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ScienceDirect
Journal of Food Engineering 79 (2007) 1104–1109
JOURNAL OF FOOD ENGINEERING
www.elsevier.com/locate/jfoodeng

Research note

Enthalpies of mixing and heat capacities of mixtures containing acetates and ketones with corn oil at 25 °C

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Received 27 February 2004; received in revised form 7 September 2005; accepted 17 January 2006
Available online 3 April 2006

Abstract

This study concerns the determination of molar enthalpies of mixing for mixtures composed by acetates (ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate and isobutyl acetate) and ketones (2-butanone, 3-pentanone and 4-methyl-2-pentanone) + corn oil at 25 °C and atmospheric conditions. In the design of heat transfer and process equipment employed in the oils and seed processing industry, the knowledge of enthalpy of the organic solvent–oil mixtures is a determinant factor. All the binaries show the same trend, a decrease of temperature is observed when the mixture is carried out. An effect endothermic takes place as consequence of the new reorganization of molecules. The aim of this study was therefore to calculate the heat capacities at constant pressure for the studied systems.

Keywords: Enthalpy of mixing; Heat capacity; Mixtures; Corn oil; Ester; Ketone

1. Introduction

Fats and oils as they exist in nature must be processed before they are suitable for use as edible fats and oils. There are two current methods of recovering oil, squeezing it from the seed using a press (hydraulic, screw or a combination) or it is extracted using a solvent, although frequently the two methods are combined, depending on the nature of the seed and the cost of the operation. Mechanical extraction is simpler and safer but less efficient than solvent extraction, in which the flakes (or press meal) are soaked in the solvent, normally hexane.

Oilseeds as natural and biologically active materials, contain many colour and flavor precursors as degradation and breakdown products, becoming refining steps completely necessary. Corn oils contain relatively large amount of waxes that must be removed so that the oil does not cloud when refrigerated (winterization or dewaxing). Desired fractions from a mixture of triglycerides dissolved in a suitable solvent are selectively crystallized at different temperatures after which the fractions are separated and the solvent removed. Because of the hazardous nature of hexane and the lack of knowledge about the behavior with other kind of solvents, this paper continue our research program involving the study of bulk and excess properties of binary mixtures containing vegetable oils and organic solvents (González, Iglesias, Lanz, & Resa, 1999; González, Resa, & Lanz, 2000; González, Resa, Ruiz, & Gutiérrez, 1996, 1997; Resa, González, Fanega, Ortiz de Landaluce, & Lanz, 2002). We report in this document experimental measurements of molar enthalpy of mixing (ΔH^{m}) as function of solvent composition for mixtures involving esters (ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate and isobutyl acetate) and ketones (2-butanone, 3-pentanone and 4-methyl-2-pentanone) at 25 °C and atmospheric pressure. Indeed, calculated heat capacities (Cp^{m}) for the studied mixtures are reported. Corn oil was characterized according to spanish standard procedures and its fatty acids composition determined. Physical properties of the corn oil as density (ρ), refractive index (n_D) and speed of sound (u) were measured as function of temperature in the range 25–50 °C.

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doi:10.1016/j.jfoodeng.2006.01.088

Measurements of bulk properties as the previously cited, and of molar enthalpies provide insight into the molecular arrangements in liquids and help one to understand the thermodynamic properties of liquid mixtures. Much data has been reported on heat capacities of oils and fats (Coupland & McClements, 1997; Kowalski, 1988; Morad, Mustafa Kamal, Panau, & Yew, 2000), but none refers specifically to mixtures. Several studies present information about physical properties of vegetable oils (Coupland & McClements, 1997; De Dios Alvarado, 1995), or mixtures of fatty acids (Flores Luque, Galán Vallejo, Cantero Moreno, & Quiroga Alonso, 1979; Flores Luque, Gómez Herrera, & Galán Vallejo, 1977; Mantell Serrano, Muñoz Cueto, Galán Vallejo, & Rodríguez Rodríguez, 1995) but nothing has been found for corn oil with organic solvents.

