

Simplifying Hansen Solubility Parameters for Complex Edible Fats and Oils

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Abstract Hansen solubility parameters (HSPs), often used to predict the miscibility between two compounds, are an alternative tool in evaluating the ability of the solvent to interact via dispersion, dipole-dipole, and hydrogen bonding interactions. The aim of this paper is to find a simple way to calculate HSPs for complex mixtures of triglycerides (TAGs). HSPs were calculated using two approaches: the first assumes that the contributions to the dispersion, dipole-dipole, and hydrogen bonding interactions may be subdivided into larger functional moieties (i.e., fatty acids and fatty acid methyl esters) that are additive, while the second approach assumes that vegetable oils are comprised of mixtures of simple TAGs in the same mass fractions as the fatty acids. The HSPs obtained using the two approaches are compared to reference values determined using the “Hansen Solubility Parameters in Practice” software (HSPiP) considering the complex TAG profile for each vegetable oil.

HSPs for vegetable oils, obtained with the HSPiP software, did not correspond well to the HSPs obtained from the group contribution approach, when using fatty acids, fatty acids + glycerol or fatty acid methyl esters. In contrast, the HSPs calculated for vegetable oils, assuming that all TAGs are simple and in the same mass fractions as the fatty acids, provide similar values to the HSPs obtained from the HSPiP software.

Therefore, it is possible to calculate the HSPs for complex oils by simply knowing the fatty acid composition. Knowledge of HSPs may be used to rationalize the ability of certain low molecular weight molecules to develop organogels in vegetable oils as well as the crystallization of triglycerides.

Keywords Hansen solubility parameters · Fatty acids · Fatty acid methyl esters · Triglycerides · HSPiP software

Introduction

Foods contain significant quantities of fats and oils, which are essential to impart desirable elastic and viscous properties. Foods high in fat often contain a continuous phase of low melting temperature triglycerides (TAGs) and a dispersed phase of crystalline fat that is predominately *trans* or long chain saturated fatty acids [1–3]. When the mixture of TAGs is heated above the melting temperature and subsequently cooled below the supersaturation temperature, either a sol remains (i.e., the dispersed phase is dissolved in the continuous phase) or the dispersed phase crystallizes. In the first scenario, the high melting temperature TAGs and TAGs from the oil have high affinity for one and other interacting to form a solution. In the second scenario, upon cooling beyond the supersaturated state, the dispersed phase crystallizes and precipitates out of solution [1, 3, 4]. A continuous 3D colloidal crystal network forms when an intricate balance is found between these two scenarios whereby the intermolecular forces driving solubilization and contrasting forces enable crystallization that facilitates the entrapment of the continuous oil phase.

In a similar manner to fat crystal networks, organogels are a result of the crystallization of self-assembled fibrillar networks (SAFiNs) by solubilizing a gelator in oil and subsequently

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cooling the sol below the supersaturation temperature. Gelator molecules self-assemble via nonspecific (i.e., dipole-dipole, dipole-induced, and instantaneous dipole-induced forces) and specific (i.e., hydrogen bonds) intermolecular non-covalent interactions developing a 3D network confining oil via surface tension and capillary action [5]. Both the influence and nature of the gelator-gelator and gelator-oil interactions are critical in understanding the process of crystallization and/or gelification [6]. Organogelation requires a meticulous balance between contrasting parameters that determine solubility and those intermolecular forces that facilitate aggregation [7]. A solution results, if the affinity between the solvent and gelator is high. When the molecular interactions between solvent and gelator increase in dissimilarity, solubility decreases and fine crystals result. Fine crystal result because of the dissimilarity of the solvent and gelator, which facilitates new gelator-gelator interactions driven by non-covalent interactions such as hydrogen-bonding and π - π stacking. Further increasing the dissimilarity results in coarser crystals comprised of isotopically orientated gelator molecules. When an intermediate balance of these forces is reached, thin entangled anisotropic fibers effectively entrap the continuous phase [6–9].

Through the use of HSPs the miscibility behaviors of liquid mixtures, polymer blends and polymer solvent compatibility, dispersion and solubility of organic and inorganic materials in organic liquids could be assessed [10]. The aim of this paper is to simplify the HSP calculation to determine, with relative ease, the HSPs for specific complex edible oils. This will be done using the “Hansen Solubility Parameters in Practice” software (HSPiP 4th Edition version 4.1.07) [11] via the “Simplified Molecular Input Line Entry Specification” (SMILES).

Theory and Methodology

Hildebrand solubility parameters describes miscibility of apolar solvents assuming they rely on London or dispersion forces [10, 12–14]. As knowledge about these parameters advanced, the Hildebrand solubility parameter (δ_t) became widely used, especially in polymer physics [15, 16] and is calculated using:

$$\delta_{t(\text{Hildebrand})} = \left(\frac{\Delta E_i^v}{V_i} \right)^{1/2} = \left[\frac{(\Delta H_i^v - RT)}{V_i} \right]^{1/2} \quad (1)$$

where $\delta_{t(\text{Hildebrand})}$ is the sum of the interactions holding liquid together, [12, 17, 18] ΔE_i^v is the cohesive energy density (i.e., the energy of vaporization), V_i is the molar volume, R is the ideal gas constant, and T is the absolute temperature.

