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Excess enthalpies for pseudobinary mixtures containing vegetable oils at the temperatures 298.15 K, 353.15 K and 383.15 K

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ABSTRACT

This paper presents excess enthalpies for the following systems containing refined vegetable oils: soybean oil + methanol (at 353.15 K/722 kPa), soybean oil + ethanol (at 353.15 K/687 kPa and 383.15 K/653 kPa), soybean oil + *n*-hexane (at 353.15 K/722 kPa and 383.15 K/756 kPa), soybean oil + propan-2-ol (at 298.15 K/998 kPa), sunflower oil + methanol (at 353.15 K/791 kPa), sunflower oil + ethanol (at 353.15 K/894 kPa and 383.15 K/860 kPa), sunflower oil + *n*-hexane (at 353.15 K/756 kPa and 383.15 K/894 kPa), sunflower oil + propan-2-ol (at 298.15 K/929 kPa), rapeseed oil + methanol (at 353.15 K/963 kPa), rapeseed oil + ethanol (at 353.15 K/998 kPa and 383.15 K/1136 kPa), and rapeseed oil + *n*-hexane (at 353.15 K/894 kPa and 383.15 K/1136 kPa). The measurements were carried out with a commercially available isothermal flow calorimeter. The experimental H^E values have been correlated using the Redlich-Kister polynomial equation. The results for systems with propan-2-ol and some values of partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, obtained in this study have been compared to those available in the literature. The results were also discussed in terms of molecular interactions.

1. Introduction

Vegetable oils and related compounds play an important role for the food processing industry as well as for the pharmaceutical, cosmetics, chemical, and petrochemical industries. The vegetable oils can be used as feedstock in the production of several edible and non-edible industrial goods. But nowadays the interest in these components is growing since they are considered as potential renewable source of biofuels.

Commercially important vegetable oils, as others edible fat and oils, have as main constituents the triacylglycerols (TAGs), which are formed by the condensation reaction of glycerol and fatty acids. Partial acylglycerols (mono- and diacylglycerols) and free fatty acids (FFA) are normally present as minor compounds, and also traces of phospholipids, sterols, tocopherols and tocotrienols, vitamins, and coloring matters as carotenes and chlorophylls. Most natural vegetable oils are complex mixtures of many different triacylglycerols, and their exact composition further varies according to the specific source [1–3].

In vegetable oil industrial processes there are several purification and separation steps, such as solvent extraction and solvent recovery steps [4–6], fatty acids distillation [7], fatty alcohols fractionation, production and purification of partial acylglycerols [7–9], physical refining (mainly deacidification process) [10,11], and deodorization of vegetable oils [12,13]. The same occurs in the biodiesel production with specific steps for biofuel purification and recovery of the alcoholic reactant used in excess [14–16]. In all these cases thermophysical properties and phase equilibrium data are of utmost importance for equipment design and optimization [17–19].

Despite the great variety and practical importance of fatty compounds, experimental data for fatty mixtures as vegetable oils are scarce in the literature and even less data are available for pure fatty components. Therefore, our research group has conducted a series

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List of symbols

H^E	excess enthalpy or heat of mixing
TAG	triacylglycerol
FA	fatty acid
FFA	free fatty acid
VLE	vapor–liquid equilibrium
LLE	liquid–liquid equilibrium
G^E	excess Gibbs energy
AOCS	American Oil Chemists' Society
GC	gas chromatography
M	molar mass
C z:y	z = number of carbons and y = number of double bonds
x	molar fraction
w	mass fraction
T	trans isomers
W	water content
IV	iodine value
L	lauric acid
M	myristic acid
P	palmitic acid
Po	palmitoleic acid
Ma	margaric acid
S	stearic acid
O	oleic acid
Li	linoleic acid
Le	linolenic acid
A	arachidic acid
Ga	gadoleic acid
Be	behenic acid
Lg	lignoceric acid
Ne	nervonic acid
UNIFAC	UNIversal Functional Activity Coefficient
x_1	mole fraction of component 1
x_2	mole fraction of component 2
A_i	adjustable parameter of the Redlich-Kister equation
m	number of parameters of the Redlich-Kister equation
RMSD	root mean square deviation
N	number of experimental values
T	absolute temperature
$H_i^{E,\infty}$	partial molar excess enthalpy at infinite dilution of compound i

Subscripts

i	identification of Redlich-Kister parameter
exptl	experimental data
calcd	calculated data

Superscripts

E	excess property
∞	at infinite dilution

of studies involving data measurement and model development for the estimation and prediction of fatty compound properties [20–30].

Excess enthalpy or heat of mixing (H^E) is an important thermodynamic property, because, when measured at different temperatures, together with phase equilibrium (as vapor–liquid equilibrium—VLE and liquid–liquid equilibrium—LLE) data it can be used for the revision and extension of group contribution methods, such as Modified UNIFAC (Dortmund) or for fitting reliable temperature-dependent G^E model parameters [31–33], since H^E data sets measured at various temperatures deliver the correct temperature dependence of the activity coefficients, which is described quantitatively by the Gibbs-Helmholtz equation [18]. This equation provides a direct relationship between the temperature dependence of the activity coefficient and the partial molar excess enthalpy [18,31]. Excess properties can also reflect differences between energetic and structural effects in a solution relative to those effects observed when its components are not mixed [33].

In the case of systems formed by fatty compounds, however, a limited number of excess enthalpy data are available in the literature. We are aware of just one report (Resa et al. [34]) dealing with excess enthalpy (H^E) measurements for mixtures containing vegetable oils, but only for mixtures with alcohols as well as at ambient temperature (298.15 K), as often occurs for most of the published data on excess enthalpy values [31]. This means that data at higher temperatures are still required. Three other papers have reported data of partial molar excess enthalpies at infinite dilution deduced from activity coefficient data: namely a recent publication from our group for three refined vegetable oils (soybean, sunflower and rapeseed oils) [25], and other reports for olive [35] and soybean [36] oils.

