 16. Variation of the Kirkwood correlation factor, g , with the mole fraction, x , of the mixture x 2-ethoxyethanol + $(1 - x)$ *n*-hexane at 298.15 K.

for the same systems. The Kirkwood correlation factor, g , from the experimental data of the density ρ , and the relative permittivity ε , for solutions of an associated compound (subscript 1) in a non-polar solvent (subscript 2) is calculated according to the following equation [20]:

$$g\mu^2 = \frac{9kT(2\varepsilon + \varepsilon_\infty)^2}{4\pi N_A x_1 (\varepsilon_\infty + 2)^2 (2\varepsilon + 1)} \times \left[\frac{\varphi(\varepsilon - 1)}{\varepsilon} - \frac{3x_2 M_2 (\varepsilon_2 - 1)}{(2\varepsilon + \varepsilon_2)\rho_2} - \frac{3x_1 M_1 (\varepsilon_\infty - 1)}{(2\varepsilon + \varepsilon_\infty)\rho_1} \right] \quad (28)$$

where μ is the dipole moment of the polar component, ρ and ε the density and the relative permittivity, respectively, M the molar mass, k Boltzman's constant, N_A Avogadro's number, and x_i is the mole fraction of component i in the mixture. In this equation $\varphi = (x_1 M_1 + x_2 M_2)/\rho$ denotes the molar volume of the mixture and $\varepsilon_\infty = n_D^2$ is the relative permittivity for the induced polarization and n_D the refractive index (the Maxwell relation).

According to the Kirkwood-Froehlich theory [20], for the systems in which the specific intermolecular interactions cause alignment of neighbouring dipoles in a parallel fashion or there is a predominance of multimers with large dipole moments, g is greater than unity, whereas the antiparallel alignment or the predominance of multimers with small dipole moments leads to g values less than unity. A value of g equal to one is expected when orientation ordering is absent, or, the effects of the two kinds of multimers cancel out. The parallel orientation (high dipole moment) favours the short range interactions, the linear multimers, and the intermolecular hydrogen bonds, while the antiparallel alignment (small dipole moment) results in multimers generally considered being cyclic. The intra-molecular hydrogen bonds lead, of course, to such cyclic structures.

As can be seen in Fig. 16, g is greater than unity at mole fractions of 2-ethoxyethanol greater than ca. 0.1. As already mentioned, in this range of mole fractions the O–H begins to bond intermolecularly and the mole fraction of intermolecular hydrogen bonds becomes greater than the mole fraction of intra-

molecular ones. From that point, the number of intermolecular hydrogen bonds is increasing rapidly with concentration according to Fig. 15. In other words, at mole fraction of 2-ethoxyethanol less than 0.1, g is less than unity, the orientation of the dipoles is antiparallel, the formation of intermolecular hydrogen bonding is not favoured and there is an excess of intra-molecular bonds. Thus, the experimental data of the excess enthalpy of mixing, the g factor of the Kirkwood-Frohlich theory [20], and the calculations of the NRHB model [15] give a rather clear picture of the molecular interactions of the studied systems of 2-ethoxyethanol.

The prediction of the NRHB model for the contribution of intermolecular hydrogen bonding is positive for all four binaries, while the contribution of the van der Waals interactions are negative (exothermic) for the system with benzene but positive (endothermic) for the other three hydrocarbons, which corroborates the above established picture. In binary mixtures of benzene with ethers there are no hydrogen bonding interactions. It is worth pointing out that the enthalpies of mixing for these binaries are negative. Typical examples are the mixtures of 1,4-dioxane with benzene at different temperatures [21] and of 1,2-dimethoxyethane (an isomer to 2-ethoxyethanol) with benzene [22,23]. The latter experimental data are compared with the predictions of the NRHB model for the system x 2-ethoxyethanol + $(1-x)$ benzene in Fig. 17 and as is shown, the experimental values for the binary with 1,2-dimethoxyethane coincide with the calculated contribution of the dispersive (non-hydrogen bonding) interactions. From literature data we also see positive enthalpies of mixing in binaries of n -alkanes or cycloalkanes with ethers. Typical examples are the mixtures of n -hexane or cyclohexane with 1,2-dimethoxyethane [24].

