J. Chem. Eng. Data **2006,** *51,* 599−603

Excess Molar Enthalpies and Hydrogen Bonding in Binary Mixtures Containing Ethers and Benzyl Alcohol at 308.15 K and Atmospheric Pressure

Carlo Castellari*

Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, Via Selmi 2, I-40 126 Bologna, Italy

---

Excess molar enthalpies, H_m^E, of binary liquid mixtures containing dibutyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol ethyl ether, diethylene glycol diethyl ether, or triethylene glycol monoethyl ether + benzyl alcohol have been measured over the entire range of composition at 308.15 K and at atmospheric pressure using a flow microcalorimeter. Data were fitted to the Redlich−Kister equation. The results show how the enthalpy of mixing is influenced by both the steric and electronic characteristic of the terminal groups that belong to the OP = [CH_2OCH_2] central unit of the ether and by the hydrogen bonding.

Introduction

The calorimetric enthalpy of mixing is strongly influenced by the hydrogen bonding of the components, and accurate measurements of excess molar enthalpy are required for a full understanding of the thermodynamic behavior of liquid mixtures with interacting components. As an example, experimental data of excess enthalpies are used to check the goodness of the spectroscopic estimates of the total enthalpies of hydrogen bonding present in the solution.[1]

In previous papers,[2−4] the excess molar enthalpies, H_m^E, of binary mixtures containing $R-[OP]_p-R'$, where OP is the repeating unit CH_2OCH_2 and $R = R' = CH_2OH$, + three aryl alcohols $Ph-(CH_2)_n-OH$, with $n = 1, 2, 3$, have been determined at 308 K. As a continuation of the research, in this article excess enthalpies of binary mixtures formed by an ether (component 1) such as dibutyl ether, ethylene glycol monoethyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, diethylene glycol ethyl ether, diethylene glycol diethyl ether, triethylene glycol monoethyl ether + benzyl alcohol (component 2) are determined at 308 K and over the whole range of composition. The molecular structure of these compounds can be represented by the formula $R-[OP]_p-R'$ (Table 1) with $OP = CH_2OCH_2$. It is thus possible to compare between the H_m^E obtained by mixing ethers with the same number p of repeating units and different end chains, and benzyl alcohol.

Glycol ethers are used in the cleaning of exhaust air and gas streams from industrial plants because of both their H-bonding power and their favorable properties (low vapor pressure, low toxicity, low viscosity, and chemical stability). Because process design using this method requires accurate thermodynamical property data, the aim of this work is to study the influence of both conformational and electronic characteristics of the terminal groups R, R′ present in the ether on the H_m^E of the mixtures.

Experimental Section

Chemicals. The sources and the purities declared by the manufacturer are reported in Table 1. The products having a mass fraction of the chemical ≥99 % were used without further treatment. Triethylene glycol monoethyl ether was purified by vacuum distillation. Before use, the substances were kept over freshly activated molecular sieves (Union Carbide type 4A) and degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy).

Densities. The densities of pure compounds ρ were determined experimentally at 308.15 K as a test of quality using a vibrating-tube density meter (Anton Paar, model DMA 60/602, Graz, Austria) operating in static mode. The temperature inside the vibrating-tube cell was measured using a digital thermometer (Anton Paar, type CTK 100) and was regulated to better than ±0.01 K using a water circulating bath (Heto, type 01 DBT 623, Birkeròd. Denmark). The uncertainty in the density was $\pm 1.5 \times 10^{-5}$ g·cm^{-3}. The densities of the pure liquids are presented in Table 1, along with literature values for comparison.

Calorimetric Measurements. The excess molar enthalpies, H_m^E, were measured by a isothermal flow microcalorimeter (LKB, model 2107, Producer AB, Bromma, Sweden) thermostated at (308.15 ± 0.01) K. The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath, and a personal computer for data acquisition and processing. Two automatic liquid burets (ABU Radiometer, Copenhagen, Denmark) pump the pure liquids into the cells. The temperature of the water bath is controlled to within ±0.01 K.

