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Excess enthalpies and excess heat capacities of the ternary system ethanol + tetrahydrofuran + cyclohexane at 298.15 K

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Abstract

Excess enthalpies and excess heat capacities at 25°C for the ternary system ethanol + tetrahydrofuran + cyclohexane, and for the related binary mixtures, were determined by means of a flow calorimetric apparatus built in our laboratory. Experimental data were described with a Redlich–Kister-type equation. Both H^E and C_p^E ternary data show large positive contributions.

Theoretical models were used for the description or prediction of experimental results. In the case of binary systems, the examined models are able to reproduce satisfactorily the experimental data for H^E, though less satisfactorily for C_p^E. Ternary experimental data are predicted by the modified UNIFAC method (Dortmund, Germany) but not by the Nitta–Chao model. Both these models are unsuccessful in predicting ternary C_p^E data.

Keywords: Cyclohexane; Ethanol; Excess enthalpy; Excess heat capacity; Model; Ternary system; THF; UNIFAC

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1. Introduction

Excess thermodynamic properties of asymmetric mixtures of two or more organic compounds are a proper basis for the study of the behaviour of these systems in

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terms of the non-random distribution of molecules and, in particular, for pointing out phenomena of preferential solvation. In the past, some of the most successful semi-empirical approaches to phase equilibria in liquid mixtures (Wilson, NRTL, UNIQUAC) were developed on the local composition concept. More recently, the rigorous fluctuation theory of mixtures of Kirkwood and Buff has proved to be particularly appropriate both for the development of new VLE and LLE models and as a tool for the study of the microscopic structure of mixtures with strong asymmetric interactions [1]. As to this latter point, a series of investigations has been carried out in this laboratory [2] which, using the Kirkwood–Buff theory have allowed the integrals of the radial distribution functions from thermodynamic excess properties to be calculated, yielding information on the local environment of the molecules in binary mixtures. We have deemed it interesting to extend this type of treatment to ternary mixtures, in order to examine the evolving of the preferential solvation of a third compound as the concentrations of the other two solvating components change, and to relate the observed Kirkwood–Buff integrals to interactions among functional groups and to the structure of the solvents. For this investigation, we have chosen the four ternary systems which can be obtained by mixing three out of four compounds of different polarity, namely cyclohexane (cyHex), tetrahydrofuran (THF), ethanol (EtOH), and dimethylformamide (DMFA). In addition to the measurements of VLE and volumetric properties, we are also engaged in the determination of the excess enthalpies H^E and excess heat capacities C_p^E necessary for the study of the change with temperature of VLE. In this paper we present the first results regarding excess enthalpies and heat capacities at 25°C for the ternary system EtOH + THF + cyHex and for the constituent binary mixtures. The discussion of the data in terms of the Kirkwood–Buff theory will be postponed until results for the other systems are available. We will examine here the application of the UNIQUAC [3], UNIFAC [4] and Nitta–Chao [5] models to the H^E and C_p^E data for this system.

2. Experimental

2.1. Materials

All products were high purity reagents and were used without further purification. Their purity was tested by gas chromatography and the water content by Karl–Fischer analysis. No significant difference was found with respect to the declared impurity content: cyclohexane, RS grade, C. Erba reagent, purity >99.8%; tetrahydrofuran, puriss, Fluka reagent, purity >99.5%, with water <0.005%; ethyl alcohol, RPE 99.9%, C. Erba anhydrous reagent, with water content <0.1%; n-heptane, used as primary reference liquid in the heat capacity measurements, was RPE, C. Erba reagent with purity >99.5%.

2.2. Calorimetric apparatus

2.2.1. Heat capacity measurements

Measurements of the heat capacities of the studied mixtures were performed with a Picker-type [6] flow calorimeter, described in detail in previous papers [7,8]. The following modifications were introduced. A supplementary loop was added for the introduction of a second sample, thus allowing the measurement in a single run of the heat capacity of two liquids, pushed in sequence into the measuring cell. This configuration permits the specific heat of two samples relative to the common transport liquid to be determined or, alternatively, the specific heat of one liquid with respect ot the second taken as the reference. This procedure is particularly useful in the case of organic mixtures, for which possible marked differences in heat capacity with respect to the pure component used as transport liquid may sensibly reduce the accuracy of the apparatus [9]. In this way, the use of a proper reference in the second loop allows application of a "stepwise" technique [10] without substituting the transport liquid.

A further modification concerns the heating resistors (a thin wire of constantane, $R \approx 20\ \Omega$) of the two cells, which were wound directly around the cell itself and fixed with a thin layer of epoxy resin. This allowed a more efficient heat transfer to the flowing liquid. A few other improvements were the computer-monitoring of the apparatus, which now permits the automatic reading of all necessary quantities and the control of all functions via the software, except the manual shifting of the loop valves.

The relationship used for calculating the specific heat with our method is

$$c_{p,\mathrm{S}} = c_{p,\mathrm{R}}[(d_\mathrm{R} P_\mathrm{S})/(d_\mathrm{S} P_\mathrm{R})]F \tag{1}$$

where $c_{p,\mathrm{S}}$, $c_{p,\mathrm{R}}$, d_S and d_R are the specific heat and density of the unknown sample and of the reference liquid, respectively; P_S and P_R are the power given to the sample and reference cell in order to obtain the same temperature increase of the two liquids (in our case typically approx. 2 K with a volumetric flow $\varphi = 0.025$ cm^3 s^{-1} and $P_\mathrm{R} \approx 85$ mW). The coefficient F is the correction factor which accounts for heat losses. Analogously to the F_2 term introduced in a previous paper [7], F can be expressed as a function of the specific heat and density of the sample and reference liquids through the relationship

$$F = \left(1 - \frac{k}{c_{p,\mathrm{S}} d_\mathrm{S} \varphi}\right) \Big/ \left(1 - \frac{k}{c_{p,\mathrm{R}} d_\mathrm{R} \varphi}\right) \tag{2}$$

where φ is the volumetric flow used in the experiment and k is a measure of the heat exchange rate between the measuring cell and the surroundings. As a first approximation, k depends only on temperature and the vacuum conditions in the apparatus. Following the above-mentioned modifications of the cells, we could ascertain that this term alone, contrary to what was previously observed [7], is sufficient to correct the experimental data for heat losses. In addition, this term meets the requirement discussed by Carter and Wood [11] of a value of unity for infinite liquid flow or in the absence of heat losses.