However, principal interactions between solvents are not limited to London dispersion forces (apolar groups), and extend to permanent dipole-dipole interactions (polar groups) and hydrogen bonding [19]. Therefore, the $\delta_{t(\text{Hildebrand})}$ parameter is insufficient to describe the behavior of molecules with apolar and polar functional groups. This deficiency led to the development of the HSPs. The HSPs estimate the miscibility of apolar, polar and hydrogen-bonding solvents [20], decomposing δ_t into three individual parameters (Eq. 2): dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) cohesive solubility parameters [21–25].

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2)$$

Additionally, the Hansen solubility parameters (i.e., δ_d , δ_p , δ_h) can be calculated using the Hoftyzer and van Krevelen method [26]:

$$\delta_d = \frac{\sum F_{di}}{V} \quad (3)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V} \quad (4)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V} \quad (5)$$

Where F_{di} is the dispersive functional group value, F_{pi} is the polar functional group value and E_{hi} is the hydrogen bonding functional group value.

HSPs Determined Using the Group Contribution Method

The HSPs for fatty acids found in edible oils (cocoa butter, canola oil, coconut oil, fish oil and soybean oil) were calculated using the HSPiP software (4th Edition version 4.1.07) [11] via the simplified molecular-input line-entry (SMILE) input function. Assuming the contributions to the thermodynamic property from each functional group are additive [27], F_{di} , F_{pi} and E_{hi} of the corresponding cohesive solubility parameters were calculated for TAGs by simplifying the molecule to groups based on the 3 fatty acids, 3 fatty acids and 1 glycerol or 3 fatty acid methyl esters using Eqs. 3 to 5. Finally, the HSPs of the TAGs mixture (i.e., the vegetable oils) were calculated using Eqs. 6 to 8. Herein, the aim was that the HSPs calculation for the TAGs in vegetable oils was simplified into large group contributions.

$$\delta_{d \text{ mixture}} = \sum_{i=1}^{i=n} \delta_{di} x_i \quad (6)$$

Table 1 Hildebrand solubility parameters (δ_t) and Hansen solubility parameters (δ_d , δ_p , δ_h) determined by the Eq. 2 and the HSPiP software respectively, for saturated and unsaturated fatty acids

Saturated fatty acids					Unsaturated fatty acids				
Carbon number	δ_d	δ_p	δ_h	δ_t	Carbon number	δ_d	δ_p	δ_h	δ_t
4:0	16.0	6.5	12.9	21.6	16:1	16.5	3.4	6.4	18.0
5:0	16.0	6.0	11.9	20.8	16:3	17.1	3.2	7.2	18.8
6:0	16.1	5.5	11.1	20.3	18:1	16.5	3.1	5.7	17.7
7:0	16.1	5.2	10.3	19.8	18:2	16.8	3.1	6.2	18.2
8:0	16.1	5.1	9.5	19.4	18:3	17.0	3.2	6.5	18.5
9:0	16.2	4.4	8.7	18.9	18:4	17.3	2.9	6.8	18.8
10:0	16.2	4.2	8.3	18.7	20:1	16.6	2.6	5.3	17.6
11:0	16.2	4.1	7.9	18.5	20:2	16.8	2.6	5.7	17.9
12:0	16.2	4.0	7.4	18.3	20:3	17.0	3.2	6.5	18.5
13:0	16.3	3.6	6.8	18.0	20:4	17.2	2.8	6.5	18.6
14:0	16.3	3.4	6.6	17.9	20:5	17.4	2.9	6.7	18.9
15:0	16.3	3.3	6.3	17.8	21:5	17.4	2.6	6.3	18.7
16:0	16.3	3.4	6.0	17.7	22:1	16.5	2.7	4.8	17.4
17:0	16.3	3.0	5.6	17.5	22:4	17.2	2.4	6.0	18.4
18:0	16.3	3.3	5.5	17.5	22:5	17.4	2.5	6.2	18.6
19:0	16.3	2.8	5.2	17.3	22:6	17.6	2.5	6.6	19.0
20:0	16.3	2.9	5.0	17.3	24:1	16.5	2.3	4.5	17.3
21:0	16.3	2.6	4.7	17.2	24:4	17.1	2.4	5.5	18.1
22:0	16.3	2.5	4.6	17.1	24:6	17.5	2.3	6.0	18.6
23:0	16.3	2.5	4.5	17.1	Hydroxy fatty acids				
24:0	16.2	2.6	4.3	17.0	18:0 12OH	16.4	4.5	8.6	19.1
25:0	16.3	2.3	4.0	16.9					

$$\delta_{p \text{ mixture}} = \sum_{i=1}^{i=n} \delta_{pi} x_i \quad (7)$$

$$\delta_{h \text{ mixture}} = \sum_{i=1}^{i=n} \delta_{hi} x_i \quad (8)$$

In Eqs. 6–8, $\delta_{d \text{ mixture}}$, $\delta_{p \text{ mixture}}$ and $\delta_{h \text{ mixture}}$ are the HSPs calculated using Eqs. 3 to 5 for the triglycerides present in the vegetable oils, and x_i is the corresponding TAG or fatty acid mass fraction.