Molar fractions of mixtures were computed from densities and volumetric flow rates of components pumped into the mixing cell. Details and operating procedures of the apparatus have been reported elsewhere.[5,6] The uncertainties in T, H^E, and x_1 are estimated to be ±0.01 K, less than 1 %, and $\pm 2 \times 10^{-4}$, respectively. The miscibility of the components was tested prior to calorimetric experiments. In each mixture, the two components were found to be completely miscible over the whole concentration range.

The total flow rates are usually kept at about 0.4 cm^3·min^{-1}, but in dilute regions, the total flow rates may increase up to 0.8 cm^3·min^{-1}. The calorimeter was calibrated by the Joule effect, and the calibration was repeated after each experiment. The performance of the apparatus was checked at 298.15 K on the systems hexane + cyclohexane and methanol + water.[7] The agreement between our data and literature values was better than 0.5 % over most of the concentration range (Figure 1). Moreover, the microcalorimeter was checked at 308.15 K on

---

* E-mail: carlo.castellari@unibo.it. Tel: + 39-051-2094327. Fax: + 39-051-2094325.

10.1021/je0504212 CCC: $33.50

Table 1. Experimental Densities ρ at $T = 308.5$ K and Literature Data of Pure Components: R−[OP]$_p$−R′

compound	$\Delta_{vap}H$/kJ·mol^{-1}	R	R′	p	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit
dibutyl ether[c]	44.715[22]	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$	1	0.75522	0.764440[a; 17]
ethylene glycol monoethyl ether[c]	49.99[23]	CH_3	CH_2OH	1	0.91600	0.91165[b; 18]
diethylene glycol	78.56[24]	CH_2OH	CH_2OH	1	1.10586	1.10588[2]
ethylene glycol dimethyl ether[c]	36.76[25]	H	H	2	0.85028	0.84464[b; 18]
ethylene glycol diethyl ether[c]	(37 ± 4)[e]	CH_3	CH_3	2	0.82622	0.841[a]
diethylene glycol ethyl ether[c]	54.43[26]	CH_3	CH_2OH	2	0.97467	0.98468[a; 19]
triethylene glycol	84.6[27]	CH_2OH	CH_2OH	2	1.11259	1.11261[2]
diethylene glycol diethyl ether[c]		CH_3	CH_3	3	0.89308	0.9035[a; 20]
triethylene glycol monoethyl ether[d]		CH_3	CH_2OH	3	1.00880	1.0161[a; 21]
tetraethylene glycol		CH_2OH	CH_2OH	3	1.11232	1.11231[2]
benzyl alcohol	49.8[28]				1.03364	1.03370[2]

[a] 298.15 K. [b] 313.15 K. [c] Aldrich, purity ≥99 %. [d] Fluka Technical, purities: 94 % before distillation, >99 % after distillation. [e] Estimated from Trouton's law.

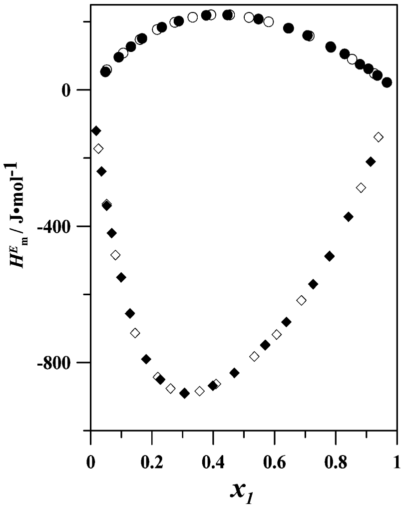

Figure 1. Comparison of excess molar enthalpies at 298.15 K. Hexane (1) + cyclohexane (2): ●, this work; ○, Gmehling.[7] Methanol (1) + water (2): ◆, this work; ◇, Gmehling.[7]