By substituting F into Eq. (1) and rearranging, one obtains the equation

$$\frac{F_{\mathrm{R}}}{c_{p,\mathrm{R}} R_{\mathrm{d}} R_{\mathrm{p}}} c_{p,\mathrm{S}}^{2} - c_{p,\mathrm{S}} + \frac{k}{\varphi d_{\mathrm{S}}} = 0 \tag{3}$$

where $R_{\mathrm{d}} = d_{\mathrm{R}}/d_{\mathrm{S}}$, $R_{\mathrm{p}} = P_{\mathrm{S}}/P_{\mathrm{R}}$ and $F_{\mathrm{R}} = 1 - k/(c_{p,\mathrm{R}} d_{\mathrm{R}} \varphi)$. Solution of Eq. (3) yields, for $c_{p,\mathrm{S}}$, an expression analogous to Eq. (1) where the coefficient F is given by

$$F = \frac{1}{2F_{\mathrm{R}}} + \left[\frac{1}{F_{\mathrm{R}}}\left(\frac{1}{4F_{\mathrm{R}}} - \frac{k}{R_{\mathrm{p}} c_{p,\mathrm{R}} d_{\mathrm{R}} \varphi}\right)\right]^{1/2} \tag{4}$$

It is then possible through Eq. (4) to calculate the correction factor F using the data relative to each single experiment, provided the k value is known. The latter constant has been determined in separate experiments in which changes in the heat capacity of the liquid which flows in the sample cell are simulated by flow changes, both positive and negative, through the relationship

$$k = \frac{c_{p,\mathrm{R}} d_{\mathrm{R}} \varphi (R_{\mathrm{p}} - R_{\varphi})}{R_{\mathrm{p}}/R_{\varphi} - R_{\varphi}} \tag{5}$$

In Eq. (5), $R_{\varphi} = \varphi'/\varphi$ is the ratio between the modified and the standard working volumetric flow, while $R_{\mathrm{p}} = P_{\varphi'}/P_{\varphi}$ is the ratio between the power applied to the modified and standard flow, respectively, chosen so as to maintain a constant liquid temperature.

The term F defined by Eq. (2) and the analogous coefficient f used by others [12] are related by

$$f = \frac{R_{\mathrm{p}} F - 1}{R_{\mathrm{p}} - 1} \tag{6}$$

As an example, Table 1 reports the corresponding values of F and f at different R_{p} ratios as the constant k, the working flow, and the type of solvent are changed. The data of Table 1 clearly indicate the dependence of the two empirical correction coefficients on the working conditions. Both tend to unity for $k \to 0$ or $\varphi \to \infty$. The term f remains surprisingly constant at fixed k and φ, for different values of the power ratio R_{p}. Only when k is rather large (or equivalently φ is proportionally small) is a change in f observed in the rather large range of R_{p} values considered here.

The constant k of our apparatus was determined using n-heptane in physical calibration experiments, with the pressure inside the cell compartment being 5×10^{-3} Pa. Three runs conducted with φ values of 1.667×10^{-2}, 2.5×10^{-2} and 3.333×10^{-2} $\mathrm{cm^3\ s^{-1}}$ allowed a k value of $(3.5 \pm 0.1) \times 10^{-3}$ $\mathrm{J\ K^{-1}\ s^{-1}}$ to be calculated, which was subsequently used to calculate the heat capacity data of pure liquids and liquid mixtures throughout this work.

Data obtained at 25°C for pure cyHex, THF and EtOH, using n-heptane as the reference, are reported in Table 2. Molar heat capacities C_p determined in this work are slightly lower than those measured by Fortier et al. [13], with a maximum deviation of 0.6% in the case of THF. Although being aware of the higher accuracy of the data reported by the latter authors, nevertheless we deemed it necessary, for the sake of homogeneity, to use our data for the calculation of excess heat capacities determined throughout this work.

Table 1
Comparison between heat loss correction factors of Eqs. (4) and (6) [a]

	n-Heptane								Water	
	$\varphi = 1.5$ $k = 5 \times 10^{-4}$		$\varphi = 1.5$ $k = 2 \times 10^{-3}$		$\varphi = 1.5$ $k = 5 \times 10^{-3}$		$\varphi = 100$ $k = 5 \times 10^{-3}$		$\varphi = 1.5$ $k = 5 \times 10^{-3}$	
R_p	F	f	F	f	F	f	F	f	F	f
1.20	1.00224	1.0134	1.00967	1.0580	1.02868	1.1721	1.00033	1.0020	1.00877	1.0526
1.10	1.00122	1.0134	1.00530	1.0583	1.01588	1.1747	1.00018	1.0020	1.00480	1.0528
0.99	0.99986	1.0139	0.99941	1.0584	0.99820	1.1782	0.99998	1.0020	0.99946	1.0535
0.90	0.99850	1.0135	0.99344	1.0590	0.97975	1.1822	0.99978	1.0020	0.99406	1.0535
0.80	0.99662	1.0135	0.98510	1.0596	0.95291	1.1884	0.99951	1.0020	0.98654	1.0538

[a] Values of f and F are here calculated with a number of digits which allows the effect of R_p changes to be revealed. Experimental precision would require one digit less. φ in $cm^3\ min^{-1}$; k in $J\ K^{-1}\ s^{-1}$.

Table 2
Molar heat capacity of the pure compounds at 298.15 K

Compound	R_p	d/g cm^{-3}	F	C_p/J K^{-1} mol^{-1} [b]
n-Heptane [a]	–	0.67951 [c]	–	224.781 ± 0.005 [c]
Ethanol	1.22577	0.78537	1.02027	111.86 ± 0.05
Cyclohexane	0.94650	0.77387	0.99359	155.89 ± 0.06
Tetrahydrofuran	0.98648	0.88212	0.99845	122.74 ± 0.06

[a] Compound used as the transport liquid. [b] Quoted uncertainties are standard deviations obtained in at least 5 experiments. [c] Ref. [13].

2.2.2. Enthalpy measurements

Heats of mixing for the calculation of excess enthalpies H^E of the system under study were determined by means of a single-cell flow calorimeter built in our laboratory. The apparatus takes advantage of the basic instrumentation of the system which measures specific heats, as described in the previous section. However, the calorimetric assembly containing the mixing cell was devised and built as a separate element with respect to the old system previously described [7]. It consists of two small massive copper cylindrical blocks, 1.5 cm in diameter and 10 cm high. The first cylinder (A) has the function of bringing the liquids to the working temperature while the second (B) is the true calorimetric cell where the liquids are mixed. The external surface of each cylinder has a spiral groove around 75% of its area in which are lodged and sealed for good thermal contact inconel tubing (0.14 cm external diameter) through which the liquids flow. On the remaining surface is wound, and fixed with epoxy resin, an electrical heating resistor of constantan (approx. 40 Ω). Inside each block is also placed a platinum probe (Pt_{100}) for temperature readings via a thermometric bridge (ASL, model F17A) having a resolution of 2×10^{-4} K. Two 90-cm-long inconel tubes around block A allow the two liquids to reach the block temperature, which is regulated by a high-precision thermostatic system (ASL bridge (model F16) + controller (model 300)) connected to the heating resistor and driven by a platinum probe lodged inside the block in the vicinity of the latter resistor. Under steady conditions, the temperature of cylinder A oscillates around the programmed value within $\pm 5 \times 10^{-4}$ K.

