



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



Patrícia C. Belting<sup>a,b,1,2</sup>, Jürgen Gmehling<sup>a</sup>, Rainer Bölts<sup>a,1</sup>, Jürgen Rarey<sup>a,1</sup>,  
 Roberta Ceriani<sup>c</sup>, Osvaldo Chiavone-Filho<sup>d</sup>, Antonio J.A. Meirelles<sup>b,\*,2</sup>

<sup>a</sup> Carl von Ossietzky Universität Oldenburg, Technische Chemie (FKV), D-26111 Oldenburg, Federal Republic of Germany

<sup>b</sup> Food Engineering Department, Faculty of Food Engineering, University of Campinas, Av. Monteiro Lobato 80, Cidade Universitária Zeferino Vaz, 13083-862 Campinas-SP, Brazil

<sup>c</sup> Faculty of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Cidade Universitária Zeferino Vaz, 13083-852 Campinas-SP, Brazil

<sup>d</sup> Chemical Engineering Department, Federal University of Rio Grande do Norte, Av. Senador Salgado Filho S/N, 59066-800 Natal-RN, Brazil

### ARTICLE INFO

#### Article history:

Received 16 January 2014

Received in revised form 25 April 2014

Accepted 27 April 2014

Available online 5 May 2014

#### Keywords:

Molar excess enthalpy

Heat of mixing

Refined vegetable oil

Isothermal flow calorimetry

### 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.

© 2014 Elsevier B.V. All rights reserved.

### 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

\* Corresponding author. Tel.: +55 19 3521 4037; fax: +55 19 3521 4027.

E-mail address: [tomze@fea.unicamp.br](mailto:tomze@fea.unicamp.br) (A.J.A. Meirelles).

<sup>1</sup> Present address.

<sup>2</sup> Permanent address.

**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 $i$
<b>Subscripts</b>	
$i$	identification of Redlich-Kister parameter
$exptl$	experimental data
$calcd$	calculated data
<b>Superscripts</b>	
$E$	excess property
$\infty$	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<sup>-1</sup>.

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].

Download English Version:

<https://daneshyari.com/en/article/202344>

Download Persian Version:

<https://daneshyari.com/article/202344>

[Daneshyari.com](https://daneshyari.com)