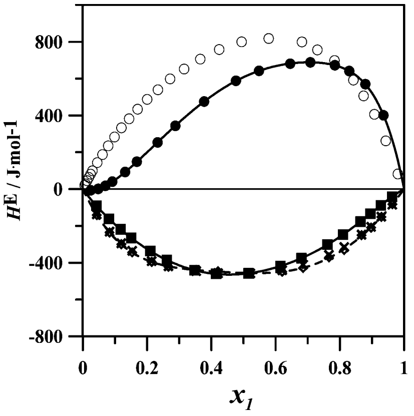

Figure 2. Experimental excess molar enthalpies H^E_m. This work: ●, dibuthyl ether (1) + benzyl alcohol (2); ■, ethylene glycol monoethyl ether (1) + benzyl alcohol (2); ×, diethylene glycol (1) + benzyl alcohol (2). Literature data: ◇, diethylene glycol (1) + benzyl alcohol (2), Francesconi et al.;[2] ○, dibuthyl ether (1) + methanol (2), Villamañan et al.[10] Curves, Redlich−Kister equation (eq 1).

the system diethylene glycol + benzyl alcohol. The values of H^E_m agree with the data determined in a previous work[2] (Figure 2), within the limits of experimental errors.

Data Reduction

Each set of experimental results of H^E_m has been fitted by the method of least squares, with all points weighted equally, to the calculated values $H^E_{m(calc)}$ using a Redlich−Kister polynomial

$$H^E_{m(calc)} = x_1x_2\sum_{k\geq 0} a_k\,(x_1 - x_2)^k \qquad (1)$$

where a_k represents the adjustable parameters and x_1 and x_2 are the mole fractions of components 1 and 2, respectively.

A suitable objective function to be minimized is

$$\phi = \sum_{k=1}^{N}[H^E_{m(calc)} - H^E_m]^2_k \qquad (2)$$

where N is the number of experimental points.

The standard deviations $\sigma(H^E_m)$ are defined as

$$\sigma(H^E_m) = \left|\frac{\phi_{min}}{N - n}\right|^{0.5} \qquad (3)$$

where n is the number of adjustable parameters a_k.

Results and Discussion

The experimental excess molar enthalpies, H^E_m, at 308.15 K are reported in Table 2 as a function of the molar fraction, x_1, of the ethers. The estimated adjustable parameters a_k (eq 1) and the relative standard deviations $\sigma(H^E_m)$ (eq 3), obtained in the fitting, are listed in Table 3.

The experimental results are presented in Figures 1−3 together with $H^E_{m(calc)}$ (solid-line curves). Each Figure shows the data of mixtures with the same value of p, which is the number of repeating units CH_2OCH_2. In these Figures are also shown, for comparison, some literature values together with $H^E_{m(calc)}$ (broken-line curves). The results will be qualitatively explained by considering that $H^E_m \propto (E_{11} + E_{22} - 2E_{12})$, where E_{ij} represents the interaction energy between molecules i and j. Because E_{ii} is proportional to the vaporization enthalpy, values of $\Delta_{vap}H$, quoted in the literature, are listed in Table 1.

Figure 2 ($p = 1$). Dibutyl Ether + Benzyl Alcohol. For this system, the H^E_m values are positive (with a maximum of 688 J·mol^{-1} at $x_1 = 0.71$).The steric hindrance of the butyl moieties and the presence of intramolecular C−H···O interactions inside the ether most likely contribute to these results. Both factors lower the acceptor character of the oxygen atom, decreasing the strength of the intermolecular O···H−O bonds between the ether and butyl alcohol, that is, E_{12}. However, the trend in H^E_m versus x_1 is quite different at extreme values of concentration; in particular, the alcohol-rich region presents values of H^E_m that are asymptotically close to zero. Consequently, it can be