The two liquids mix together in cylinder B. The mixture is made homogeneous by passing through a few crossed constrictions and then flowing inside 150 cm of coiled tubing which allows a good exchange of the mixing heat with the cylinder. The electrical resistor wound on block B is connected with a stabilized DC power supply, whose voltage can be varied manually with high resolution ($\pm 2 \times 10^{-4}$ V, corresponding to $\pm 2 \times 10^{-5}$ W under 2 V). The power dissipated by this resistance is calculated by measuring with a digital voltmeter (Keithley, model 197) the voltage drop on the resistance itself and on a second standard resistor of analogous value, put in series with the first, externally to the calorimeter. Block B also contains a small loop, only a few coils, through which is passed a slow flow of gaseous N_2 cooled via the Peltier effect. This device permits a controlled refrigeration of the calorimetric cell and is used both with discrete injections, for bringing the cell to the working temperature, or with a continuous flow when mixtures with negative excess enthalpies are examined.

The two blocks are enclosed in two small thin-walled glass containers and both are lodged at the center of a cylindrical thin-walled copper container C (10 cm diameter, 20 cm high) maintained at constant temperature (± 0.01 K) by a heating resistor wound on the external surface of the cylinder, and connected to an electronic thermoregulator driven by a platinum probe. Proper function of this thermostat is provided by a refrigerating loop where water circulates pumped by an external thermostat. The whole apparatus is placed inside a large box completely filled with expanded polyurethane.

For performing H^E measurements, the two liquids are taken from two small reservoirs and forced to circulate into the calorimetric system at a predetermined total flow rate (usually 1 cm^3 min^{-1}) and mutual flow ratio, by two HPLC pumps (Shimadzu, model LC6). The liquids are pre-thermostatted each flowing into 3 m of PTFE tubing (internal diameter 0.5 mm) wound around the central part of cylinder C. They reach final thermal equilibrium at the working temperature in the thermostatic block A, then undergo mixing in the calorimetric cell B, and the mixture is finally collected in an external container.

At the beginning of the measurement, with steady liquids, the temperature of cell B is regulated to the same value as cell A, preselected as the working temperature. The power dissipated by the heating resistor of cell B is then regulated so as to obtain a stationary value of temperature with time, which is observed as a zero-slope line on the monitor of the PC which also records the vector of the temperature values. The pumps are then activated and the power absorbed by the mixing process (all excess enthalpies observed in this work were positive) is manually compensated for, obtaining, under the new conditions, a linear trend of temperature with time with a small, but finite, slope. This procedure allows a single experiment to be completed in about 10 min.

The power P_{mix} associated with the mixing under study is calculated through the expression

$$P_{mix} = \frac{V_H V_S}{R_S} - C_B(s_f - s_i + \delta) + P' \qquad (7)$$

where V_H and V_S are the voltages read on the heating resistor and on standard resistor R_S respectively, s_f and s_i are the final and initial slope of the function temperature versus time (in K s^{-1}), while C_B (J K^{-1}) is the heat capacity of cell B. The latter quantity was calculated as $C_B = \Delta P/\Delta s$, where Δs is the slope change observed for a change ΔP of the heating power supplied to the calorimetric cell. The observed value was 45.0 ± 0.5 J K^{-1}. The term δ is a small correction (generally, at $\varphi = 1$ cm^3 min^{-1}, $C_B\delta < 1 \times 10^{-3}$ W) to account for the small slope change caused by the friction of the flowing liquids; it was determined in separate experiments by having the same liquid pushed by both pumps at different flow ratios. The value of δ is independent of the nature of the liquid and depends, in a reproducible manner, on the flow value. The term P' takes a non-zero value when

Table 3
Excess enthalpies H^E in J mol^{-1} for the system benzene (1)–cyclohexane (2) at 298.15 K

x_1	This work [a]	Ref. [14]	Ref. [15]	x_1	This work [a]	Ref. [14]	Ref. [15]
0.05	148.0	148.3	148.0	0.60	776.5	776.3	775.5
0.10	281.5	281.4	282.6	0.70	690.1	689.5	690.8
0.20	503.4	501.8	507.0	0.80	537.5	535.3	541.9
0.30	663.8	661.5	668.0	0.90	311.2	308.1	318.1
0.40	762.6	760.7	765.0	0.95	167.2	164.7	172.4
0.50	800.2	799.3	800.2				

[a] Calculated through the equation $H^E = x_1(1-x_1)\ [3200.7 + 140.4(2x_1 - 1) + 144.8(2x_1 - 1)^2 + 103.1(2x_1 - 1)^3]$ which fitted the experimental data with a standard deviation of 1.4 J mol^{-1}.

at least one of the liquids to be mixed is itself a pre-formed mixture. When one single liquid is a mixture which is then mixed with one pure component, P' may be calculated using

$$P' = \frac{H_1^E \varphi_1}{\left(\sum_{i=1}^{n} x_i V_i + V_1^E\right)} \tag{8}$$

In Eq. (8), H_1^E, V_1^E and φ_1 are the excess enthalpy, excess volume and the volumetric flow, respectively, of the mixture being diluted, and x_i and V_i are the mole fraction and molar volume of its n components.

The excess enthalpy H^E of the final mixture was eventually calculated by the equation

$$H^E = \frac{P_{\text{mix}}}{\left[\varphi_1 \bigg/ \left(\sum_{i=1}^{n} x_i V_i + V_1^E\right) + \varphi_2 / V_2\right]} \tag{9}$$

where P_{mix} is the experimental power calculated through Eq. (7), and φ_2 and V_2 are the flow and the molar volume of liquid 2, the pure component used as the diluent, respectively.

The flow of the pumps was regularly checked by weight.

Our calorimetric apparatus was tested by measurements on the binary system benzene–cyclohexane. Experimental data from the present work, at rounded values of mole fraction, are compared with data of Stokes et al. [14] and Grolier [15] in Table 3. A good agreement is observed, particularly with the results of Stokes.

The densities of all liquids used in this work were measured by means of a vibration densimeter, Anton Paar, Model DMA60, equipped with the cell DMA 602.