In this work, systematic H^E measurements for binary mixtures with refined vegetable oils (soybean, sunflower and rapeseed oils) were carried out at temperature from 298.15 to 383.15 K using a commercially available isothermal flow calorimeter. The systems presented in this paper were chosen to extend the H^E database at higher temperatures, which is required for the further development of Modified UNIFAC (Dortmund).

2. Experimental

2.1. Materials

Refined soybean oil was purchased from Vandermoortele Deutschland GmbH, refined sunflower and refined rapeseed oils were purchased from Brökelmann + Co and Oelmühle GmbH + Co. The refined vegetable oils were further dried over molecular sieve and subjected to vacuum for at least 24 h. These procedures removed any water and volatile impurities present in the vegetable oils. The water content of all chemicals and vegetable oils was analyzed using the Karl Fischer titration technique. The results obtained have shown the water content was less than 100 mg kg^{-1}.

The three alcohols and n-hexane used in this work, including their purity (verified by gas chromatography) and suppliers, are summarized in Table 1. The chemicals were not subjected to further purification.

The compositions of the refined vegetable oils investigated, expressed in terms of the corresponding fatty acids (FA), were determined by gas chromatography of fatty acid methyl esters using the official method (1–62) of the American Oil Chemists' Society (AOCS) [37] and are presented in Table 2. Prior to the chromatographic analysis, the fatty acids of the samples were converted to their respective methyl esters using the method of Hartman and Lago [38], as already used by Lanza et al. [39], Silva et al. [40] and Follegatti-Romero et al. [28]. The chromatographic analyses were carried out using an Agilent 6850 Series CG capillary gas chromatography system under the same experimental conditions described by Belting et al. [25].

The free fatty acid content of refined vegetable oils was determined by titration according to the official AOCS method Ca 5a-40 [37]. The Iodine value (IV) was calculated from the fatty acid composition according to the official AOCS method Cd 1c-85 [37].

The probable triacylglycerol (TAG) compositions (Table 3) were obtained by gas chromatography and by the algorithm suggested by Antoniossi Filho et al. [41], as described in previous work [25].

Table 1
Information about the chemicals used.

Component	Supplier	Purification method[a]	Purity analysis method	Mass fraction purity	W[c] (mg kg^{-1})
Methanol	VWR International GmbH	–	GC[b]	>0.998	80
Ethanol	VWR International GmbH	–		>0.998	48
Propan-2-ol	Riedel-de Haen	–		>0.998	50
n-Hexane	Carl Roth GmbH	–		>0.99	30

[a] No further purification method was required.
[b] Gas chromatography.
[c] W = Water content.

Table 2
Fatty acid composition of refined vegetable oils investigated.

Fatty acid nomenclature	Trivial	Symbol	Cz:y[a]	M[b] (g mol^{-1})	Soybean oil		Sunflower oil		Rapeseed oil	
IUPAC					100x[c]	100w[d]	100x	100w	100x	100w
Dodecanoic	Lauric	L	C12:0	200.32	0.05	0.03	0.07	0.05	0.06	0.05
Tetradecanoic	Myristic	M	C14:0	228.38	0.10	0.09	0.11	0.09	0.09	0.07
Pentadecanoic			C15:0	242.40	0.04	0.04	0.05	0.04	0.04	0.04
Hexadecanoic	Palmitic	P	C16:0	256.43	11.46	10.55	6.94	6.36	4.89	4.46
cis-hexadec-9-enoic	Palmitoleic	Po	C16:1	254.42	0.11	0.10	0.13	0.12	0.22	0.20
Heptadecanoic	Margaric	Ma	C17:0	270.45	0.09	0.09	0.04	0.04	0.06	0.06
cis-heptadeca-10-enoic			C17:1	268.43	0.06	0.06	0.04	0.04	0.07	0.07
Octadecanoic	Stearic	S	C18:0	284.49	3.40	3.47	3.02	3.07	1.78	1.79
cis-octadeca-9-enoic	Oleic	O	C18:1	282.47	28.90	29.30	25.52	25.76	62.98	63.18
cis,cis-octadeca-9,12-dienoic	Linoleic	Li	C18:2	280.45	48.73	49.04	62.47	62.61	18.64	18.56
trans-trans-octadeca-9,12-dienoic	Linoelaidic		C18:2*T*[e]	280.45	0.19	0.19	0.40	0.40	0.10	0.10
All-*cis*-octadeca-9,12,15-trienoic	Linolenic	Le	C18:3	278.44	5.20	5.20	0.09	0.09	7.47	7.39
All-*trans*-octadeca-9,12,15-trienoic			C18:3*T*[e]	278.44	0.57	0.57			1.14	1.13
Icosanoic	Arachidic	A	C20:0	312.54	0.32	0.36	0.21	0.23	0.51	0.57
cis-icos-9-enoic	Gadoleic	Ga	C20:1	310.52	0.27	0.30	0.20	0.22	1.27	1.40
Docosanoic	Behenic	Be	C22:0	340.59	0.38	0.47	0.52	0.64	0.25	0.30
Docos-13-enoic	Erucic		C22:1	338.57					0.34	0.40
Tetracosanoic	Lignoceric	Lg	C24:0	368.65	0.12	0.16	0.18	0.24	0.10	0.13
cis-tetracos-15-enoic	Nervonic	Ne	C24:1	366.63					0.10	0.13
FFA[f]						0.0002		0.0002		0.0002
W[g] (mg kg^{-1})						<72		<73		<70
IV[h]						123.18		130.67		107.43

[a] C z:y, where z = number of carbons and y = number of double bonds.
[b] M = Molar mass.
[c] Molar fraction.
[d] Mass fraction.
[e] *Trans* isomers.
[f] Free fatty acid expressed as mass fractions of oleic acid.
[g] W = Water content.
[h] IV = Calculated iodine value.