Table 2 Hildebrand solubility parameters (δ_t) and Hansen solubility parameters (δ_d , δ_p , δ_h) determined by the Eq. 2 and the HSPiP software respectively, for saturated and unsaturated fatty acids methyl esters

Saturated methyl esters					Unsaturated methyl esters				
Carbon number	δ_d	δ_p	δ_h	δ_t	Carbon number	δ_d	δ_p	δ_h	δ_t
C4:0	15.8	4.9	6.2	17.7	C16:1	16.3	2.7	3.6	16.9
C5:0	15.8	4.6	5.9	17.5	C16:3	16.9	2.5	4.2	17.6
C6:0	15.9	4.3	5.7	17.4	C18:1	16.3	2.4	3.2	16.8
C7:0	15.9	4.1	5.3	17.3	C18:2	16.6	2.4	3.6	17.2
C8:0	16.0	4.0	4.9	17.2	C18:3	16.8	2.5	3.8	17.4
C9:0	16.0	3.5	4.5	17.0	C18:4	17.1	2.2	4.1	17.7
C10:0	16.0	3.3	4.4	16.9	C20:1	16.4	2.0	2.9	16.8
C11:0	16.0	3.2	4.1	16.8	C20:2	16.6	2.0	3.4	17.1
C12:0	16.0	3.2	3.9	16.8	C20:3	16.8	2.1	3.7	17.3
C13:0	16.1	2.8	3.6	16.7	C20:4	17.0	2.2	4.0	17.6
C14:0	16.1	2.7	3.5	16.7	C20:5	17.2	2.3	4.2	17.9
C15:0	16.1	2.6	3.4	16.7	C21:5	17.2	1.9	4.0	17.8
C16:0	16.0	2.7	3.2	16.5	C22:5	17.2	1.9	4.0	17.8
C17:0	16.1	2.3	3.0	16.5					
C18:0	16.1	2.3	3.0	16.5					
C19:0	16.1	2.2	2.9	16.5					
C20:0	16.0	2.3	2.7	16.4					
C21:0	16.1	2.0	2.5	16.4					
C22:0	16.1	1.9	2.6	16.4					
C23:0	16.1	1.9	2.5	16.4					
C24:0	16.0	2.0	2.4	16.3					
C25:0	16.1	1.8	2.3	16.4					

Table 3 Hansen solubility parameters (δ_d , δ_p , δ_h) of cocoa butter determined with the HSPiP software (Reference values) in comparison with the parameters calculated using Eqs. 3 to 8

TAG ^a	Reference values (MPa ^{1/2})			FA ^b (MPa ^{1/2})			FA + glycerol ^c (MPa ^{1/2})			FAME ^d (MPa ^{1/2})			Mass fraction ^e
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	
POP	16.4	2.3	2.3	16.4	1.9	5.9	16.5	2.0	9.6	16.1	1.5	3.2	0.158
PPLn	16.6	2.1	2.6	16.5	1.9	6.2	16.7	2.0	9.8	16.3	1.5	3.4	0.046
POS	16.6	2.1	2.2	16.4	1.9	5.7	16.5	1.9	9.5	16.1	1.4	3.1	0.401
POO	16.5	2.2	2.3	16.4	1.8	5.8	16.6	1.9	9.5	16.2	1.4	3.2	0.086
SOS	16.8	2.0	2.2	16.4	1.9	5.6	16.5	1.9	9.4	16.2	1.3	3.1	0.223
SOO	16.7	2.0	2.2	16.4	1.8	5.6	16.6	1.9	9.4	16.2	1.4	3.1	0.085
HSP _{TAGs mixture}	16.6	2.1	2.2	16.4	1.9	5.7	16.5	1.9	9.5	16.2	1.4	3.1	

^a Ca Caprylic, C Capric, La Lauric, M Myristic, P Palmitic, Pl Palmitoleic, S Stearic, O Oleic, L Linoleic, Ln Linolenic, A Arachidonic, E Eicosapentanoic, Dp Docosapentanoic and Dh Docosahexanoic

^b Hansen solubility parameters calculated based on the contribution of the three fatty acids in the TAG

^c Hansen solubility parameters calculated based on the contribution of the three fatty acids and glycerol in the TAG

^d Hansen solubility parameters calculated based on the contribution of the three fatty acids methyl esters derived from the TAG

^e Mass fraction of each TAG in the cocoa butter

HSPs Determined Using the Simple TAGs Contribution Method

Another approach was to use the fatty acid composition of each vegetable oil and assuming that the vegetable oils are comprised of only simple TAGs (i.e., TAGs

composed by the same fatty acid in all the glycerol positions, OOO, PPP, SSS, etc.). The HSPs of the simple TAGs were obtained using their SMILES. The HSPs for the vegetable oils were calculated by multiplying the HSPs for the simple TAGs, determined using the HSPiP software, by the mass fraction of the corresponding fatty

Table 4 Hansen solubility parameters (δ_d , δ_p , δ_h) of coconut oil determined with the HSPiP software (Reference values) in comparison with the parameters calculated using Eqs. 3 to 8