3. Results

Experimental values of H^E and C_p^E for the three binary systems examined here are reported in Tables 4 and 5, respectively. Both properties were represented with

Table 4
Binary excess molar enthalpies H^E in J mol^{-1} at 298.15 K

EtOH(1)–THF(2)		EtOH(1)–cyHex(3)		THF(2)–cyHex(3)	
x_1	H^E	x_1	H^E	x_2	H^E
0.0102	51.0	0.1020	426.2	0.0201	61.8
0.0204	95.2	0.1708	520.2	0.0302	94.1
0.0281	127.9	0.3166	617.5	0.0351	107.6
0.0406	181.1	0.4427	639.8	0.0401	126.2
0.0557	235.2	0.5526	617.9	0.0411	135.5
0.0705	290.0	0.6495	564.7	0.0451	142.3
0.0828	334.8	0.9434	147.4	0.0970	286.1
0.0902	357.0			0.1014	291.4
0.1096	413.4			0.1287	351.6
0.1340	468.8			0.2101	516.7
0.1606	531.6			0.2495	571.2
0.1860	593.2			0.3065	645.0
0.2110	632.9			0.3631	694.9
0.2583	696.0			0.4431	739.8
0.3738	785.4			0.5205	734.4
0.4490	799.2			0.5708	725.9
0.4815	796.3			0.5946	705.4
0.5255	779.2			0.5946	712.7
0.5821	738.9			0.6657	651.2
0.6763	642.8			0.6661	649.4
0.7338	558.0			0.7563	534.4
0.7647	507.4			0.7996	465.2
0.8187	412.6			0.8417	392.1
0.8479	349.2			0.8693	330.7
0.8819	282.1			0.9031	254.8
0.9225	189.4			0.9620	107.1
0.9261	177.9				
0.9618	94.1				

a rational Redlich–Kister polynomial

$$Y_{ij}^{E} = \frac{x_i x_j \sum_{k=1}^{k=5} A_k (x_i - x_j)^{k-1}}{1 + A_0 (x_i - x_j)} \qquad (Y = H, C_p) \qquad (10)$$

where subscripts i and j ($i < j$) refer to the mixture components: EtOH (1), THF (2), cyHex (3). Table 6 reports the values of the A_k coefficients and the standard deviation of the fit, obtained using a non-linear least-squares treatment of the data reported in Tables 4 and 5.

Experimental values of H^E and C_p^E for the ternary system are reported in Tables 7 and 8. The data were fitted to the equation

$$Y_{123}^{E} = x_1 x_2 x_3 \sum_{m=0}^{3} \sum_{n=0}^{m} B_{mn} x_1^{m-n} x_2^{n} + \sum_{i=1}^{2} \sum_{j=i+1}^{3} Y_{ij}^{E} \qquad (Y = H, C_p) \qquad (11)$$

Table 5
Binary excess molar heat capacities C_p^E in J mol^{-1} K^{-1} at 298.15 K

EtOH(1)–THF(2)		EtOH(1)–cyHex(3)		THF(2)–cyHex(3)	
x_1	C_p^E	x_1	C_p^E	x_2	C_p^E
0.0400	0.04	0.0195	4.60	0.0517	−0.44
0.1018	0.82	0.0370	6.91	0.1070	−0.80
0.1140	0.51	0.0770	8.74	0.1970	−0.98
0.1680	1.04	0.0800	8.54	0.2950	−1.13
0.2000	1.79	0.0966	8.49	0.4210	−1.09
0.2300	1.32	0.1482	9.99	0.4460	−1.09
0.2989	2.48	0.1490	9.19	0.5170	−0.98
0.4010	2.80	0.1640	9.51	0.5790	−0.92
0.5010	3.27	0.1994	10.10	0.7080	−0.70
0.5073	2.67	0.2090	10.01	0.8285	−0.45
0.5576	2.97	0.2440	10.10	0.9130	−0.26
0.5982	2.82	0.3000	9.94		
0.6040	2.88	0.3100	9.91		
0.6060	2.53	0.3100	10.14		
0.6960	2.63	0.3430	9.80		
0.7002	2.43	0.3760	9.65		
0.7480	2.03	0.4130	8.95		
0.7900	1.71	0.4990	8.03		
0.8007	1.77	0.5580	7.50		
0.8680	1.39	0.6030	6.56		
0.9021	0.91	0.6570	5.88		
0.9120	0.83	0.6920	5.38		
0.9500	0.23	0.6998	5.42		
0.9910	0.05	0.7620	3.84		
		0.8030	3.23		
		0.8280	3.04		
		0.8770	1.93		
		0.8970	1.76		
		0.9580	0.67		

where Y_{ij}^E are the corresponding binary excess properties given by Eq. (10). Best values of coefficients B_{mn} and standard deviations of the fit are reported in Table 9.

Our binary data compare well with published data, when available, as may be seen from Fig. 1. Our excess enthalpies for the system EtOH + cyHex are practically coincident with those of Nagata and Kazuma [16]. We fitted our data of this mixture to Eq. (10) together with the experimental points of these authors. Our data are also in good agreement with those measured by Stokes and Adamson (±0.7% on average) [17] and larger by approx. 1.5% than those of Zhu et al. [18]. The data given by Hwang and Robinson [19], who smoothed a few previous experimental data, appear anomalously larger, particularly in the cyHex-rich region.

Table 6
Coefficients A_k of Eq. (10)

Property	Binary system	A_0	A_1	A_2	A_3	A_4	A_5	σ [a]
H^E in J mol^{-1}	EtOH(1)–THF(2)	–	3155.6	−700.68	323.92	−473.16	251.02	2.9
	EtOH(1)–cyHex(3) [b]	0.97174	2536.5	2046.8	601.01	463.64	–	1.2
	THF(2)–cyHex(3)	–	2974.4	−161.33	–	–	226.11	3.2
C_p^E in J mol^{-1} K^{-1}	EtOH(1)–THF(2)	–	11.841	1.5285	−5.3222	–	–	0.29
	EtOH(1)–cyHex(3)	0.95879	32.770	5.7819	−7.7744	–	–	0.22
	THF(2)–cyHex(3)	–	−4.0320	2.6898	−2.3931	–	–	0.04

[a] Standard deviation of the fit. [b] The fit included 20 experimental points from Ref. [16].

