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Data, analysis and modeling of physical properties for process design of systems involving lipids

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ABSTRACT

Pure component and mixture properties are necessary for synthesis, design, and analysis of processes for the production of edible oils, fats, biodiesel, and other lipids. The lack of measured data for these systems makes it necessary to develop reliable predictive models based on limited data. We have systematically collected data for vapor–liquid equilibrium (VLE), solid–liquid equilibrium (SLE) and related pure component properties involving lipid systems as a first step toward developing relevant property models. The established consistency tests to evaluate the VLE data of lipid systems as well as lipid properties are briefly reviewed. For SLE systems, where consistency tests based on the Gibbs–Duhem equation cannot be implemented, a consistency test has been developed. It involves limiting conditions and regression of the parameters for a new thermodynamic model that combines solute activity coefficients in the liquid phase at infinite dilution and a theoretically based term to account for the non-ideality in dilute solutions. This model gives noticeably better descriptions of experimental data in lipid systems than do traditional models. Examination of various objective functions for regressing model parameters showed that some variation of parameter values and differences in accuracy can be found, though they are not large. Some original UNIFAC group contribution parameters for lipids have been revised by fitting to the lipid database.

1. Introduction

The world's production of oils and fats has grown from 79.2 million tons in 1990 to nearly 176 million tons in 2011 [1]. Most of the substances involved are lipids, which are organic components insoluble in polar solvents (such water), and soluble in organic solvents (such as chloroform and acetone) and alcohol. Lipids are molecules that totally or in part originate from carbanion-based condensations of thioesters, as fatty acids, and/or originate by carbocation-based condensations of isoprene units, as sterols [2]. This work considers the main classes of lipids present in edible oils and biodiesel production systems, namely, fatty acids, esters (methyl and ethyl), triacylglycerols (TAGS), diacylglycerols (DAGS), monocylglycerols (MAGS), phospholipids, tocopherols, squalenes, among others (see Table 1 for examples of lipids considered in this work). This growth in the production and consumption of oils and fats challenges the lipid processing industry to design and develop better products and processes.

Lipids are often not tabulated in common property databases and their polyfunctional structure requires careful model analysis. The availability and reliability of data and modeling of the properties and phase equilibria for pure lipids and their mixtures are summarized in the present work. The collected SLE data of lipids (CAPEC_Lipids_Mixtures_Database) provides saturation compositions of solid components in solution at specific temperatures. Finding the solid structure and/or considering its effect on the saturation composition of the liquid is not an objective of this particular work. Rather, because measurement uncertainties or quality estimates are unavailable for many literature experimental data, we focus on the analysis of data quality for systems where the solid is probably well characterized.

In this work, VLE data have been evaluated following the consistency tests recommended by NIST [22], based on the Gibbs–Duhem equation, pure component limits, and accuracy in regressing excess Gibbs Energy models. Further, we have considered options for objective functions in parameter regression, including least-squares and maximum likelihood estimation, especially because

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Table 1
UNIFAC groups for lipids.

Compounds	CH_3	CH_2	CH	CH=CH	CH=C	C=C	ACH	AC	AC—CH_3	CH_2 cyc	CH cyc	C cyc	CH=C cyc	C=C cyc	OH	AC—OH	CH_3COO	CH_2COO	CH—O	O cyc	CH_2NH_2	COOH	PHO_4	P=O	O^-
Fatty acids (FA)	X	X		X																		X			
Methyl esters (ME)	X	X		X													X								
Ethyl esters (EE)	X	X		X														X							
Triacylglycerols (TAGS)	X	X	X	X														X							
Diacylglycerols (DAGS)	X	X	X	X											X			X							
Monoclyglycerols (MAGS)	X	X	X	X											X			X							
Phospholipids	X	X	X	X											X			X	X		X		+	+	+
Tocopherols	X	X	X				X	X	X	Y		Y				X				Y					
Tocotrienol	X	X					X	X	X	Y		Y				X				Y					
Carotenes	X			X	X	X					Y	Y	Y	Y											
Lutein	X			X	X	X					Y	Y		Y	X										
Lycopene	X	X		X	X							Y													
Squalene	X	X			X																				
Zeaxanthin	X		X	X	X	X					Y			Y	X										
Campesterol	X	X	X								Y	Y	Y		X										
Cholesterol	X	X	X								Y	Y	Y		X										
Sitosterol	X	X	X								Y	Y	Y		X										
Stigmasterols	X	X	X	X							Y	Y	Y		X			X							
Sterol glycosides	X	X	X	X	X						Y	Y	Y		X			X		Y					+

the latter considers measurement uncertainties in the experimental data. In addition, we have worked to improve the performance of the original UNIFAC group contribution model by fine-tuning some group interaction parameters using the lipids database, which has been extended to include many SLE data. For most SLE systems, the entire composition range is not covered, so the Gibbs–Duhem equation cannot be applied. Furthermore, pure component temperature limits are often less certain, and the excess Gibbs Energy models typically used for non-ideality in VLE may not be reliable for SLE. To address this situation, we have proposed an alternative set of consistency tests, including a new approach for modeling dilute solution SLE. The proposed new thermodynamic model combines solute infinite dilution activity coefficients in the liquid phase with a theoretically based term to account for the non-ideality for dilute solutions relative to infinite dilution. This model was found to give noticeably better descriptions of experimental data than do traditional thermodynamic models (NRTL, UNIQUAC and UNIFAC) for lipid systems.

2. Pure component properties of lipids

Measured data for thermodynamic and related pure component properties and mixtures for a wide range of lipids and their mixtures have been found in the open literature and databases such as NIST-TDE® and DIPPR®. These data have been collected for the CAPEC_Lipids_Database. More than 13,500 data points for the following eight pure component properties covering nearly 290 lipids have been collected: normal boiling point (T_b), critical temperature (T_c), critical pressure (P_c), critical volume (V_c), normal melting point (T_m), standard Gibbs energy of formation (G_f), standard enthalpy of formation (H_f), and standard enthalpy of fusion (H_{fus}). In the database, the components with limited information are those commonly found in vegetable oils, more specifically acylglycerols and tocopherols.

The properties of pure components are typically predicted using the structurally dependent parameters of group-contribution (GC) methods. GC methods for predicting primary properties have been developed by many authors [3–5]. Multi-level property estimation approaches have been developed via data regression by Constantinou and Gani [6], Marrero and Gani [7], and Hukkerikar et al. [8] for a wide range of chemical, biochemical, and environmentally related pure components. There are many methods for prediction of temperature dependent properties of pure components, including lipids, such as those of Basařová and Svoboda [9], Kolská et al. [10,11], Ceriani et al. [12,13]. Several GC based methods have been reported for predicting lipid solution properties such as density, viscosity, thermal conductivity, specific enthalpies, and surface tension of lipid systems. For example, Rabelo et al. [15] developed a model to predict the liquid viscosities of mixtures of fatty acids, and Eiteman and Goodrum [16] developed a model to calculate the densities and viscosities of low molecular weight mixtures of triacylglycerols.

3. Phase equilibria of lipid systems

3.1. Database

Property model development requires reliable data and their evaluation. For the purposes of this work, a search of the literature was made to collect, within a limited time, as many data as possible. The criteria for data selection were details of measurement technique; measurement accuracy; different ranges of temperature, pressure, and molar fractions considered by the author; the use of a method of analysis or a model to describe the experimental data; and, whether the data source brought in results for different