TAG ^a	Reference values (MPa ^{1/2})			FA ^b (MPa ^{1/2})			FA + glycerol ^c (MPa ^{1/2})			FAME ^d (MPa ^{1/2})			Mass fraction ^e
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	
CaCC	16.4	2.8	3.5	16.2	2.6	8.7	16.4	2.6	12.7	16.0	2.0	4.6	0.011
CaCLa	16.2	2.9	3.3	16.2	2.5	8.4	16.4	2.6	12.5	16.0	2.0	4.4	0.034
CCLa	16.4	2.6	3.2	16.2	2.4	8.0	16.4	2.5	12.1	16.0	1.9	4.2	0.128
CLaLa	16.2	2.7	3.0	16.2	2.3	7.7	16.4	2.4	11.9	16.0	1.9	4.1	0.178
LaLaLa	16.1	2.7	2.8	16.2	2.3	7.4	16.4	2.4	11.7	16.0	1.8	3.9	0.207
LaLaM	16.2	2.5	2.7	16.2	2.2	7.1	16.5	2.3	11.4	16.0	1.7	3.8	0.161
LaLaO	16.2	2.5	2.6	16.3	2.1	6.7	16.5	2.2	10.8	16.1	1.7	3.6	0.018
LaMM	16.4	2.3	2.6	16.3	2.1	6.9	16.5	2.2	11.2	16.1	1.6	3.6	0.101
LaMO	16.4	2.3	2.5	16.4	2.0	6.5	16.5	2.1	10.6	16.1	1.6	3.5	0.021
LaMP	16.3	2.4	2.5	16.3	2.1	6.6	16.5	2.2	10.7	16.0	1.6	3.5	0.031
LLO	16.5	2.0	2.7	16.7	1.8	6.0	16.8	1.9	9.6	16.5	1.4	3.5	0.031
LaOO	16.4	2.3	2.4	16.4	1.9	6.2	16.6	2.0	10.0	16.2	1.5	3.4	0.016
LaPP	16.2	2.5	2.4	16.3	2.1	6.4	16.4	2.1	10.3	16.0	1.6	3.4	0.0145
LOO	16.6	2.1	2.5	16.6	1.8	5.9	16.7	1.8	9.5	16.4	1.4	3.3	0.0145
PLO	16.5	2.2	2.5	16.5	1.8	6.0	16.7	1.9	9.6	16.3	1.4	3.3	0.009
MPO	16.5	2.2	2.3	16.4	1.9	6.1	16.5	2.0	9.9	16.1	1.5	3.3	0.008
OOO	16.6	2.1	2.3	16.5	1.8	5.7	16.6	1.8	9.4	16.3	1.4	3.2	0.002
POP	16.4	2.3	2.3	16.4	1.9	5.9	16.5	2.0	9.6	16.1	1.5	3.2	0.008
PPP	16.2	2.4	2.2	16.3	2.0	6.0	16.4	2.0	9.7	16.0	1.6	3.2	0.002
HSP _{TAGs mixture}	16.2	2.5	2.8	16.2	2.2	7.2	16.4	2.3	11.4	16.0	1.8	3.8	

^a Fatty acid legend as in Table 3

^b Hansen solubility parameters calculated based on the contribution of the three fatty acids in the TAG

^c Hansen solubility parameters calculated based on the contribution of the three fatty acids and glycerol in the TAG

^d Hansen solubility parameters calculated based on the contribution of the three fatty acids methyl esters derived from the TAG

^e Mass fraction of each TAG in the coconut oil

Table 5 Hansen solubility parameters (δ_d , δ_p , δ_h) of canola oil determined with the HSPiP software (Reference values) in comparison with the parameters calculated using Eqs. 3 to 8

TAG ^a	Reference values (MPa ^{1/2})			FA ^b (MPa ^{1/2})			FA + glycerol ^c (MPa ^{1/2})			FAME ^d (MPa ^{1/2})			Mass fraction ^e
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	
POP	16.4	2.3	2.3	16.4	1.9	5.9	16.5	2.0	9.6	16.1	1.5	3.2	0.008
POO	16.5	2.2	2.3	16.4	1.8	5.8	16.6	1.9	9.5	16.2	1.4	3.2	0.057
SOO	16.7	2.0	2.2	16.4	1.8	5.6	16.6	1.9	9.4	16.2	1.4	3.1	0.017
OOO	16.6	2.1	2.3	16.5	1.8	5.7	16.6	1.8	9.4	16.3	1.4	3.2	0.136
LLP	16.4	2.1	2.7	16.6	1.8	6.1	16.8	1.9	9.7	16.4	1.4	3.5	0.048
POL	16.5	2.2	2.5	16.5	1.8	6.0	16.7	1.9	9.6	16.3	1.4	3.3	0.075
LLO	16.5	2.0	2.7	16.7	1.8	6.0	16.8	1.9	9.6	16.5	1.4	3.5	0.223
OOL	16.6	2.1	2.5	16.6	1.8	5.9	16.7	1.8	9.5	16.4	1.4	3.3	0.242
LLLn	16.4	2.0	3.0	16.9	1.8	6.3	17.0	1.9	9.8	16.7	1.4	3.7	0.009
OLLn	16.4	2.1	2.8	16.8	1.8	6.1	16.9	1.9	9.7	16.6	1.4	3.5	0.123
PPLn	16.6	2.1	2.6	16.5	1.9	6.2	16.8	1.9	9.8	16.3	1.5	3.4	0.015
PPL	16.3	2.3	2.5	16.5	1.9	6.1	16.6	2.0	9.7	16.2	1.5	3.3	0.006
LLnLn	16.3	2.1	3.1	16.9	1.8	6.4	17.0	1.9	9.9	16.7	1.4	3.7	0.042
HSP _{TAGs mixture}	16.5	2.1	2.6	16.6	1.8	6.0	16.8	1.9	9.6	16.4	1.4	3.4	