Table 2. Experimental Excess Molar Enthalpies H_m^E of Binary Mixtures Containing Ethers (1) + Benzyl Alcohol (2) at 308.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
Dibutyl Ether (1) + Benzyl Alcohol (2)						Diethylene Glycol Ethyl Ether (1) + Benzyl Alcohol (2)					
0.0247	−6.7	0.2327	253.3	0.7082	688.3	0.0289	−197.0	0.2629	−871.7	0.7405	−617.2
0.0481	1.0	0.2880	343.5	0.7845	672.6	0.0561	−346.3	0.3223	−919.3	0.8106	−487.0
0.0705	17.8	0.3776	475.4	0.8292	641.3	0.0819	−461.0	0.4164	−941.3	0.8509	−400.8
0.0918	40.3	0.4765	588.2	0.8792	569.7	0.1063	−551.5	0.5170	−896.3	0.8954	−295.7
0.1317	92.7	0.5482	642.2	0.9357	400.7	0.1514	−680.8	0.5880	−832.2	0.9448	−164.6
0.1682	148.7	0.6454	680.9			0.1921	−769.6	0.6816	−711.7		
Ethylene Glycol Monoethyl Ether (1) + Benzyl Alcohol (2)						Diethylene Glycol Diethyl Ether (1) + Benzyl Alcohol (2)					
0.0424	−90.8	0.3471	−441.4	0.8097	−247.8	0.0234	−167.6	0.2236	−849.3	0.6973	−530.6
0.0814	−162.0	0.4148	−460.7	0.8645	−176.6	0.0458	−304.4	0.2774	−891.6	0.7756	−401.6
0.1173	−218.4	0.5154	−457.8	0.8948	−133.6	0.0672	−416.7	0.3655	−890.6	0.8217	−320.3
0.1505	−265.6	0.6147	−419.0	0.9273	−88.4	0.0876	−508.3	0.4635	−825.5	0.8736	−224.5
0.2100	−336.1	0.6802	−375.4	0.9623	−41.6	0.1259	−647.3	0.5353	−749.8	0.9325	−114.8
0.2617	−385.3	0.7613	−301.9			0.1611	−741.8	0.6334	−624.7		
Ethylene Glycol Dimethyl Ether (1) + Benzyl Alcohol (2)						Triethylene Glycol Monoethyl Ether (1) + Benzyl Alcohol (2)					
0.0395	72.3	0.3305	−335.1	0.7979	364.3	0.0241	−196.9	0.2284	−927.3	0.7031	−764.7
0.0760	56.7	0.3969	−334.7	0.8555	489.3	0.0470	−353.3	0.2830	−987.4	0.7804	−610.4
0.1098	2.9	0.4968	−261.2	0.8876	517.0	0.0689	−476.3	0.3719	−1036.3	0.8257	−510.0
0.1413	−62.5	0.5969	−122.5	0.9221	485.9	0.0898	−574.6	0.4704	−1030.0	0.8766	−385.8
0.1979	−182.3	0.6638	12.8	0.9595	344.9	0.1290	−716.9	0.5422	−985.1	0.9343	−226.8
0.2476	−264.9	0.7476	227.2			0.1648	−813.5	0.6398	−869.1		
Ethylene Glycol Diethyl Ether (1) + Benzyl Alcohol (2)											
0.0296	−49.4	0.2678	−548.9	0.7453	−183.5						
0.0575	−122.3	0.3278	−553.6	0.8144	−38.5						
0.0838	−202.2	0.4225	−512.1	0.8541	42.8						
0.1087	−275.7	0.5232	−449.0	0.8977	109.5						
0.1546	−398.1	0.5940	−395.7	0.9461	124.3						
0.1960	−478.1	0.6870	−285.9								

Table 3. Adjustable Parameters a_k (Equation 1) and Standard Deviations $\sigma(H_m^E)$ (Equation 3) of Binary Mixtures Containing Ethers (1) + Benzyl Alcohol (2) at 308.15 K

component 1	a_0	a_1	a_2	a_3	a_4	a_5	$\sigma(H_m^E)$
dibutyl ether	2431.08	1633.94	214.88	1677.69	1471.21	1388.22	0.7
ethylene glycol monoethyl ether	−1852.89	268.08	106.14	282.65			3.0
ethylene glycol dimethyl ether	−1032.78	2191.84	2155.50	1936.23	6419.61		0.8
ethylene glycol diethyl ether	−1856.89	1280.38	−1400.49	3105.59	4853.66	−1825.84	0.6
diethylene glycol ethyl ether	−3635.15	1170.93	−741.10	820.74	−1027.54		3.3
diethylene glycol diethyl ether	−3158.51	2057.22	−1438.42	941.41			1.5
triethylene glycol monoethyl ether	−4063.35	1158.09	−668.74	1353.63	−1792.32		0.4

assumed that when the ether is surronded by a great number of benzyl alcohol dimers[8,9] the interaction energy between unlike molecules balances the self-association energy of components. On the contrary, in the ether-rich region, the alcohol−ether H bonding is weaker than the alcohol−alcohol and ether−ether interactions ($2E_{12} < E_{11} + E_{22}$). Similar behavior was found for the system dibuthyl ether/methanol[10] at 298.15 K (Figure 2, open circles). In effect, the two curves are skewed toward the region of high dibuthyl ether concentration and are similar, allowing for the decrease in $\Delta_{vap}H$ of the components (and hence of E_{11} and E_{22}) with the increase in temperature.