Before judging the overall performance of the NRHB model, it is useful to compare its calculations for the binary mixture of 2-ethoxyethanol + n -octane at 298.15 K with the corresponding calculations by two group contribution models reported in Ref.

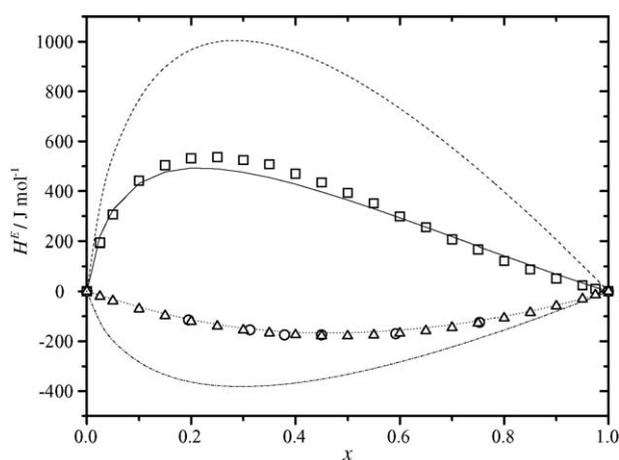


Fig. 17. Comparison of the experimental [7] excess molar enthalpies, H^E , at 298.15 K for the system x 2-ethoxyethanol + $(1-x)$ benzene, (\square), with the predictions of the NRHB model for the contributions from intermolecular hydrogen bonds (---), dispersive interactions (\cdots), intra-molecular hydrogen bonds (-·-·-) and the total H^E (—). The contribution of dispersive interactions is compared with the experimental H^E for the system x 1,2-dimethoxyethane + $(1-x)$ benzene: (\circ), data from Ref. [22]; (\triangle), data from Ref. [23].

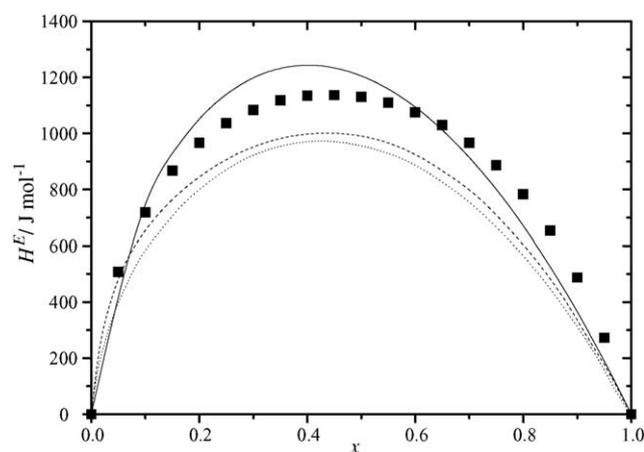


Fig. 18. Excess molar enthalpies, H^E , at 298.15 K for the system x 2-ethoxyethanol + $(1-x)$ n -octane. Comparison of the experimental data [7] (\blacksquare), with the calculated ones by three models: UNIFAC[26] (---), DISQUAC[27] (\cdots), and NRHB (—).

[25]. In Fig. 18 a comparison is made of the experimental data from Ref. [7] and the calculations with UNIFAC [26], DISQUAC [27] and NRHB. Tamura et al. [25] have applied the first two models to these experimental data and have observed a similar behaviour of both models, the UNIFAC being slightly superior. As shown in Fig. 18, NRHB is at least as good as UNIFAC. The significant advantage, of course, of NRHB over UNIFAC and DISQUAC is its capacity to calculate the separate contributions of the molecular interactions to the overall enthalpy of mixing.