^a Fatty acid legend as in Table 3

^b Hansen solubility parameters calculated based on the contribution of the three fatty acids in the TAG

^c Hansen solubility parameters calculated based on the contribution of the three fatty acids and glycerol in the TAG

^d Hansen solubility parameters calculated based on the contribution of the three fatty acids methyl esters derived from the TAG

^e Mass fraction of each TAG in the canola oil

acid present in the vegetable oil. The results obtained with the two approaches were compared with those

obtained using the HSPiP software considering the actual complex TAG composition of each vegetable oil.

Table 6 Hansen solubility parameters (δ_d , δ_p , δ_h) of fish oil determined with the HSPiP software (Reference values) in comparison with the parameters calculated using Eqs. 3 to 8

TAG ^a	Reference values (MPa ^{1/2})			FA ^b (MPa ^{1/2})			FA + glycerol ^c (MPa ^{1/2})			FAME ^d (MPa ^{1/2})			Mass fraction ^e
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	
DhDhDh	16.4	1.3	4	17.6	1.4	6.6	17.6	1.5	9.6	17.4	1.1	4.3	0.0611
DpDhDh	16.5	1.3	3.9	17.5	1.4	6.5	17.6	1.5	9.5	17.3	1.1	4.2	0.4337
EEDp	16.6	1.4	3.7	17.4	1.6	6.5	17.5	1.7	9.7	17.2	1.2	4.1	0.1649
EDpDp	16.2	2.2	3.0	17.4	1.5	6.4	17.5	1.6	9.5	17.2	1.2	4.1	0.0268
PIDhDh	16.4	1.6	3.6	17.3	1.6	6.5	17.4	1.7	9.7	17.1	1.2	4.1	0.0468
DpDpDp	16.7	1.3	3.6	17.4	1.4	6.2	17.5	1.5	9.3	17.2	1.1	4.0	0.0386
PEE	16.3	1.9	3.3	17.1	1.8	6.5	17.1	1.8	9.8	16.8	1.4	3.9	0.0132
ODhDp	16.7	1.6	3.3	17.2	1.5	6.2	17.3	1.6	9.4	17.0	1.2	3.9	0.0253
ODpDp	16.8	1.6	3.2	17.1	1.5	6.1	17.2	1.6	9.3	16.9	1.2	3.8	0.0087
PIODh	16.3	2.2	2.7	16.9	1.7	6.3	17.0	1.8	9.7	16.7	1.3	3.8	0.0077
SDpDp	16.9	1.5	3.1	17.1	1.6	6.0	17.2	1.7	9.3	16.9	1.2	3.7	0.0532
PPDh	16.2	2.3	2.6	16.8	1.8	6.2	16.9	1.8	9.6	16.5	1.4	3.7	0.0333
PODp	16.6	1.9	2.8	16.8	1.7	6.0	16.9	1.8	9.5	16.5	1.3	3.5	0.0027
PISDp	16.6	1.8	2.8	16.8	1.7	6.0	16.9	1.8	9.6	16.6	1.3	3.6	0.0027
SOE	16.6	1.9	2.8	16.8	1.8	6.0	16.9	1.8	9.6	16.5	1.3	3.5	0.0027
SDpO	16.8	1.8	2.7	16.8	1.7	5.8	16.9	1.8	9.4	16.6	1.3	3.5	0.0569
PIOO	16.4	2.2	2.4	16.5	1.8	5.9	16.6	1.9	9.6	16.3	1.4	3.3	0.0124
PPPI	16.2	2.4	2.4	16.4	2.0	6.1	16.5	2.0	9.8	16.1	1.6	3.3	0.0091
HSP _{TAGs mixture}	16.5	1.5	3.6	17.3	1.5	6.4	17.4	1.6	9.5	17.1	1.2	4.1	

^a Fatty acid legend as in Table 3

^b Hansen solubility parameters calculated based on the contribution of the three fatty acids in the TAG

^c Hansen solubility parameters calculated based on the contribution of the three fatty acids and glycerol in the TAG

^d Hansen solubility parameters calculated based on the contribution of the three fatty acids methyl esters derived from the TAG

^e Mass fraction of each TAG in the fish oil

Results and Discussion

The δ_d , δ_p and δ_h of common saturated and unsaturated fatty acids and their methyl ester derivatives are shown in Tables 1 and 2, respectively. Overall, the behavior of δ_d , δ_p and δ_h of the fatty acids methyl esters is similar to the homologues fatty acids. Irrespective of the fatty acid chain length, δ_d for the saturated fatty acids and the methyl esters remains constant at $\sim 16 \text{ MPa}^{1/2}$ (Tables 1 and 2). The overall contribution from the London dispersion forces to the cohesive energy density remains constant with increasing chain length. This is because the molecular volume increases linearly to the change in energy making the energy density constant. On the other hand, as the carbon number increases δ_p decreases, indicating that as chain length increases the ability to orientate their electric charge decreases [28]. Finally, the decrease in δ_h , as a function of increasing chain length, indicates that the hydrogen-bonding capacity per unit volume decreases due to the larger apolar contribution by the additional methyl groups. However, this behavior was less prevalent for the unsaturated fatty acids and the corresponding methyl esters.