Table 3
Probable triacylglycerol composition of refined vegetable oils investigated.

Main TAG[a]	Cz:y[b]	M[c] (g mol^{-1})	Soybean oil		Sunflower oil		Rapseed oil	
			100x[d]	100w[e]	100x	100w	100x	100w
POP	C50:1[c]	833.36	1.46	1.40			0.55	0.52
PLiP	C50:2	831.34	3.29	3.14	1.34	1.27		
POS	C52:1	861.42	0.89	0.89			0.59	0.58
POO	C52:2	859.40	5.42	5.35	2.06	2.02	8.26	8.07
POLi	C52:3	857.38	11.92	11.74	7.79	7.63	5.94	5.79
PLeO	C52:4	855.36					2.83	2.75
PLiLi	C52:4	855.36	14.85	14.59	11.80	11.52		
PLeLi	C52:5	853.35	1.95	1.91				
SOO	C54:2	887.46	1.74	1.77	0.66	0.67	2.66	2.68
SOLi	C54:3	885.43	6.87	6.99	3.60	3.64		
OOO	C54:3	885.43	2.79	2.83	2.69	2.72	34.98	35.21
OOLi	C54:4	883.42	13.39	13.58	16.74	16.89	23.44	23.54
OLiLi	C54:5	881.40	16.61	16.82	29.60	29.80		
OOLe	C54:5	881.40					14.39	14.42
LiLiLi	C54:6	879.38	16.95	17.12	23.71	23.82		
OLiLe	C54:6	879.38					4.15	4.15
LiLiLe	C54:7	877.37	1.87	1.88				
OOA	C56:2	915.51					0.60	0.63
OOGa	C56:3	913.50					1.00	1.04
OLiGa	C56:4	911.48					0.60	0.62

[a] Groups with a total triacylglycerol (TAG) composition lower than 0.5% were ignored.
[b] C z:y, where z = number of carbons (except carbons of glycerol) and y = number of double bonds.
[c] M = Molar mass.
[d] Molar fraction.
[e] Mass fraction.

The average molar mass of the vegetable oils was calculated using the respective fatty acid compositions presented in Table 2, assuming that all fatty acids are esterified to the glycerol molecules to form triacylglycerols. The values obtained for the refined soybean, sunflower and rapeseed oils are 874.04 g mol^{-1}, 875.55 g mol^{-1}, and 882.83 g mol^{-1}, respectively.

2.2. Apparatus and experimental procedure

The molar excess enthalpy (H^E) data were measured using a commercially available isothermal flow calorimeter from Hart Scientific (model 7501). The apparatus and procedure have been previously described by Gmehling [31]. In the calorimeter, two syringe pumps (model LC 2600, ISCO) provide a flow of constant composition and temperature through a thermostated flow cell equipped with a pulsed heater, a calibration heater, and a Peltier cooler mounted in a stainless steel cylinder. A back pressure regulator keeps the pressure constant (up to 2×10^4 kPa) and prevents evaporation and degassing effects. Flow rates were selected to cover the entire composition range. This device enables the detection of endothermic and exothermic mixing effects since the Peltier cooler works at constant power, producing a constant heat loss from the calorimeter cell, which is compensated by the pulsed heater. The energy per pulse was determined by electrical calibration with precision of approximately 0.5%. From the recorded frequency change of the pulsed heater (between base line and actual measurements) and the flow rates, the molar excess enthalpies could be obtained using the value of the energy evolved per pulse, the densities of both components at pump temperature, the given pressure and the molar mass of the compounds. The densities of the refined vegetable oils were obtained (by interpolation) from experimental data measured using a vibrating tube densimeter (Anton Paar Model 4500) with a precision of (5×10^{-5} g cm^{-3}), and the vegetable oil molar masses were estimated as described above. The densities and molar mass of the other components were taken from the Dortmund Data Bank (DDB) [42]. The experimental uncertainties are: ±0.01 K in temperature and less than 0.0005 in mole fraction. The uncertainty in H^E measurements was estimated to be less than 1%.

The results have been fitted using a Redlich-Kister polynomial equation (Eq. (1)) and the objective function presented in Eq. (2) as a function of composition.

$$\frac{H^E}{x_1 x_2} = \sum_{i=1}^{m} A_i (2x_1 - 1)^{i-1} \tag{1}$$

$$F = \sum \left[\left(\frac{H^E}{x_1 x_2} \right)_{exptl} - \left(\frac{H^E}{x_1 x_2} \right)_{calcd} \right]^2 \tag{2}$$

where H^E is the molar excess enthalpy, A_i are the adjustable parameters obtained by the least-square method, m is the number of parameters, x_1 and x_2 are the mole fractions of the compounds 1 and 2, respectively, and the subscripts *exptl* and *calcd* indicate the experimental and calculated data, respectively. Note that compound 2 corresponds to one of the edible oils that are considered as pseudocomponents.

3. Results and discussion

The 17 experimental excess enthalpy (H^E) data sets are given in Tables 4–14 with information about the temperature and the pressure used in the measurements. During the H^E measurements, no reaction was observed because of the short residence time in the calorimeter cell caused by the flow principle.