Table 7
Excess molar enthalpies H^E in J mol^{-1} of the ternary system EtOH(1)–THF(2)–cyHex(3) at 298.15 K

x_1	x_2	H^E	x_1	x_2	H^E
0.3466	0.3064	1186.3	0.2384	0.3244	1194.8
0.1467	0.7063	820.4	0.2020	0.4275	1183.4
0.2962	0.4073	1192.2	0.1664	0.5283	1106.3
0.4484	0.1024	913.3	0.1316	0.6269	966.6
0.3973	0.2049	1089.1	0.0976	0.7233	779.9
0.0975	0.8048	587.8	0.0643	0.8175	512.4
0.0486	0.9027	327.8	0.8272	0.0799	426.9
0.1962	0.6073	1018.0	0.7520	0.1636	599.6
0.2463	0.5074	1135.0	0.6733	0.2511	735.0
0.0178	0.9156	256.7	0.5909	0.3428	837.7
0.0362	0.8282	478.7	0.5044	0.4390	902.1
0.0553	0.7378	696.9	0.4136	0.5399	900.9
0.0751	0.6440	869.6	0.3181	0.6461	831.1
0.0957	0.5466	1014.2	0.5897	0.0943	823.2
0.1170	0.4456	1103.7	0.5275	0.1899	1000.3
0.1392	0.3407	1132.6	0.4644	0.2867	1098.2
0.1622	0.2316	1076.8	0.4006	0.3847	1138.5
0.1862	0.1181	897.5	0.3360	0.4839	1119.0
0.4367	0.4572	1003.0	0.2705	0.5845	1034.9
0.5153	0.3596	980.8	0.2042	0.6863	872.0
0.5912	0.2652	907.7	0.1370	0.7895	612.7
0.6647	0.1739	786.8	0.0689	0.8940	361.5
0.7358	0.0855	619.2	0.5467	0.0454	731.4
0.3555	0.5582	967.0	0.4368	0.0564	807.2
0.2713	0.6627	861.4	0.6440	0.0356	645.8
0.0937	0.8834	398.9	0.7307	0.0269	540.3
0.0757	0.1245	749.8	0.8085	0.0191	421.6
0.0655	0.2424	905.0	0.8786	0.0121	290.7
0.0558	0.3542	955.2	0.9421	0.0057	151.9
0.0466	0.4608	938.1	0.6536	0.0742	688.2
0.0379	0.5614	862.6	0.3889	0.0441	763.5
0.0318	0.9097	286.5	0.1484	0.0168	541.5
0.3138	0.1107	946.9	0.4877	0.0553	782.0
0.2756	0.2188	1123.9	0.5753	0.0653	756.0

Concerning the system THF + cyHex, our H^E values are in fair agreement with those of Arm and Bankay [20] and Murakami et al. [21], while they are larger at $x \approx 0.5$ by approx. 30 J mol^{-1} than those of Cabani and Ceccanti [22]. Our H^E data are also larger than data published by Bolinaga et al. [23] at 30°C and much larger, up to 80 J mol^{-1}, with respect to those by Geier and Bittrich [24] at 21°C in the THF-rich region, even after converting these data to 25°C using C_p^E values measured in the present work. No H^E data are available to our knowledge for the mixture EtOH + THF, which shows a slightly asymmetric trend and a maximum ($H^E = 800$ J mol^{-1} at $x_{\mathrm{EtOH}} = 0.45$) that is higher than those of the other two systems.

Table 8
Excess molar heat capacities C_p^E in J mol^{-1} K^{-1} of the ternary system EtOH(1)–THF(2)–cyHex(3) at 298.15 K

x_1	x_2	C_p^E	x_1	x_2	C_p^E
0.4916	0.0430	7.54	0.5950	0.1500	5.25
0.4095	0.2029	6.26	0.5010	0.2810	5.15
0.4616	0.1013	7.12	0.4210	0.3990	4.54
0.3567	0.3057	5.35	0.3390	0.5170	3.92
0.2541	0.5053	4.06	0.2435	0.6513	2.58
0.3060	0.4043	4.75	0.8500	0.0905	1.89
0.1524	0.7033	2.36	0.7494	0.1508	3.17
0.2031	0.6047	3.17	0.6005	0.2397	4.37
0.5130	0.9000	0.53	0.1700	0.4905	2.78
0.1022	0.8011	1.32	0.1242	0.3750	2.83
0.5677	0.4050	4.11	0.1002	0.1005	6.02
0.5687	0.3549	4.05	0.1417	0.0502	8.08
0.0590	0.1005	5.18	0.1265	0.1485	5.76
0.0505	0.0506	5.51	0.1127	0.2485	3.94
0.2980	0.3010	5.28	0.0903	0.3997	2.10
0.2014	0.1993	6.01	0.0603	0.6002	0.47
0.2521	0.1603	6.76	0.0091	0.8027	−0.47
0.2840	0.0530	8.78	0.0047	0.9016	−0.37
0.1642	0.4504	2.90	0.0166	0.6967	−0.47
0.2114	0.3003	4.82	0.0194	0.7916	−0.31
0.1359	0.5502	1.94	0.1084	0.0690	6.80
0.1038	0.6505	1.31	0.0171	0.8868	−0.16
0.6660	0.0497	5.37			

Table 9
Ternary coefficients B_{mn} of Eq. (11)

	$B_{mn}(H) \times 10^{-5}$ in J mol^{-1}	$B_{mn}(C_p) \times 10^{-2}$ in J mol^{-1} K^{-1}
B_{00}	0.3899	0.8839
B_{10}	−1.6069	−2.4020
B_{11}	−1.0556	−3.0415
B_{20}	2.5818	2.0157
B_{21}	3.1953	4.8776
B_{22}	1.4846	2.9420
B_{30}	−1.3785	–
B_{31}	−2.5295	–
B_{32}	−1.8688	–
B_{33}	−0.8711	–
σ [a]	11	0.18

[a] Standard deviation of the fit.