For unsaturated fatty acids and methyl esters δ_d and δ_h , increase as a function of the number of π -bonds (Tables 1

and 2). Particularly for δ_d , the results indicate that the presence of the double bonds results in greater London dispersion forces. Similarly, increasing the number of double bonds in the molecule causes δ_h to increase (Tables 1 and 2). Although the double bonds increase London dispersion forces in the molecule (δ_d), the structural organization of the unsaturated chain limits the inter-molecular interactions throughout the hydrocarbon chain. However, since the carboxyl and methyl-ester groups are at the end of the molecule, the molecular capability to develop hydrogen bonds is favored as the number of double bonds increases. δ_p has little variation depending on the unsaturation degree, but this does not present a clear tendency. δ_p and δ_h are both greater for fatty acids than fatty acid methyl esters because the polarity for carboxylic acids is greater than esters. The conversion of the functional group from carboxylic acid to an ester decreases the polarity (δ_p) of the molecule and the molecular capacity to form hydrogen bonds (δ_h).

Generally, HSPs are effected by the addition and subtraction of all functional groups, in the case of lipids, the addition of hydroxyl, amine, and carboxylic acid groups have the greatest effect on increasing δ_h and to a lesser extent δ_p . Functional groups, such as ketones, aldehydes and esters will

Table 7 Hansen solubility parameters (δ_d , δ_p , δ_h) of soybean oil determined with the HSPiP software (Reference values) in comparison with the parameters calculated using Eqs. 3 to 8

TAG ^a	Reference values (MPa ^{1/2})			FA ^b (MPa ^{1/2})			FA + glycerol ^c (MPa ^{1/2})			FAME ^d (MPa ^{1/2})			Mass fraction ^e
	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	δ_d	δ_p	δ_h	
POP	16.4	2.3	2.3	16.4	1.9	5.9	16.5	2.0	9.6	16.1	1.5	3.2	0.002
POS	16.6	2.1	2.2	16.4	1.9	5.7	16.5	1.9	9.5	16.1	1.4	3.1	0.001
POO	16.5	2.2	2.3	16.4	1.8	5.8	16.6	1.9	9.5	16.2	1.4	3.2	0.009
SOO	16.7	2.0	2.2	16.4	1.8	5.6	16.6	1.9	9.4	16.2	1.4	3.1	0.007
LLL	16.5	2.0	2.9	16.8	1.8	6.2	16.9	1.9	9.7	16.6	1.4	3.6	0.3
OOO	16.6	2.1	2.3	16.5	1.8	5.7	16.6	1.8	9.4	16.3	1.4	3.2	0.046
LLP	16.4	2.1	2.7	16.6	1.8	6.1	16.8	1.9	9.7	16.4	1.4	3.5	0.064
POL	16.5	2.2	2.5	16.5	1.8	6.0	16.7	1.9	9.6	16.3	1.4	3.3	0.037
LLO	16.5	2.0	2.7	16.7	1.8	6.0	16.8	1.9	9.6	16.5	1.4	3.5	0.269
OOL	16.6	2.1	2.5	16.6	1.8	5.9	16.7	1.8	9.5	16.4	1.4	3.3	0.139
LLLn	16.4	2.0	3	16.9	1.8	6.3	17.0	1.9	9.8	16.7	1.4	3.7	0.02
LLS	16.6	2.0	2.7	16.6	1.8	6.0	16.8	1.9	9.6	16.4	1.4	3.4	0.036
OLLn	16.4	2.1	2.8	16.8	1.8	6.1	16.9	1.9	9.7	16.6	1.4	3.5	0.017
OOLn	16.5	2.1	2.6	16.7	1.8	6.0	16.8	1.9	9.6	16.5	1.4	3.4	0.004
PLLn	16.3	2.2	2.8	16.7	1.9	6.2	16.8	1.9	9.8	16.5	1.5	3.5	0.004
POLn	16.3	2.2	2.6	16.6	1.9	6.1	16.7	1.9	9.7	16.4	1.5	3.4	0.001
PPL	16.3	2.3	2.5	16.5	1.9	6.1	16.6	2.0	9.7	16.2	1.5	3.3	0.008
PPLn	16.6	2.1	2.6	16.5	1.9	6.2	16.7	2.0	9.8	16.3	1.5	3.4	0.001
SLP	16.5	2.1	2.4	16.5	1.9	5.9	16.6	1.9	9.6	16.2	1.4	3.3	0.008
SLS	16.8	1.9	2.4	16.5	1.9	5.7	16.6	1.9	9.5	16.3	1.3	3.2	0.001
SOL	16.7	2.0	2.5	16.5	1.8	5.8	16.7	1.9	9.5	16.3	1.4	3.3	0.026
HSP _{TAGs mixture}	16.5	2.0	2.7	16.7	1.8	6.0	16.8	1.9	9.6	16.5	1.4	3.5	