A description of the enthalpic real mixture behavior of these liquids will be made from the analysis of the experimental excess enthalpies data presented in this paper.

The results obtained for systems of alcohol + vegetable oil (see Tables 5–7, 9–11, 13 and 14) present high excess enthalpies. These systems are strongly endothermic, as also observed by Resa et al. [34] at 298.15 K, and the H^E values increase with increasing temperature.

The mixture alcohols + vegetable oil can show limited miscibility and thus a positive deviation from Raoult's law depending on temperature and composition. Silva et al. [28] and Chiyoda et al. [43] showed that the miscibility of vegetable oils and absolute ethanol increases with increasing temperature. At temperatures and concentrations studied in this work, no miscibility gap was observed. Our data are in agreement with the results obtained by Follegatti-Romero et al. [29] and Silva et al. [28], which presented the extrapolated critical solution temperatures (predicted by NRTL model) for the systems: soybean oil + ethanol (342.25 K), sunflower oil + ethanol (343.55 K) and rapeseed oil + ethanol (347.00 K), always lower than the experimental temperatures used in this work.

The H^E data of n-hexane + vegetable oil (see Tables 4, 8 and 12) are mostly positive but relatively small and they decrease with increasing temperature. This is a typical behavior for mixtures between a slightly polar compound (vegetable oil) and a non-polar compound (n-hexane), as observed by Gmehling [44]. However, these binary mixtures at 383.15 K and at high concentrations of n-hexane (above 0.94 molar fraction) presented negative values of H^E.

Table 4
Experimental H^E data for the system n-hexane (1) + soybean oil (2) at 353.15 K/722 kPa and 383.15 K/756 kPa.

x_1[a]	H^E[b] (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
353.15 K and 722 kPa					
0.0551	29.9	0.3871	192.2	0.7207	263.3
0.1104	60.0	0.4425	214.5	0.7764	255.6
0.1650	89.9	0.4980	234.6	0.8323	228.0
0.2210	114.9	0.5536	248.1	0.8881	191.6
0.2758	140.4	0.6095	261.0	0.9440	122.7
0.3321	167.7	0.6648	269.1		
383.15 K and 756 kPa					
0.0502	10.7	0.5978	106.4	0.9395	1.3
0.0993	26.1	0.6981	95.6	0.9496	−4.4
0.1982	48.7	0.7986	68.5	0.9596	−6.5
0.2986	77.7	0.8488	45.8	0.9698	−8.9
0.3976	92.7	0.8992	19.9	0.9798	−7.8
0.4981	103.0	0.9244	6.5	0.9899	−5.1

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.

[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 5
Experimental H^E data for the system methanol (1) + soybean oil (2) at 353.15 K/722 kPa.

x_1[a]	H^E[b] ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)
353.15 K and 722 kPa					
0.0569	595.0	0.4073	3478.3	0.7033	3680.2
0.1184	1231.8	0.4680	3728.1	0.7623	3313.2
0.1727	1721.5	0.5265	3818.8	0.8217	2683.4
0.2333	2280.6	0.5848	3886.9	0.8811	1826.1
0.2912	2748.1	0.6435	3811.5	0.9405	925.2
0.3505	3134.5				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 6
Experimental H^E data for the system ethanol (1) + soybean oil (2) at 353.15 K/687 kPa and 383.15 K/653 kPa.

x_1[a]	H^E[b] ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)
353.15 K and 687 kPa					
0.0570	583.6	0.4087	3670.9	0.7027	3927.3
0.1157	1216.0	0.4666	3988.9	0.7621	3610.0
0.1745	1767.9	0.5260	4108.2	0.8212	3118.2
0.2321	2274.0	0.5843	4193.6	0.8808	2417.9
0.2902	2857.8	0.6432	4126.6	0.9403	1452.8
0.3492	3318.2				
383.15 K and 653 kPa					
0.0571	625.4	0.4090	3894.7	0.7029	4559.6
0.1158	1335.3	0.4668	4215.3	0.7623	4261.5
0.1746	1949.5	0.5262	4554.9	0.8216	3747.3
0.2323	2490.6	0.5846	4671.8	0.8809	2964.5
0.2904	3057.3	0.6442	4679.8	0.9404	1798.0
0.3494	3498.8				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 7
Experimental H^E data for the system propan-2-ol (1) + soybean oil (2) at 298.15 K/998 kPa.

x_1[a]	H^E[b] ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)
298.15 K and 998 kPa					
0.0535	465.4	0.3864	2857.8	0.6829	2985.9
0.1082	953.6	0.4429	3012.5	0.7444	2746.8
0.1601	1450.3	0.5023	3133.7	0.8070	2366.4
0.2167	1911.6	0.5619	3149.8	0.8705	1832.0
0.2711	2341.0	0.6214	3119.4	0.9348	1075.3
0.3285	2632.1				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 8
Experimental H^E data for the system *n*-hexane (1) + sunflower oil (2) at 353.15 K/756 kPa and 383.15 K/894 kPa.

x_1[a]	H^E[b] ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)	x_1	H^E ($\mathrm{J\,mol^{-1}}$)
353.15 K and 756 kPa					
0.0553	29.5	0.3878	187.2	0.7213	264.1
0.1107	61.0	0.4433	210.3	0.7769	254.9
0.1654	83.0	0.4988	226.0	0.8327	233.0
0.2215	113.5	0.5543	243.9	0.8884	190.2
0.2764	134.5	0.6102	255.8	0.9442	123.3
0.3327	166.6	0.6655	264.8		
383.15 K and 894 kPa					
0.0505	8.5	0.5993	111.2	0.9198	13.7
0.0999	21.9	0.6994	99.8	0.9399	1.9
0.1992	48.7	0.7595	86.0	0.9499	−0.3
0.2999	74.2	0.8296	61.2	0.9599	−5.1
0.3991	98.3	0.8798	36.2	0.9700	−5.8
0.4997	109.3	0.8998	22.7	0.9800	−4.9