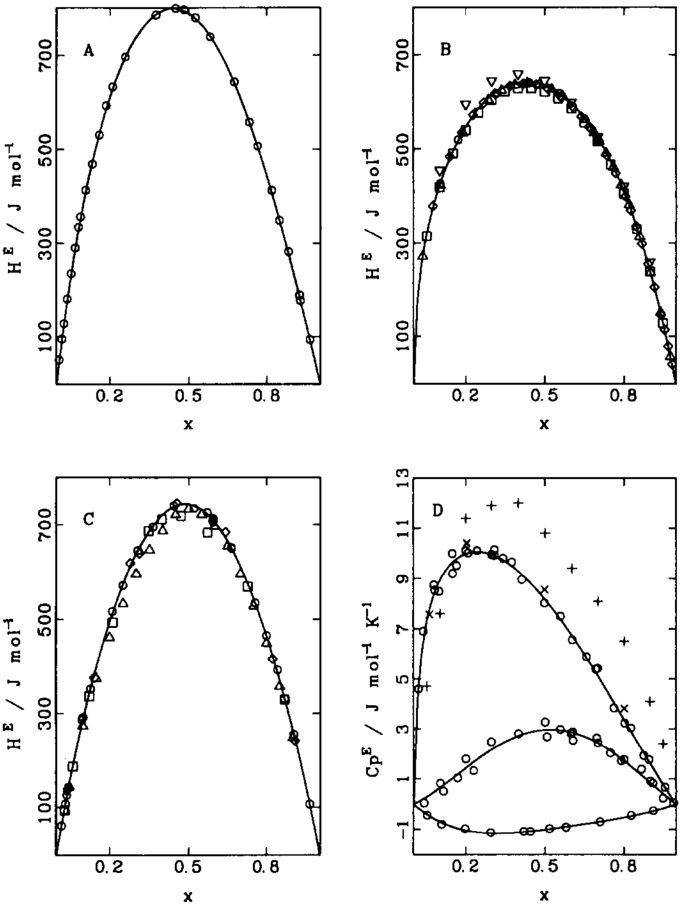

Fig. 1. Plot of experimental data from the present work (○) and best-fitting Redlich–Kister (Eq. (10)) curves (——). A, EtOH + THF; B, EtOH + cyHex: △, Ref. [16]; □, Ref. [18]; ◇, Ref. [17]; ▽, Ref. [19]. C, THF + cyHex: □, Ref. [22]; ◇, Ref. [21]; △, Ref. [20]. D, from top to bottom, curves and symbols refer to: EtOH + cyHex; EtOH + THF; THF + cyHex: ×, Ref. [26]; +, calculated from H^E data of Refs. [16] and [27]. In all cases, x is the molar fraction of the first component of the binary mixture.

As far as C_p^E values are concerned, the system EtOH + cyHex exhibits positive values with the clear asymmetric trend characteristic of alcohol + hydrocarbon mixtures [25]. Our values are in good agreement with the data of Klesper [26] and also with C_p^E values which can be calculated from H^E measurements by Nagata and coworkers at 25°C [16] and 35°C [27]. A perfectly symmetric curve, with moderately positive values, is instead exhibited by the EtOH + THF mixture, while the THF + cyHex system displays slightly negative values (minimum of $H^E = -1.1$ J mol^{-1} K^{-1} at $x_{THF} = 0.3$).

The excess enthalpies of the ternary system (see Fig. 2A) present a high maximum (approx. 1200 J mol^{-1}) near the center of the diagram, largely deter-

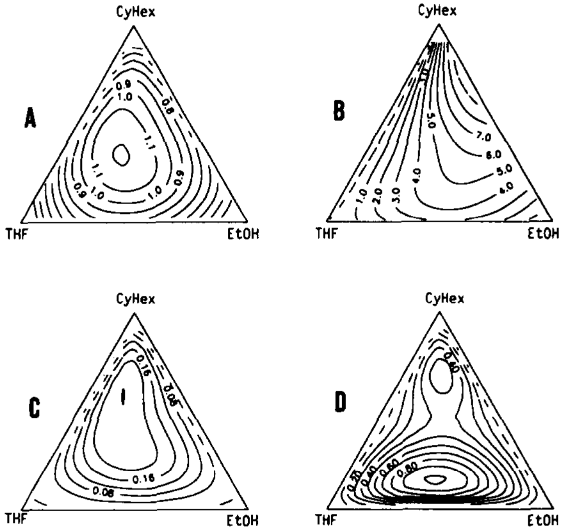

Fig. 2. Representation of contours for constant values of H^E (A), of C_p^E (B), and excess ternary contribution to H^E (C), and to C_p^E (D), for the ternary system EtOH + THF + cyHex. Units are kJ mol^{-1} and J mol^{-1} K^{-1} for H and C_p, respectively.

mined by the ternary excess contribution which displays a maximum in the same region (approx. 240 J mol^{-1}, see Fig. 2C). The quantity C_p^E, however, does not show maximum points inside the triangle even though two small maxima of the ternary contribution are present (see Fig. 2B and D).

3.1. Predictive models

A few predictive models were tested as to their capability to reproduce excess enthalpies and excess heat capacities of the systems examined in this work: the UNIQUAC [3], the UNIFAC, in the version recently proposed by Gmehling et al. [4], and the Nitta–Chao [5] models.

3.1.1. Original UNIQUAC

By differentiating with respect to temperature the term g^E/RT in the original expression given by Abrams and Prausnitz [3], one obtains the following expression for the excess enthalpy of a system containing n components

$$H^E = RT \sum_{j=1}^{n} q_j x_j \left[\frac{\sum_{i=1}^{m} q_i x_i \delta_{ij}^* \exp(-\delta_{ij})}{\sum_{i=1}^{m} q_i x_i \exp(-\delta_{ij})} \right] \tag{12}$$

where $\delta_{ij} = \Delta u_{ij}/RT$, $\delta_{ij}^* = -T(\partial\delta_{ij}/\partial T)_{P,x}$, $m = n$, and $\delta_{ij} = \delta_{ij}^* = 0$ for $i = j$. The q_i terms are parameters proportional to the molecular surface, defined as $q_i = A_{wi}/A_{ws}$, where A_{wi} is the molecular surface area calculated according to Bondi [28] and

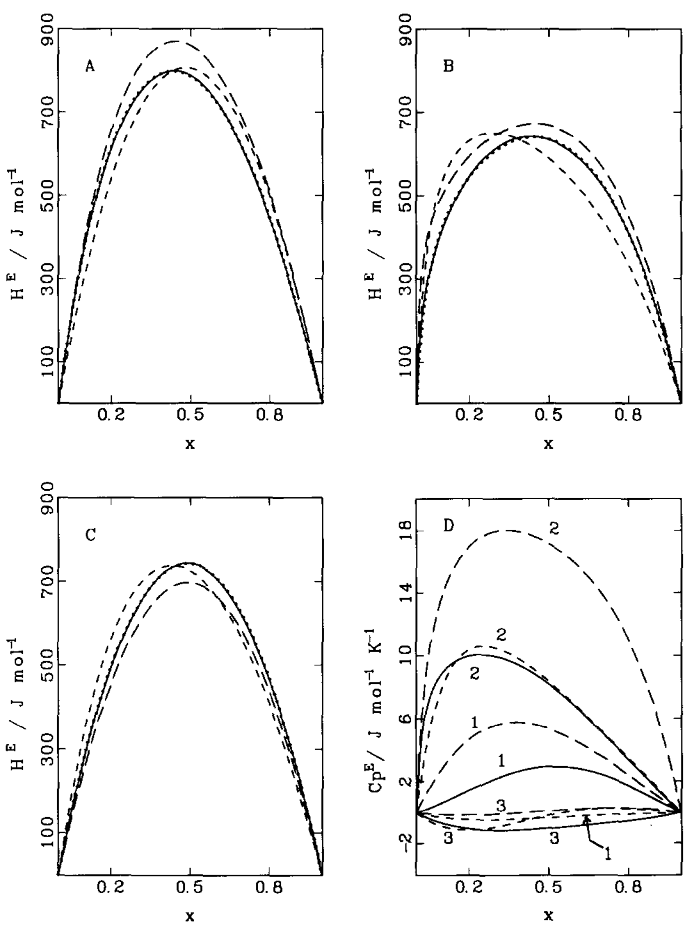

Fig. 3. Comparison of experimental data best-fitting curves (Eq. (10)) with prediction of theories and models: ——, Redlich–Kister curves; · · ·, UNIQUAC; — —, UNIFAC; - -, Nitta–Chao. A and D, 1, EtOH + THF; B and D, 2, EtOH + cyHex; C and D, 3, THF + cyHex. In A, B and C, curves (——) and (· · ·) practically coincide.