^a Fatty acid legend as in Table 3

^b Hansen solubility parameters calculated based on the contribution of the three fatty acids in the TAG

^c Hansen solubility parameters calculated based on the contribution of the three fatty acids and glycerol in the TAG

^d Hansen solubility parameters calculated based on the contribution of the three fatty acids methyl esters derived from the TAG

^e Mass fraction of each TAG in the soybean oil

increase δ_p and to a lesser extent will increase δ_h . These functional groups have very little effect on δ_d , which is primarily effected by the addition of methyl and aromatic groups. The replacement of a single bond with an unsaturated double bond does not contribute to δ_p or δ_h but would see a decrease in δ_d .

Table 8 Hansen solubility parameters (δ_d , δ_p , δ_h) determined for the vegetable oils using the HSPiP software and calculated using the Hansen solubility parameters (δ_d , δ_p , δ_h) for the symmetrical triglycerides (TAGs) and fatty acid mass fraction

Sample	TAGs ^a	δ_d	δ_p	δ_h	Mass fraction of TAGs in oils	
Cocoa butter	PPP	16.2	2.4	2.2	0.30	
	SSS	16.9	1.9	2.1	0.31	
	OOO	16.6	2.1	2.3	0.38	
	LnLnLn	16.5	2.0	2.9	0.02	
	HSPs _{TAGsmixture}	16.6	2.1	2.2		
	HSPs HSPiP _{Software}	16.6	2.1	2.2		
Coconut oil	CaCaCa	16.2	3.4	4.0	0.02	
	CCC	16.5	2.5	3.3	0.16	
	LaLaLa	16.1	2.7	2.8	0.56	
	MMM	16.6	2.1	2.5	0.14	
	PPP	16.2	2.4	2.2	0.03	
	OOO	16.6	2.1	2.3	0.05	
	LLL	16.5	2.0	2.9	0.03	
	HSPs _{TAGsmixture}	16.2	2.5	2.8		
	HSPs HSPiP _{Software}	16.2	2.5	2.8		
Canola oil	PPP	16.2	2.4	2.2	0.07	
	SSS	16.9	1.9	2.1	0.01	
	OOO	16.6	2.1	2.3	0.49	
	LLL	16.5	2.0	2.9	0.35	
	LnLnLn	16.5	2.0	2.9	0.08	
	HSPs _{TAGsmixture}	16.5	2.1	2.6		
	HSPs HSPiP _{Software}	16.5	2.1	2.6		
	Fish oil	PPP	16.2	2.4	2.2	0.03
SSS		16.9	1.9	2.1	0.03	
PIPIPI		16.1	2.4	2.8	0.04	
OOO		16.6	2.1	2.3	0.04	
EEE		16.2	1.7	3.8	0.13	
DpDpDp		16.7	1.3	3.6	0.33	
DhDhDh		16.4	1.3	4.0	0.40	
HSPs _{TAGsmixture}		16.5	1.5	3.6		
HSPs HSPiP _{Software}		16.5	1.5	3.6		
Soybean oil		PPP	16.2	2.4	2.2	0.05
		SSS	16.9	1.9	2.1	0.03
	OOO	16.6	2.1	2.3	0.27	
	LLL	16.5	2.0	2.9	0.64	
	LnLnLn	16.2	2.1	3.2	0.02	
	HSPs _{TAGsmixture}	16.5	2.0	2.7		
	HSPs HSPiP _{Software}	16.5	2.0	2.7		

^a Fatty acid legend as in Table 3

The Tables 3 to 7 show HSPs for TAGs present in cocoa butter, coconut oil, canola oil, fish oil, and soybean oil, respectively. For each vegetable oil, the HSPs for the TAGs were determined using the HSPiP software or calculated using Eqs. 3 to 5 as previously described (see “HSPs Determined Using the Group Contribution Method”). The use of Eqs. 3 to 5 assume that the HSPs of each TAG in the vegetable oils, result from the contribution of the three fatty acids in the TAG, the three fatty acids and glycerol in the TAG, or the three fatty acid methyl esters derived from the TAG (FA, FA + glycerol, and FAME, respectively). The HSPs for each TAG mixture are shown in Tables 3 to 7 and are determined by HSPiP software or calculated using Eqs. 6 to 8. Within this context, independent of the type of vegetable oil, δ_d was calculated

Table 9 Hansen solubility parameters (δ_d , δ_p , δ_h) determined for triglycerides with the HSPiP software using the SMILES