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 9
Experimental H^E data for the system methanol (1) + sunflower oil (2) at 353.15 K/791 kPa.

x_1[a]	H^E[b] (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
353.15 K and 791 kPa					
0.0570	596.5	0.4082	3508.2	0.7038	3670.3
0.1135	1242.1	0.4690	3729.1	0.7628	3290.9
0.1686	1731.2	0.5274	3876.5	0.8221	2663.6
0.2340	2257.9	0.5857	3926.2	0.8814	1821.6
0.2920	2704.7	0.6444	3850.6	0.9406	925.6
0.3513	3215.4				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 10
Experimental H^E data for the system ethanol (1) + sunflower oil (2) at 353.15 K/894 kPa and 383.15 K/860 kPa.

x_1[a]	H^E[b] (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
353.15 K and 894 kPa					
0.0573	543.2	0.4101	3606.3	0.7049	3885.6
0.1163	1094.7	0.4694	3949.2	0.7638	3563.5
0.1753	1761.7	0.5285	4064.2	0.8203	3077.4
0.2359	2243.0	0.5875	4114.3	0.8819	2388.9
0.2938	2794.5	0.6460	4095.2	0.9409	1423.9
0.3525	3323.2				
383.15 K and 860 kPa					
0.0574	522.4	0.4084	4018.0	0.7039	4640.6
0.1163	1205.9	0.4680	4409.7	0.7628	4355.2
0.1753	1822.8	0.5262	4679.9	0.8220	3830.9
0.2331	2424.8	0.5857	4847.4	0.8813	3042.6
0.2914	2951.3	0.6446	4836.1	0.9406	1855.5
0.3505	3560.4				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 11
Experimental H^E data for the system propan-2-ol (1) + sunflower oil (2) at 298.15 K/929 kPa.

x_1[a]	H^E[b] (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
298.15 K and 929 kPa					
0.0524	591.1	0.3873	3055.4	0.6846	3057.8
0.1079	1168.2	0.4457	3203.3	0.7464	2796.9
0.1626	1728.7	0.5048	3284.1	0.8086	2398.4
0.2178	2164.4	0.5642	3283.1	0.8717	1872.6
0.2742	2519.7	0.6238	3206.2	0.9354	1108.3
0.3302	2830.8				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 12
Experimental H^E data for the system *n*-hexane (1) + rapeseed oil (2) at 353.15 K/894 kPa and 383.15 K/1136 kPa.

x_1[a]	H^E[b] (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
353.15 K and 894 kPa					
0.0998	45.3	0.5012	229.0	0.9003	173.5
0.2012	96.5	0.6008	250.5	0.9502	114.0
0.3013	147.0	0.7008	259.9	0.9801	48.5
0.4008	190.8	0.8007	239.9		
383.15 K and 1136 kPa					
0.1002	23.3	0.4994	100.4	0.8999	23.7
0.1998	47.3	0.5998	105.5	0.9400	−6.7
0.2996	72.5	0.6996	89.7	0.9602	−9.5
0.4000	92.3	0.7998	58.1	0.9901	−3.3

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

In Figs. 1–4 the experimental results for the vegetable oil systems are compared with the Redlich-Kister fits. The symbols represent the experimental data and the lines correspond to the fitting carried out with the Redlich-Kister polynomial equation. It is worth noting that, at the present moment, vapor–liquid equilibrium (VLE) data are not available in literature for the systems studied and liquid–liquid equilibrium (LLE) data are available for only a few of them [26,39,45]. Therefore, instead of simultaneous data regression using e.g. NRTL, we have used the Redlich-Kister equation to fit the H^E results only.

Comparing the results from mixtures of different vegetable oils with the same compound at the same temperature, very similar

Table 13
Experimental H^E data for the system methanol (1) + rapeseed oil (2) at 353.15 K/963 kPa.

x_1[a]	H^{Eb} (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
353.15 K and 963 kPa					
0.0577	526.3	0.4508	3736.0	0.7654	3461.2
0.1200	1168.9	0.5509	4010.9	0.8241	2800.5
0.1750	1650.4	0.5999	4019.4	0.8828	1835.1
0.2361	2270.9	0.6480	4019.7	0.9413	925.2
0.2944	2829.1	0.7063	3854.2	0.9801	330.9
0.3540	3281.7				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

Table 14
Experimental H^E data for the system ethanol (1) + rapeseed oil (2) at 353.15 K/998 kPa and 383.15 K/1136 kPa.

x_1[a]	H^{Eb} (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
353.15 K and 998 kPa					
0.0573	581.1	0.4100	3783.1	0.7049	3999.5
0.1163	1243.0	0.4694	4062.7	0.7638	3656.0
0.1753	1845.6	0.5285	4214.9	0.8229	3150.8
0.2331	2443.2	0.5875	4251.0	0.8819	2437.1
0.2937	2978.6	0.6459	4195.5	0.9409	1457.1
0.3525	3427.7				
383.15 K and 1136 kPa					
0.0578	641.5	0.4120	3921.4	0.7061	4531.0
0.1171	1287.7	0.4700	4244.3	0.7645	4208.4
0.1764	1863.7	0.5294	4492.8	0.8234	3689.2
0.2345	2401.7	0.5876	4659.6	0.8823	2910.6
0.2930	2974.8	0.6471	4657.0	0.9412	1777.0
0.3522	3454.1				

[a] Standard uncertainty $u(x_1)$ 0.0005 in mole fraction.
[b] Relative standard uncertainty of excess enthalpy $u_r(H^E) = u(H^E)/|H^E| < 0.01$.

trends were found, as can be seen in Figs. 1 and 2. Therefore, only the diagram for the case of soybean oil was represented (Fig. 3).