Ethylene Glycol Monoethyl Ether (Synonym: 2-Ethoxyethanol) + Benzyl Alcohol. The system presents negative H_m^E values over the whole range of composition (with a minimum of −457 J·mol^{-1} at $x_1 = 0.51$). Because both the components are strongly associated with high $\Delta_{vap}H$ (nearly 50 kJ·mol^{-1}, see Table 1), negative excess enthalpies of mixing require strong H-bonding between the components. In effect, an X-ray analysis reveals that the ethylene glycol monoethyl ether is able to give a medium-strong intermolecular H-bond.[11] The curve is symmetrical and quite similar to the analogous plot of diethylene glycol + benzyl alcohol reported in Figure 2 ($H_m^E = -458$ J·mol^{-1}, $x_1 = 0.52$, at the minimum)[2]. However, the substitution of a CH_3 with a CH_2OH group in component 1 increases (~36 %) the heat of vaporization (Table 1) but has no effect on the difference $E_{11} - 2E_{12}$ as a consequence of a parallel strengthening of the H-bonds between different molecules of the mixture.

Figure 3 ($p = 2$). Ethylene Glycol Dimethyl Ether (Synonym: 1,2-Dimethoxyethane) + Benzyl Alcohol. The H_m^E values of this system are roughly positive for $x_1 < 0.1$ and $x_1 > 0.65$ (517 J·mol^{-1}, $x_1 = 0.89$, at the maximum) and negative between these concentrations (−335 J·mol^{-1}, $x_1 = 0.33$, at the minimum). 1,2-Dimethoxymethane can assume different conformations. However, in the liquid state, the energies and stability of some of the five principal conformers are still controversial. It is assumed that in solution the intermolecular hydrogen bonding ability and the concentration of the solution are both basic factors in the populations of the conformers.[12] As a result, the sigmoidal character of the H_m^E curve could be related to changes in the conformational preference of 1,2-dimethoxyethane with concentration. Positive enthalpies of mixing should be partially derived from the stabilization of "hydrophobic" conformers in which the etheric oxygen atoms are involved in C−H···O intramolecular interactions.

Ethylene Glycol Diethyl Ether (Synonyms: 1,2-Diethoxyethane; 3,6-Dioxaoctane) + Benzyl Alcohol. The heat of mixing is negative (−554 J·mol^{-1}, $x_1 = 0.33$, at the minimum) in the alcohol-rich region and slightly positive for a high ether concentration (124 J·mol^{-1}, $x_1 = 0.95$, at the maximum). The H_m^E curve is almost parabolic, and the role of the change in conformer population appears to be less marked than in the previous system.

It should be noted that in going from ethylene glycol dimethyl ether to ethylene glycol diethyl ether the minimum in the H_m^E

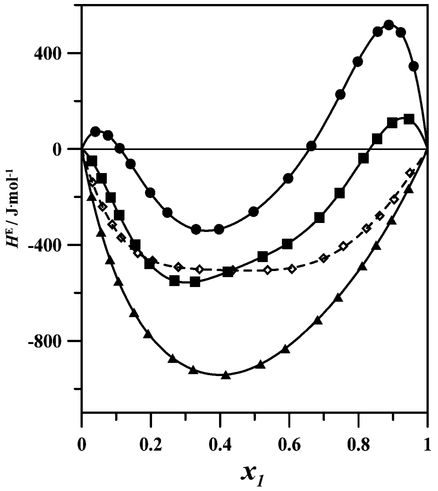

Figure 3. Experimental excess molar enthalpies H_m^E. This work: ●, ethylene glycol dimethyl ether (1) + benzyl alcohol (2); ■, ethylene glycol diethyl ether (1) + benzyl alcohol (2); ▲, diethylene glycol ethyl ether (1) + benzyl alcohol (2). Literature data: ◇, triethylene glycol (1) + benzyl alcohol (2), Francesconi et al.[2] Curves, Redlich−Kister equation (eq 1).