TAGs	δ_d	δ_p	δ_h	δ_t
Tributylin	16.3	3.9	5.7	17.7
Trivalerin	16.6	3.7	5.3	17.8
Tricaproin	16.6	3.4	5.0	17.7
Trioenanthin	16.3	3.3	4.5	17.2
Tricaprylin	16.2	3.4	4	17.0
Tripelargonin	16.6	2.6	3.4	17.1
Tricaprin	16.5	2.5	3.3	17.0
Triundecanoin	16.3	2.5	3.1	16.8
Trilaurin	16.1	2.7	2.8	16.6
Tritridecanoin	16.6	2.1	2.4	16.9
Trimyristin	16.6	2.1	2.5	16.9
Tripentadecanoin	16.4	2.2	2.4	16.7
Tripalmitin	16.2	2.4	2.2	16.5
Tripalmitolein	16.1	2.4	2.8	16.5
Trimargarin	16.9	1.9	2.0	17.1
Tristearin	16.9	1.9	2.1	17.1
Triolein	16.6	2.1	2.3	16.9
Trivaccenin	16.7	1.9	2.6	17.0
Trilinolein	16.5	2.0	2.9	16.9
Trilinolenin	16.2	2.1	3.2	16.6
Tristearidonin	17.0	1.5	3.5	17.4
Trinonadecanoin	16.7	2.0	2.1	16.9
Triarachidin	16.6	2.2	2.0	16.9
Triecosenoin	17.3	1.7	2.2	17.5
Triarachidonin	16.6	1.7	3.6	17.1
Triecosapentaenoin	16.2	1.7	3.8	16.7
Triheneicosanoin	17.5	1.8	1.8	17.7
Tribehenin	17.4	1.8	1.9	17.6
Triclupanodonate	16.7	1.3	3.6	17.1
Tridocosahexaenoin	16.4	1.3	4.0	16.9
Tritricosanoin	17.3	1.9	2.0	17.5
Trilignocerin	17.2	2.1	1.9	17.4

based on fatty acids, fatty acids and glycerol, and fatty acid methyl esters and each calculated parameter was similar to the corresponding parameter determined using the HSPiP software. In contrast, δ_p values calculated for FA and FA + glycerol were similar to those calculated using the HSPiP software. These results indicate that the polarity of these structures is not greatly affected by the configuration used to calculate this parameter. It may be expected that the presence of glycerol, as an independent molecule, added to the three fatty acids (i.e., FA + glycerol) would result in a significant increase in δ_p , however the value of δ_p is similar to the parameter determined by the HSPiP software. For the FAME, the presence of the methyl group attached to the ester group decreases the polarity of the molecule, and thus the corresponding δ_p values were lower than those determined with the HSPiP software.

Finally, the δ_h values calculated for the vegetable oils, particularly those resulting from the contribution of FA and FA + glycerol, were significantly higher than those determined using the software (Tables 3 to 7). Compared with the TAGs, the presence of the carboxylic functional group in the FA and FAME provide the ability to establish hydrogen bonds. In the same context, the presence of the three hydroxyl groups in the glycerol results in higher capacity to develop hydrogen bonds and as a consequence has the highest value of δ_h .

The HSPs for vegetable oils, calculated using the contributions of the FA, FA + glycerol, or FAME, did not show good correlations compared to the HSPs values obtained with the HSPiP software. Therefore, the larger group contribution method was abandoned and instead it was assumed that vegetable oils (i.e., complex mixtures of TAGs) are comprised of only simple TAGs (i.e., tristearin, triolein) in the same mass fraction as the fatty acids. The HSPs for mixtures of TAGs, obtained using the FA composition and assuming that all TAGs are simple, and the individual HSPs for simple TAGs (see “HSPs Determined Using the Simple TAGs Contribution Method”) were compared with the HSPs determined with the HSPiP software (HSP HSPiP software; Table 8). The HSP for each complex oil had the same values as the HSPs obtained using the HSPiP software. Hence, it is possible to obtain the HSPs for complex TAGs mixtures simply using the FA composition. This allows for very simple approximations of the HSPs for very complex vegetable oils. The position and distribution of the fatty acids on the TAGs do not modify the HSPs for the TAG mixtures. Therefore, the HSPs for complex mixtures of TAGs can be easily calculated using the fatty acid composition and assuming that simple TAGs are in the same ratios as the fatty acids. The HSPs for the simple TAGs, constituted by the most common fatty acids in vegetable oils and fats are shown in Table 9.

Conclusions

The HSPs of complex mixtures of TAGs were calculated first by assuming that the contributions to the dispersion, dipole-dipole, and hydrogen bonding interactions from each functional group in the TAGs are additive; and, second by utilizing simple TAGs based on the fatty acid composition. The first approach using group contributions to calculate the HSPs, based on independent units (i.e., fatty acids, fatty acids + glycerol and fatty acid methyl esters) did not correlate well to the HSPs for the vegetable oils (i.e., TAGs) using the HSPiP software. The HSPs for complex mixtures of TAGs, calculated using group contributions, do not provide adequate estimates of the HSPs. Simplifying the calculations by assuming that vegetable oils are composed of simple TAGs, in the same ratios as fatty acids, it is possible to estimate of δ_d , δ_p and δ_h . Using this simplified approach provided the same result for different complex fats and oils obtained using the HSPiP software and the actual TAGs present in those samples. Therefore, we do not need the actual TAG profile to calculate the HSP of the oil, but instead only require the fatty acid composition.

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