The comparison of excess enthalpy data obtained for different mixtures with soybean oil at 353.15 K is presented in Fig. 3. Analysing the diagrams, it can be seen that all investigated mixtures show endothermic behavior. Furthermore the following hierarchy was found for the H^E values in increasing order: *n*-hexane < methanol < ethanol. The non-ideality of these mixtures can be attributed on one hand to structural effects: interstitial accommodation, changes in free volume, and differences in shape and size of the mixed components and, on the other hand, to the energetic effects, this means molecular interactions that can be weakened or destroyed or established during the mixing process [46].

From Figs. 2 and 3 it can be concluded that the molar excess enthalpies for mixtures with alcohols present large positive values. This behavior is usually observed when polar and associating compounds, such as alcohols, are mixed with polar but non associating molecules, such as esters, which constitute the vegetable oils. Our results are therefore consistent with the rule established by Abbott et al. [33], in their “field guide to the excess functions”. This type of mixtures belongs to “region I” (enthalpy dominates) and have usually positive and large H^E values. This suggests that the overall amount of interactions of these two unmixed compounds diminishes upon mixing due to complex molecular effects in operation.

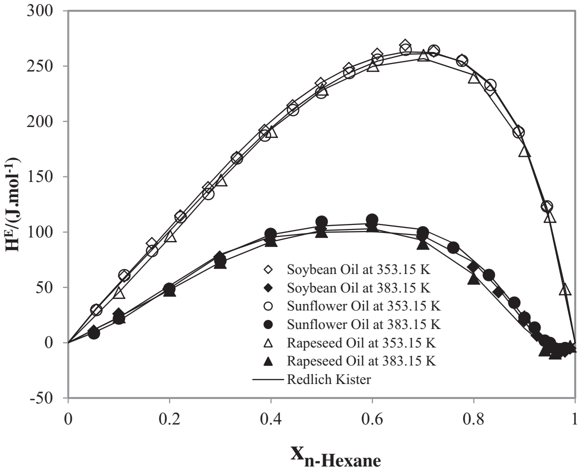

Fig. 1. Excess enthalpies (H^E) for the systems: *n*-hexane (1) + soybean oil (2) at 353.15 K (◇) and at 383.15 K (◆), *n*-hexane (1) + sunflower oil (2) at 353.15 K (○) and at 383.15 K (●), and *n*-hexane (1) + rapeseed oil (2) at 353.15 K (△) and at 383.15 K (▲).

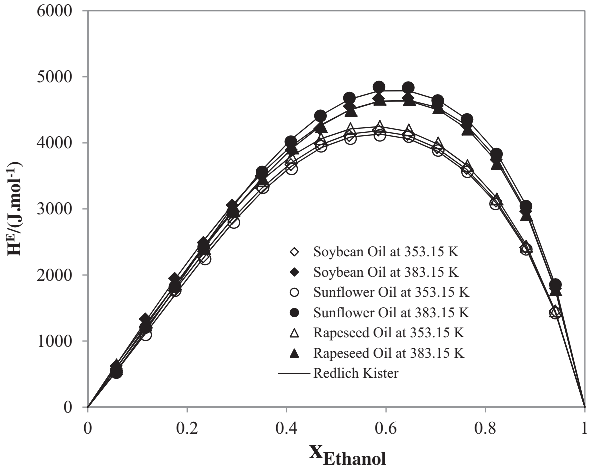

Fig. 2. Excess enthalpies (H^E) for the systems: ethanol (1) + soybean oil (2) at 353.15 K (◇) and at 383.15 K (◆), ethanol (1) + sunflower oil (2) at 353.15 K (○) and at 383.15 K (●) and ethanol (1) + rapeseed oil (2) at 353.15 K (△) and at 383.15 K (▲).

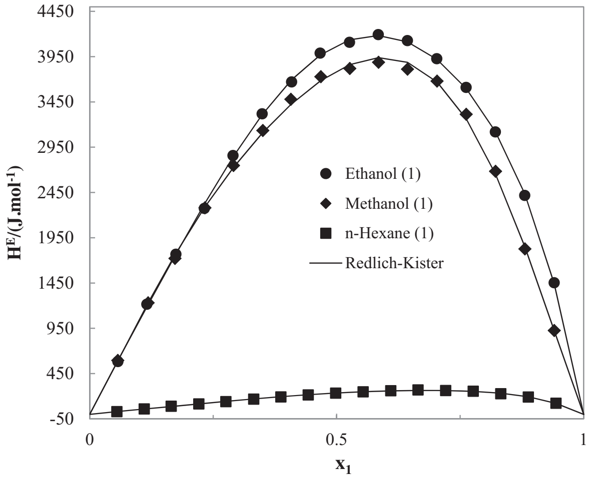

Fig. 3. Comparison of the experimental H^E data of mixtures of different solvents (1) with soybean oil (2) at 353.15 K.