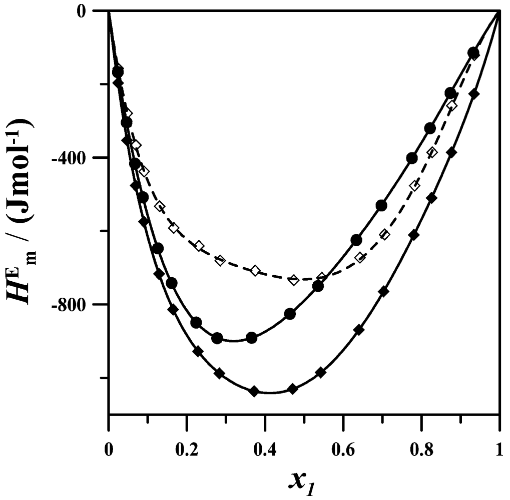

Figure 4. Experimental excess molar enthalpies H_m^E. This work: ●, diethylene glycol diethyl ether (1) + benzyl alcohol (2); ■, triethylene glycol monoethyl ether (1) + benzyl alcohol (2). Literature data: ◇, tetraethylene glycol (1) + benzyl alcohol (2), Francesconi et al.[2] Curves, Redlich−Kister equation (eq 1).

curve roughly doubles. Because the substitution of two hydrogen atoms with two methyl groups does not appreciably affect the term E_{11} (Table 1), the term E_{12} must increase strongly, and it can be assumed that the methyl groups raise the negative charges on the oxygen atoms with a consequent increase in hydrogen bonding between the ether and alcohol.

Diethylene Glycol Ethyl Ether (Synonyms: 2-(2-Ethoxyethoxy)ethanol, Carbitol) + Benzyl Alcohol. The H_m^E values are negative and present a strong minimum of −941 J·mol^{-1} at $x_1 = 0.42$ that results in almost twice the value of the one corresponding to the system triethylene glycol + benzyl alcohol (−504 J·mol^{-1}, $x_1 = 0.54$, at the minimum)[2]. The strong minimum of the heat of mixing agrees with the chelating functionalities of diethylene glycol ethyl ether.[13] Finally, the substitution of a CH_3 with a CH_2OH group increases the heat of vaporization of component 1 by the same amount found for the previous case $p = 1$ (Table 1), but in this case, the strength of the self-association bonding is not fully compensated for by an analogous increase in the intermolecular H-bonding between triethylene glycol and benzyl alcohol.

Figure 4 (p = 3). Diethylene Glycol Diethyl Ether (Synonym: Diethylcarbitol) + Benzyl Alcohol. The H_m^E curve is parabolic and negative with a sharp minimum (−892 J·mol^{-1}, $x_1 = 0.28$) that is coherent with the presence of three oxygen atoms in the ether molecule. In effect, in the solid state, the diethylene glycol diethyl ether can act as a tridentate ligand with metals,[14] and thus it seems plausible to consider that the presence of four-center hydrogen bonds[15] in the alcoholic solutions strongly increases the term E_{12}. The position of the minimum in the H_m^E curve suggests a change in conformation of diethylene glycol diethyl ether with concentration. A conformational IR study of this compound in water demonstrated a strong preference of the gauche conformation around the C−C bond, changing with concentration and increasing remarkably with increasing water fraction, as a consequence of preferential hydrogen bonding between the oxygens in the gauche $O{-}CH_2{-}CH_2{-}O$ moiety and water.[16] The presence of the minimum of H_m^E in the alcohol-rich region seems to indicate conformational behavior similar to that observed in water.

Triethylene Glycol Monoethyl Ether + Benzyl Alcohol. The H_m^E values are negative over the whole range of concentration. The curve of the heat of mixing is parabolic and presents a strong minimum, −1037 J·mol^{-1}, that results in a correspondingly higher value for the system tetraethylene glycol + benzyl alcohol (−734 J·mol^{-1} at $x_1 = 0.47$)[2].