A_{ws} is the surface area of a standard segment (usually CH_2) here assumed as $A_{ws} = 3.161 \times 10^9$ cm^2 mol^{-1} [5].

Eq. (12) contains only binary parameters, four for each binary mixture, which were calculated by fitting this equation to our experimental binary H^E data. These parameters can be used in the same equation to predict H^E values for the ternary system. The trend of the experimental H^E values are satisfactorily reproduced for all binary systems examined here (see Fig. 3). The same parameters also reproduce H^E values for the ternary mixture (see Fig. 4).

By differentiating Eq. (12) with respect to temperature one gets a rather complex expression for C_p^E which has little application. Our experimental C_p^E data were used,

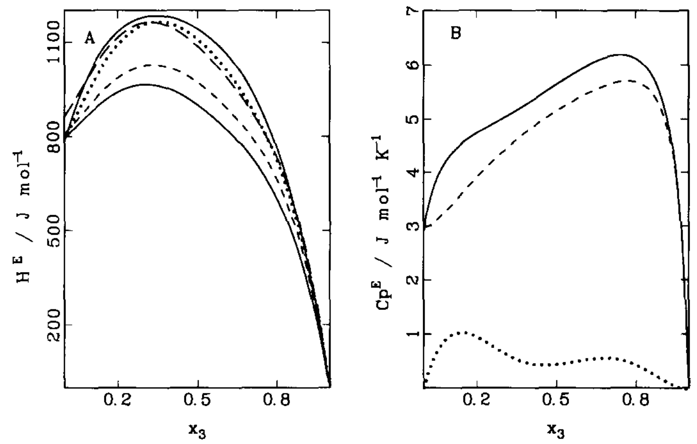

Fig. 4. Plot of excess functions of the ternary system EtOH(1) + THF(2) + cyHex(3) along the line $x_1 = x_2$. A: ——, top, Redlich–Kister curve (Eq. (11)); bottom, Redlich–Kister curve without excess ternary contribution; · · ·, UNIQUAC; — —, UNIFAC; – –, Nitta–Chao. B: ——, Redlich–Kister curve; – –, Redlich–Kister curve without excess ternary contribution; · · ·, excess ternary contribution (Eq. (11) with only the first term on right-hand side).

inside the UNIQUAC procedure, in order to obtain the temperature dependence of parameters δ_{ij} and δ^*_{ij}. Assuming a quadratic expression for the function $\Delta u_{ij} = f(T)$, we derived the following equations to represent the previous parameters within a limited temperature range around 25°C

$$\begin{aligned} \delta_{ij}(T) &= \delta_{ij}(T_0) + a_{ij}(1/T - 1/T_0) + b_{ij}(T - T_0) \\ \delta^*_{ij}(T) &= \delta^*_{ij}(T_0) + a_{ij}(1/T - 1/T_0) - b_{ij}(T - T_0) \end{aligned} \qquad (13)$$

where $T_0 = 298.15$.

The values of the parameters of Eq. (13) are reported in Table 10 together with values of the standard deviations.

Table 10
Parameters used for the UNIQUAC model

System	i-j	$\delta_{ij}(298.15)$	a_{ij}	b_{ij}	$\delta^*_{ij}(298.15)$	σ [a]
EtOH(1)–THF(2)	1–2	−0.40749	18.54	−1.566	0.52938 [b]	
	2–1	2.0465	463.20	3.455×10^{-3}	0.52347 [b]	2.1
EtOH(1)–cyHex(3)	1–3	0.17141	84.02	-3.717×10^{-4}	0.39263 [b]	
	3–1	3.6750	−1942	-3.217×10^{-2}	3.0780 [b]	4.2
THF(2)–cyHex(3)	2–3	−0.2956	[c]	[c]	0.4680	
	3–2	1.8741	[c]	[c]	0.1442	2.0
EtOH–THF–cyHex	–	–	–	–	–	25 [d]

[a] Standard deviation of the fit in J mol^{-1}. [b] Values of this parameter, not independent of the other parameters, are given only for convenience. [c] Parameter not calculated owing to the low value of C_p^E for this system. [d] Root mean square deviation.

3.1.2. Modified UNIFAC

Very recently Gmehling et al. [4] proposed an updated version of the UNIFAC method (Dortmund, Germany) [29] containing an extended list of interaction parameters between different molecular groups, supported by a very large thermodynamic data base (Dortmund Data Bank). This list, unlike others [30,31], includes contributions by cyclic ethers. The procedure can easily be applied and allows the prediction of several thermodynamic properties (G^E,H^E,γ^∞,C_p^E) even at different temperatures. Values of H^E and C_p^E predicted by this model for the systems examined in this work are compared with experimental data in Fig. 3. Calculated C_p^E values were obtained as ratios of finite increments $\Delta H^E/\Delta T$ using two H^E values calculated at two temperatures ($\Delta T = 5°C$) around 25°C.

Predicted excess enthalpies are very satisfactory for all binary mixtures and even better for the ternary system. For excess heat capacities, however, the calculated values are in all cases much larger than experimental data.

3.1.3. Nitta–Chao

This model represents a predictive methodology based on the rigorous cell liquid theory and the calculation of the molecular partition function using the hard sphere equation of state of Carnahan and Starling [32]. For practical purposes it adopts the quasi-chemical approach and the use of group contributions. These features provide the model with the capability of predicting a large number of thermodynamic properties for any kind of liquid mixture. However, it presents a higher calculation complexity and a smaller base of molecular interaction parameters. This model requires definitions of the "hard core" volume V_i^* for each molecular group i, a dispersive interaction energy ε_{ij} between groups i and j and, for systems with chemical association, the additional interaction energy, σ_{ij}. The temperature dependence of V_i^* and σ_{ij} is accounted for by introducing the additional parameters $V_{i,0}^*$ and a_i, and σ_{ij}° and σ'_{ij}, respectively.