In this type of mixture associations or electrostatic interactions (as the strong hydrogen-bonds) between like molecules (alcohol) may be partially compensated by solvation between unlike species (esters), i.e., probably strong dipolar interactions and hydrogen-bonds between the oxygen in the alcohols and the π-electrons of the ester (vegetable oil) are formed in place of the association effects or eletrostatic interactions between alcohol molecules. Comparing the results for mixtures containing methanol and vegetable oils with the ones containing ethanol and vegetable oils at the same temperature (353.15 K), we can observe that the mixtures with ethanol presented higher H^E values (see Tables 5 and 6 for soybean oil, 9 and 10 for sunflower oil, and 13 and 14 for rapeseed oil). Our results agree with those presented by Resa et al. [34]. They also verified that the disruption of the hydrogen-bonding effect, which involves the absorption of energy, increases with the size of the alcohol, i.e., alcohols with longer chain show more significant depression of hydrogen-bonding effect and consequently higher H^E values.

Comparing the H^E values of the mixtures formed by *n*-hexane + vegetable oil with mixtures of alcohol + vegetable oil, higher interaction between the *n*-hexane (nonpolar compound) and the vegetable oil (polar but non associating compound) are observed. The low value of H^E indicates that the mixture of *n*-hexane and vegetable oil shows a quasi ideal enthalpic behavior.

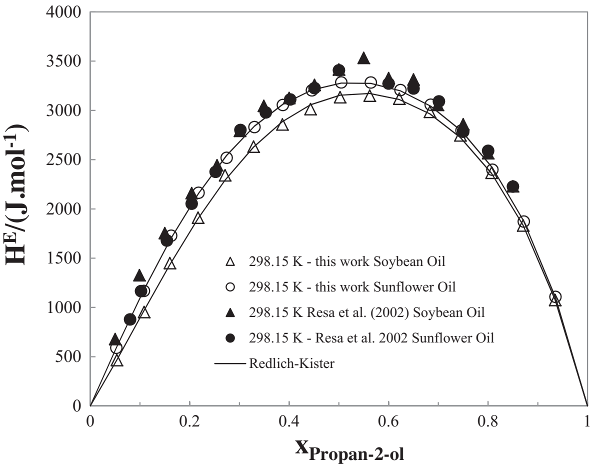

Fig. 4. Comparison of the experimental H^E data of mixtures with propan-2-ol (1) and vegetable oils at 298.15 K from this work (△ soybean oil, ○ sunflower oil) and from Resa et al. [34] (▲ soybean oil, ● sunflower oil).

The binary systems of vegetable oils + alcohols have a strongly temperature dependent miscibility gap. This special behavior can be applied, for example, for the recovery of the solvents used in vegetable oil extraction by alcohols or for the recovery of excess alcohol normaly used in the transesterification reaction in biodiesel production.

The H^E-data of the systems propan-2-ol + soybean oil and propan-2-ol + sunflower oil at 298.15 K are compared to previously published data [34] in Fig. 4. For propan-2-ol + sunflower oil, our results agree within ±2% with those obtained by other authors. In case of the system propan-2-ol + soybean oil, our data are on average 15% lower than those reported in literature. However, it should be mentioned that the equipment and methodology used in reference [34] differ considerably from the one used in this work and the vegetable oils used in both studies have slightly different compositions.

It was found (by both Resa et al. [34] and this study) that the variation of vegetable oil composition has no strong influence on the excess enthalpies, since these compounds are basically mixtures of triacylglycerols (esters) with a very similar average molar mass and similar chemical characteristics. It was observed that the variation of temperature and mixture composition had a much larger influence (see Figs. 1 and 2).

The equipment used by Resa et al. [34] operates at ambient temperature and pressure. This means that the temperatures of the two compounds and the mixture are dependent on room temperature control. Unlike temperature and mixture composition, it is reasonable to consider that pressure has little effect on H^E measurements, as long as it does not promote changes in the physical state of the mixture. In the equipment used in this work, the temperature control of the two components and of the mixture in the flow cell is performed by thermostated syringe liquid pumps and silicon oil bath, respectively. The temperatures are monitored with a Hart Scientific platinum resistance thermometer (model 1006 Micro-Therm) with an accuracy of ±0.005 K and the pressure is maintained constant (to avoid any evaporation) using a back pressure regulator. The methodology for calculating H^E is also different: in our work H^E is obtained from the energy involved per pulse of the pulsed heater, while Resa et al. [34] used the variation of the temperature after mixing the components, i.e., the results are significantly influenced by the initial temperature of the components and by ambient temperature. Since the new values were determined several times with precise control, we believe them to be more accurate.

The fitted Redlich-Kister parameters A_i and the root mean square deviation (RMSD) for all investigated mixtures are given in Table 15.

Table 16 summarizes the calculated values of the partial molar excess enthalpy at infinite dilution, $H_i^{E,\infty}$, for systems with various solvents (component 1) and refined vegetable oil (component 2) from this work (obtained by fitting a Redlich-Kister polynomial to the experimental calorimetric data) and available literature data (derived from the slopes of the linear plot of $\ln(\gamma_i^{\infty})$ versus $1/T$, according to the Gibbs-Helmholtz equation). It can be seen that the $H_i^{E,\infty}$ values obtained from the calorimetric data are in the range of the $H_i^{E,\infty}$ values obtained from the linear plots.

Table 16 shows similar values of $H_i^{E,\infty}$ for mixtures with the same solvent in the different vegetable oils and for almost all mixtures investigated the obtained values at infinite dilution correspond to endothermal partial molar excess enthalpies ($H_i^{E,\infty} > 0$), except for mixtures of vegetable oil at infinite dilution in *n*-hexane at 383.15 K, as observed in experimental H^E values (see Tables 4, 8 and 12). The positive and large $H_i^{E,\infty}$ values for alcohols at infinite dilution again reflect the weak association with the vegetable oils.

Table 15
Redlich-Kister parameters (A_i) and the root mean square deviation (RMSD) for systems with refined vegetable oil.