The H_m^E curve is more symmetrical (minimum at $x_1 = 0.37$) than the corresponding one of the previous system, suggesting less-pronounced changes in the conformation of the ether. A comparison of the results presented in the cited IR study[16], with reference to diethylene glycol diethyl ether and triethylene glycol monoethyl ether in water, has shown that the latter system presents both a less-pronounced preference for the gauche conformation around the C−C bond and a smaller effect of the ether concentration on the ratio of the gauche/trans conformation than the former one.

In conclusion, the study of the calorimetric behavior of mixtures of various short-chain ethers in benzyl alcohol has provided some information about the influence of the structural properties of component 1 on the heat of mixing. The steric and electronic characteristics of the terminal groups as well as the conformation of the whole ether molecule greatly influence the H_m^E of the mixtures, changing both the availability and the H-bond acceptor character of etheric oxygen atoms.

Acknowledgment

I thank Dr. Michele Contento (Dipartimento di Chimica “G. Ciamician”, Università degli Studi di Bologna) for his valuable assistance with chemical purification.

Literature Cited

(1) Goutev, N.; Matsuura, H. Hydrogen bonding in chloroform solutions of ethylenedioxy ethers. Spectroscopic evidence of bifurcated hydrogen bonds. *J. Phys. Chem. A* **2001**, *105*, 4741−4748.

(2) Francesconi, R.; Castellari, C.; Comelli, F. Thermodynamic study of binary mixtures containing glycols or polyethylene glycols + benzyl alcohol at 308.15 K. *J. Chem. Eng. Data* **2004**, *49*, 363−367.

(3) Castellari, C.; Francesconi, R.; Comelli, F. Excess molar enthalpies and hydrogen bonding in binary mixtures containing glycols or poly(ethylene glycols) and 2-phenylethyl alcohol at 308.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1032−1035.

(4) Castellari, C.; Francesconi, R.; Comelli, F. Excess molar enthalpies and hydrogen bonding in binary mixtures containing glycols or poly(ethylene glycols) + 3-phenylpropyl alcohol at 308.15 K. *Thermochim. Acta* **2004**, 69−73.

(5) Monk, P.; Wadsö, I. A flow micro reaction calorimeter. *Acta Chem. Scand.* **1968**, *22*, 1842−1852.

(6) Francesconi, R.; Comelli, F. Liquid-phase enthalpy of mixing for the system 1,3-dioxolane-chlorobenzene in the range 288.15−313.15 K. *J. Chem. Eng. Data* **1986**, *31*, 250−253.

(7) Gmehling, I. Excess enthalpies for 1,1,1-trichloroethane with alkanes, ketones, and esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.

(8) Guchhait, N.; Ebata, T.; Mikani, N. Discrimination of rotamers of aryl alcohol homologues by infrared-ultraviolet double-resonance spectroscopy in a supersonic jet. *J. Am. Chem. Soc.* **1999**, *121*, 5705−5711 and references therein.

(9) Robertson, E. G.; Snock, L. C.; Simons, J. P.; Mons, M. Structural landscapes in hydrogen-bonded biomolecular clusters: resonant ion-dip spectroscopy. *Central Laser Facility Annual Report* **1999/2000**, 124−128.

(10) Villamañan, M. A.; Casanova, C.; Roux, A. H.; Grolier, I. P. E. Calorimetric investigation of the interactions between oxygen and hydroxyl groups in (alcohol + ether) at 298.15 K. *J Chem. Thermodyn.* **1982**, *14*, 251−258.

(11) Kubiak, R.; Was’kowska, A.; Pietraszko, A.; Bukowska, E. Syntheses and thermal characterization of the magnesium phthalocianine complex with 2-methoxy- and with 2-ethoxyethanol. X-ray structure of (2-ethoxyethanol)magnesium phthalocyanine. *Inorg. Chim. Acta* **2005**, *358*, 453−458.

(12) Goutev, N.; Keiichi, O.; Matsuura, H. Raman spectroscopy study on the conformation of 1,2-dimethoxyethane in the liquid phase and in aqueous solution. *J. Phys. Chem. A* **2000**, *104*, 9226−9232.