Values of characteristic parameters used in this work for calculating H^E and C_p^E are reported in Tables 11 and 12. Some parameters relative to the cyclic ether

Table 11
Parameters of Nitta–Chao model characteristic of single molecular groups [a]

Group	$V_{i,0}^*$ in cm^3 mol^{-1}	a_i in K	c_i [b]	Q_i [c]
CH_3	13.46	23.7	0.338	6.71
CH_2	10.25	23.7	0.093	4.27
$CH_{2,ring}$	9.76	21.2	0.165	4.84
O	4.10	55.1	0.128	1.9
OH(O)	8.01	39.6	0.245	3.62
OH(H)	–	–	–	1.00

[a] Values taken from Ref. [35]. [b] Number of external degrees of freedom of group i; see Ref. [5]. [c] Number of contacts of group i; see Ref. [5].

Table 12
Interaction parameters ε_{ij} of Nitta–Chao model [a]

	CH_3	CH_2	$CH_{2,\mathrm{ring}}$	O_e	OH(O)	OH(H)
CH_3	2515					
CH_2	2515	2515				
$CH_{2,\mathrm{ring}}$	2572	2572	2674			
O_e	3500	3500	4300 [b]	6532		
OH(O)	3738	3738	3980 [b]	9598	6887	
OH(H)	3738	3738	3980 [b]	9598	6887	6887
				12900 [b,c]	12552 [c]	
				14000 [b,d]	17154 [d]	

[a] All values (in J mol^{-1}) taken from Ref. [35] except when otherwise indicated. [b] Calculated in the present work (see text). [c] σ°_{ij}. [d] σ'_{ij}.

oxygen, not available in the literature, and to the cyclic CH_2 group, were calculated by us through a best-fitting procedure which allowed reproduction of the vaporization heats of a series of cyclic ethers at several temperatures [33] as well as excess enthalpies and Gibbs energies [34] for the system EtOH + THF. In Figs. 3 and 4, the thermodynamic properties calculated by this model are compared with the experimental functions (Eqs. (10) and (11)) for binary and ternary mixtures, respectively. Enthalpy values of binary mixtures are satisfactorily reproduced, though a displacement of the maximum values is generally observed. Values predicted for the ternary system are, however, notably lower than the experimental ones with a deviation at the maximum of approx. 200 J mol^{-1}. This model is not capable of predicting the ternary excess contribution for the present system.

As far as the excess heat capacities are concerned, a satisfactory agreement is obtained for the EtOH + cyHex system and a still acceptable prediction is obtained for THF + cyHex, while practically zero C_p^E values are predicted for the EtOH + THF mixture over the whole composition range (see Fig. 3D).

4. Discussion

A few aspects of the trend of the thermodynamic properties observed for the mixtures considered here deserve brief discussion.

Table 13 reports useful features of the three binary systems examined: the maximum values of excess enthalpies $H^E_{\max}$, and heat capacities, $C^E_{p,\max}$, and the limiting ($x_k \to 0$) slopes of the excess enthalpies, h°_k. The mixture EtOH + cyHex presents the lowest value of $H^E_{\max}$ and at the same time the largest values of $C^E_{p,\max}$ and h°_k. This characteristic behavior, already discussed by Costas and Patterson [25,36] for other systems, was explained in terms of a marked decrease in hydrogen bonding accompanied by an increase in local structural order of the mixture as the hydrocarbon is added to pure alcohol, due to the high degree of self-association of this latter component.

Table 13
Characteristic features of binary mixtures [a]

Mixture $i+j$	$H^{\mathrm{E}}_{\mathrm{max}}$ in J mol^{-1}	$C^{\mathrm{E}}_{p,\mathrm{max}}$ in J mol^{-1} K^{-1}	h^0_i [b] in kJ mol^{-1}	h^0_j [b] in kJ mol^{-1}
1+2	800	2.9	3.75	2.56
1+3	640	9.9	22.19	2.86
2+3	743	−1.0	3.36	3.04

[a] 1, EtOH; 2, THF; 3, cyHex. [b] $h^0_k = \lim_{x_k \to 0} (H^E/x_k)$.

The behavior of the THF + cyHex mixture is practically the opposite, i.e. a notably larger $H^{\mathrm{E}}_{\mathrm{max}}$ and low values of h°_k and $C^{\mathrm{E}}_{p,\mathrm{max}}$ are shown, the latter being small and negative over the whole composition range. We may therefore reasonably argue that the cyclic ether dipole–dipole interactions in the pure liquid, and thus the orientational order, are markedly reduced by the introduction of the inert hydrocarbon.

The binary system of the two polar components, EtOH and THF, is characterized by the largest $H^{\mathrm{E}}_{\mathrm{max}}$, and intermediate values of h°_k and of the excess heat capacities, these latter now being always positive and with the $C^{\mathrm{E}}_{p,\mathrm{max}}$ value practically centered at the equimolar mixture. This behavior is certainly more difficult to interpret on the basis of the available thermodynamic data. It can only be affirmed that the large value of $H^{\mathrm{E}}_{\mathrm{max}}$ indicates a clear decrease in molecular interactions in the mixture with respect to the pure liquids, and that the increase in structural order suggested by positive excess heat capacities should be ascribed, owing to their symmetrical trend, not only to alcohol self-association but also to ether–alcohol association through hydrogen bonds involving the ether oxygen.

As to the ternary system, large positive values of H^{E} are shown, the ternary excess (Eq. (11), first term on the right-hand side) also being markedly positive. This is clearly shown in Fig. 4A which compares the trend of a series of experimental excess enthalpies, characterized by the largest observed enthalpy effects, with corresponding values calculated through Eq. (11) by taking into account only binary parameters. Excess heat capacities are also always positive over the whole ternary domain, except for a limited region with low alcohol content; the ternary excess is also positive. Again, Fig. 4B shows these excess quantities for a series of mixtures chosen in correspondence with the largest observed C^{E}_p values.

The ternary excess enthalpy effect suggests that the weakening of molecular interactions observed when going from the pure liquids to any two-component mixture is more effective when all three components are mixed together. On the same grounds, the ternary excess of heat capacity indicates a still higher structural order in the three-component mixture.

Finally, we would like to observe that the ternary excess heat capacity, unlike the enthalpy function, exhibits two different maxima, curiously both at equimolar concentration of the two polar components. We hope that this fact, as well as the general behavior of this ternary system, can be satisfactorily explained when the analysis of other thermodynamic properties, such as G^{E} and V^{E}, determined in this laboratory, will be complete.

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