Component 1	Component 2	T (K)	A_1	A_2	A_3	A_4	A_5	A_6	RMSD* (J mol^{-1})
n-Hexane	Soybean oil	353.15	941.533	566.75	255.21	499.31	486.59		2.75
n-Hexane	Soybean oil	383.15	399.105	29.601	266.36	617.32	−827.56	−1103.1	2.54
Methanol	Soybean oil	353.15	15170.4	5920.5	2392.8	−3595.4	−5403.3		37.53
Ethanol	Soybean oil	353.15	16305.1	5389.9	−538.38	3834.1	4189.3		19.63
Ethanol	Soybean oil	383.15	17621.8	7650.6	3895.1	4710.6	2085.6		33.69
Propan-2-ol	Soybean oil	298.15	12606.8	2021.2	1253.5	3635.5			21.91
n-Hexane	Sunflower oil	353.15	918.391	592.20	311.16	481.55	457.52		2.34
n-Hexane	Sunflower oil	383.15	422.334	87.553	174.64	458.22	−732.63	−881.91	2.23
Methanol	Sunflower oil	353.15	15278.9	5832.7	2041.2	−3679.3	−4903.6		37.04
Ethanol	Sunflower oil	353.15	16103.1	5420.3	−745.32	4310.3	3756.8		29.80
Ethanol	Sunflower oil	383.15	18250.8	8236.3	1137.3	6158.4	3991.7		35.32
Propan-2-ol	Sunflower oil	298.15	13096.2	1303.1	2676.7	3038.2			12.41
n-Hexane	Rapeseed oil	353.15	911.989	569.00	230.18	549.92	449.76		2.43
n-Hexane	Rapeseed oil	383.15	405.422	120.85	5.0906	73.920	−507.56	−583.44	3.74
Methanol	Rapeseed oil	353.15	15827.8	6518.1	798.51	−2723.6	−4771.5		57.01
Ethanol	Rapeseed oil	353.15	16616.9	4946.0	544.98	4665.0	2398.7		14.49
Ethanol	Rapeseed oil	383.15	17614.9	8196.9	1395.8	3988.4	5326.1		20.37

* Root mean square deviation—$\mathrm{RMSD}(H^E) = \left[\sum \frac{(H^E_{calcd} - H^E_{exptl})^2}{N}\right]^{1/2}$, where N is the number of experimental values.

Table 16
Excess enthalpies at infinite dilution ($H_i^{E,\infty}$) for systems with various solvents (1) and refined vegetable oil (2).

Component 1	Component 2	This work				Ref. [36][b]	Ref. [25][b]
		$H_1^{E,\infty}$ (kJ mol^{-1}) at 353.15 K	$H_2^{E,\infty}$ (kJ mol^{-1}) at 353.15 K	$H_1^{E,\infty}$ (kJ mol^{-1}) at 383.15 K	$H_2^{E,\infty}$ (kJ mol^{-1}) at 383.15 K	$H_1^{E,\infty}$ (kJ mol^{-1})	$H_1^{E,\infty}$ (kJ mol^{-1})
n-Hexane	Soybean oil	0.62	2.75	0.29	−0.62	0.59	1.57
Methanol	Soybean oil	9.83	14.48			9.72	9.28
Ethanol	Soybean oil	10.73	29.18	11.24	35.96	12.15	11.66
Propan-2-ol	Soybean oil	8.20[a]	19.52 [a]				
n-Hexane	Sunflower oil	0.61	2.76	0.20	−0.47		1.72
Methanol	Sunflower oil	10.26	14.57				11.68
Ethanol	Sunflower oil	9.38	28.85	8.99	37.77		22.00
Propan-2-ol	Sunflower oil	11.43 [a]	20.11 [a]				
n-Hexane	Rapeseed oil	0.47	2.71	0.29	−0.49		1.30
Methanol	Rapeseed oil	8.06	15.65				16.36
Ethanol	Rapeseed oil	9.95	29.17	12.15	36.52		17.55

[a] Data obtained at 298.15 K.

[b] Estimated from linear dependence of $\ln(\gamma_i^\infty)$ on the reciprocal absolute temperature, relative combined standard uncertainty $u_{r,c}[\ln(\gamma_i^\infty)] = \frac{u_c[\ln(\gamma_i^\infty)]}{|\ln(\gamma_i^\infty)|} = 0.2$.

Comparing the partial molar excess enthalpies values at infinite dilution of *n*-hexane in the vegetable oils used in this work to the literature, the data measured show differences of less than 0.03–1.52 kJ mol^{-1} in absolute values. Comparing our results for methanol and ethanol at infinite dilution in soybean oil with available literature data, the difference is always less than 12%. It should be considered that the values of $H_i^{E,\infty}$ from both available references have about 20% error by the fact that $H_i^{E,\infty}$ is determined from the difference of log terms.

4. Conclusions

Excess enthalpies were measured for 17 mixtures containing refined vegetable oils in the temperature range from 298.15 to 383.15 K with the objective of extending the excess enthalpy database at higher temperatures, which is required for the further development of the modified UNIFAC (Dortmund). Because at this moment VLE and LLE data are only available for part of the studied systems, the results have been fitted using the Redlich-Kister polynomial equation instead of using a thermodynamic model based on the local composition concept.

All systems investigated showed deviations from the ideal behavior and their experimental H^E data are mostly positive. The strong endothermic effect observed in mixtures with alcohols is mainly due to the disruption of hydrogen-bonds upon mixing.

A further publication in preparation will compare these findings with the results of static vapor–liquid equilibrium (VLE) measurements obtained for the same vegetable oils and compared with the results of different predictive methods. Thus, it will be possible to evaluate the need to define new groups and/or to fit new group interaction parameters for the modified UNIFAC method.

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