The NRHB model reproduces the shape, the symmetry and the values of the H^E curve for the 2-ethoxyethanol + benzene binary very well. It is essential to keep in mind that one single set of binary parameters is used in all systems and for all calculated thermodynamic properties. The very same hydrogen bonding parameters obtained from the spectroscopic measurements [9] and used previously to correlate phase compositions and saturated densities [10] are also used in the present work in order to estimate the heats of mixing. In view of this, the ability of the model to describe the diverse properties of these systems is rather satisfactory.

The parameters in Tables 8 and 9 were used for predicting the effect of temperature on the heats of mixing in alkoxyethanol + hydrocarbon systems. It is found that the heat of mixing increases as the temperature increases, as expected since there is a drastic decrease of the number of intermolecular hydrogen bonds with temperature which, according to the model, is due to the relatively large entropy change upon formation of these bonds.

6. Conclusions

The main conclusions of this work could be summarized as follows:

1. New experimental data are reported for the heat of mixing of 2-ethoxyethanol with four hydrocarbons at 298.15, 308.15

and 318.15 K, measured with a flow calorimeter, and for the Kirkwood correlation factor, g , of 2-ethoxyethanol + n -hexane at 298.15 K.

- The hydrogen bonding parameters, obtained previously from the spectroscopic measurements [9] and applied successfully on the VLE data of the 2-ethoxyethanol + CO₂ mixture [10], correlate satisfactorily the H^E data of the 2-ethoxyethanol + hydrocarbon systems. The contribution of intra-molecular hydrogen bonding to the key thermodynamic properties is in no way negligible.
- The thermodynamic properties of 2-ethoxyethanol + hydrocarbon mixtures are dictated by the interplay of dispersive forces, intermolecular and intra-molecular hydrogen bonding. The contribution of the intermolecular hydrogen bonds to the heat of mixing is endothermic, while that of intra-molecular bonds is exothermic.
- The experimental data of the heats of mixing and the Kirkwood correlation factor combined with our previous data on the vapor–liquid equilibrium compositions, the densities of the phases at equilibrium, and spectroscopic (IR) measurements, and the application of the NRHB model [15] give a fairly clear picture of the molecular interactions in the 2-ethoxyethanol + inert solvent mixtures.

List of symbols

A, B, C	parameters of fitting Eq. (1)
B	number of intra-molecular hydrogen bonds of type 1-2
E	energy
g	Kirkwood correlation factor
G	Gibbs energy
H	enthalpy
k	Boltzman's constant
K	parameters defined by Eqs. (20–22), equilibrium constants
l	Staverman's parameter
M	molar mass
n	number of experimental points
n_D	refractive index
N	number of molecules
N_r	total number of lattice sites
N_A	Avogadro's number
N_0	number of empty lattice sites
N_{10}	number of free proton donors
N_{11}, N_{12}	number of type 1-1 and 1-2 intermolecular hydrogen bonds
p	number of parameters
P	pressure
q	external intermolecular contacts
Q	partition function
r	number of segments per molecule
R	gas constant
s	surface-to-volume fraction, average number of contacts per segment
S	entropy
T	temperature
v	average segmental volume
V	volume

x	mole fraction of 2-ethoxyethanol
y	number of –O– sites
z	lattice coordination number

Greek letters

Γ	non-random factor
ε	interaction energy, relative permittivity
ζ, ξ	adjustable binary interaction parameter
θ	hole-free surface (contact) fraction
Θ	surface fraction
μ	dipole moment
ν_H	average per segment number of hydrogen bonds
ρ	density
σ	standard deviation
φ	segment fraction, molar volume

Subscripts

H	hydrogen bond
i	component of type i
o	property pertinent to holes
r	property pertinent to molecular segments
R, NR	random, nonrandom distribution
sp	specific

Superscripts

E	excess property
\sim	reduced quantity
*	scaling constant

Acknowledgments

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