(13) Evans, J. W.; Greci, M. A.; Ziller, J. Synthesis and structure of a mixed valence metal carbitoxide complex: $Eu_3[O(CH_2CH_2O)_2CH_2CH_3]_4(OC_6H_3{}^{i}Pr_2\text{-}2, 6)_3$. *Inorg. Chem. Commun.* **1999**, *2*, 530−532.

(14) Eveland, J. R.; Whitmire, K. H. Complexes of bismuth(III) chloride with oxygen donor ligands. Structural characterization of $BiCl_3 \cdot 3THF$, $BiCl_3 \cdot$diglyme and $BiCl_3 \cdot$diethylcarbitol. *Inorg. Chim. Acta* **1996**, *249*, 41−46.

(15) Jeffrey, G. A.; Saenger, V. *Hydrogen Bonding in Biological Structures.* Springer-Verlag: Berlin, 1991; p 20.

(16) Begum, R.; Matsuura, H. Conformational properties of short poly(oxyethylene) chains in water studied by IR spectroscopy. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3839−3848.

(17) Domanska, U.; Lachwa, J.; Letcher, T. M. Excess molar volumes and excess molar enthalpies of (N-methyl-2-pyrrolidone + an ether) at the temperature 298.15 K. *J. Chem. Thermodyn.* **2002**, *34*, 885−893.

(18) Ohji, H.; Tamura, K.; Ogawa, H. Excess thermodynamic properties of (2-ethoxyethanol + 1,4-dioxane or 1,2-dimethoxyethane) at temperatures between (283.15 and 313.15) K. *J. Chem. Thermodyn.* **2000**, *32*, 319−328.

(19) Martinez., R.; Gonzalez, J. A.; Garcia de la Fuente, I.; Cobos, J. C. Thermodynamic properties of *n*-alkoxyethanols + organic solvent containing 2-(2-ethoxyethoxy)ethanol and selected alkanes. *J. Chem. Eng. Data* **2000**, *45*, 1036−1039.

(20) Pal, A.; Dass, G. excess molar volumes and viscosities of diethylene glycol diethyl ether with dimethyl carbonate, diethyl carbonate, and propylene carbonate at (298.15, 308.15, and 318.15) K. *J. Chem. Eng. Data* **2000**, *45*, 487−491.

(21) Pal, A.; Dass, J. Excess molar volumes and excess partial molar volumes of triethylene glycol monoethyl ether−n-alcohol mixtures at 25 °C. *Solution Chem.* **1999**, *28*, 237−245.

(22) Majer, V.; Wagner, Z.; Svoboda, V.; Cadek, V. Enthalpies of vaporization and cohesive energies for a group of aliphatic ethers. *J. Chem. Thermodyn.* **1980**, *12*, 387−391.

(23) Antosik, M.; Fras, Z.; Malanowski, S. K. Vapor−liquid equilibrium in 2-ethoxyethanol + methanol at 313.15 to 333.15 K. *J. Chem. Eng. Data* **1999**, *44*, 219−222.

(24) Steele, W. V.; Chirico, R. D.; Cowell, A. B.; Knipmeyer, S. E.; Nguyen, A. Thermodynamic properties and ideal gas enthalpies of formation for methyl benzoate, (R)-(+)-limonene, *tert*-amyl methyl ether, *trans*-crotonaldehyde, and diethylene glycol. *J. Chem. Eng. Data* **2002**, *47*, 667−688.

(25) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nuguyen, A.; Smith, N. K. Thermodynamic properties and ideal-gas enthalpies of formation for butyl vinyl ether, 1,2-dimethoxyethane, methyl glycolate, bicyclo-[2.2.1]hept-2-ene, 5-vinylbicyclo[2.2.1]hept-2-ene, trans-azobenzene, butyl acrylate, di-*tert*-butyl ether, and hexane-1,6-diol. *J. Chem. Eng. Data* **1996**, *41*, 1285−1302.

(26) *Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1995.

(27) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Measurements of vapor pressure, heat capacity, and density along the saturation line for ϵ-caprolactam, pyrazine, 1,2-propanediol, triethylene glycol, phenyl acetylene, and diphenyl acetylene. *J. Chem. Eng. Data* **2002**, *47*, 689−699.

(28) Riddik J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

Received for review October 13, 2005. Accepted December 11, 2005.

JE0504212