2. Material and methods

2.1. Reactives

Acetates were supplied by Fluka except of propyl acetate supplied by Aldrich, while ketones purchaser was Prolabo, all the chemicals with a purity better than 0.985 mol%. Ultrasonic treatment was used for degassing and molecular sieves (type 3a, 1/16 inch, Fluka) were introduced into the bottles to reduce possible water contents in solvents. No more treatment was applied owed to their high purity grade, from the purchaser. The purities of the solvents were checked by comparing the measured density and refractive index data with those reported in the literature.

Corn oil was supplied by Koipe and analyzed to calculate its composition in fatty acids. With this aim, we used a SHIMADZU model GC-14B gas chromatograph equipped with a flame detector. The chromatographic technique and the chemical procedure for the preparation of fatty acids were described in a previous work (González et al., 1996). The obtained composition (% mol) is the following: palmitic acid (11.97), stearic acid (2.34), araquidic acid (0.77), oleic acid (29.09), linoleic acid (54.97), linolenic acid (0.86). The uncertainty in the % mol data is ±0.1% mol. From the experimental composition, the average molar mass (M_w) of corn oil has been calculated, $M_w = 872.08 \pm 0.05\ \mathrm{g\ mol^{-1}}$. Other characteristics of the oil were measured too: acid value (0.14 mg KOH), saponification value (198 mg KOH/g oil), iodine value (123.7), peroxide value (9.2 meq O_2/kg oil), and wetness and volatiles (0.04 water % in the oil). These were analyzed following standard spanish procedures, UNE rules (AMV Ed., 1997) and the obtained values are in agreement with those reported in bibliography. Other properties of the oil as density, refractive index and speed of sound were measured as function of temperature in the range 25–50 °C. Density was obtained using a vibration tube density meter Anton Paar DMA 58 with a resolution of $1 \times 10^{-5}\ \mathrm{g\ cm^{-3}}$. The oscillator period, τ, in the vibrating tube was converted into density (ρ) by using the equation,

$$\rho = A \cdot \tau^2 - B \quad (1)$$

where A and B are the apparatus constant, determined with the literature data of pure water and dry air. The refractive indices, n_D, at the sodium line were measured using a Mettler Toledo RE50 refractometer with a precision of $\pm 1 \times 10^{-5}$. An Anton Paar DSA 48 analyser carried out speed of sound measurements, with a precision of $\pm 1\ \mathrm{m\ s^{-1}}$ and was also frequently calibrated. These properties are gathered in Table 1, in the studied temperatures and compared with literature values.

2.2. Preparation of samples

To determinate the mixing enthalpy of the studied mixtures, all experiments were carried out using a Dewar calorimeter and its equipment, the whole set supplied by Phywe Systeme GMBH. Experimental set up and procedure is similar to that described in Zijlema, Witkamp, and van Rosmalen (1999). To weigh the individual components of these mixtures, we use an AND electronic Balance model HF-20006, with an accuracy of $\pm 2 \times 10^{-3}$ g, taking care no evaporation of solvent occurs.

2.3. Procedure

The organic solvent contained in an erlenmeyer flask, is temperature equilibrated using a temperature controlled bath. The Dewar vessel with the vegetable oil is heated by a heating coil. A magnetic heating stirrer and a stir bar provide agitation. To start the measures two liquids

Table 1
Experimental physical properties of corn oil as function of temperature and literature values

T (°C)	Density (kg m^{-3})		Refractive index (n_D)		Speed of sound (m s^{-1})	
	Experimental	Literature[a]	Experimental	Literature[b]	Experimental	Literature[a]
25	915.52	917.98	1.47203	1.470–1.474	1449.59	1451.65
30	912.02	914.73	1.47028		1436.35	1435.50
35	908.75	911.48	1.46842		1419.70	1419.35
40	905.41	908.23	1.46651		1403.29	1403.20
45	902.00	904.98	1.46480		1386.77	1387.05
50	899.12	901.73	1.46270		1371.00	1370.90

[a] Coupland and McClements (1997).
[b] Madrid et al. (1997).