Characterization of solvent properties of methyl soyate by inverse gas chromatography and solubility parameters

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A study on the physicochemical properties of methyl soyate (or soybean oil fatty acid methyl esters) is very important for its use as a substitute solvent in liquid–liquid separations. Towards this end, the Hildebrand solubility parameter of methyl soyate was determined using an inverse gas chromatographic technique (IGC). Solute specific retention volumes of 19 solutes (varying in solubility parameter) were determined using methyl soyate as the stationary phase. Flory–Huggins interaction parameters between the solvent (methyl soyate) and the solutes, calculated using the solute retention data, were then used in studying the miscibility of the solute in the solvent at infinite dilution. The Hildebrand solubility parameters of methyl soyate varied from 8.03 to 7.49 $\mathrm{cal}^{1/2}\mathrm{cm}^{-3/2}$ at temperatures from 50–85 °C. The solubility parameter of methyl soyate at room temperature conditions extrapolated from the experimental data was found to be 8.49 $\mathrm{cal}^{1/2}\mathrm{cm}^{-3/2}$. This value is consistent with those obtained using group contribution methods for model methyl esters of C18 fatty acids found predominantly in methyl soyate. Hansen solubility spheres were plotted using the literature data (including this study) for the interactions of methyl soyate with 41 solutes to determine the three dimensional solubility parameter of methyl soyate at room temperature. These calculated solubility parameter values were consistent with those determined experimentally *via* IGC.

Introduction

Recently, a number of studies are focused on the use of "green" solvents in the place of volatile and toxic organic solvents in industrial applications. These green solvents can include ionic liquids,[1] supercritical or high pressurized fluids,[2] and other solvents that can be derived from renewable resources.[3] The use of fatty acid methyl esters (FAMEs) derived from soybean oil, commonly known as methyl soyate, as a green solvent has been noted in a number of studies.[4–6] These studies indicate methyl soyate exhibits low flammability, low toxicity, and good biodegradability for use in industrial and domestic cleaning operations, as well as in processing of food equipments. Methyl soyate is also used as a fuel, commercially referred to as "biodiesel".[7] Apart from these myriad uses, the physicochemical properties of these FAMEs have not been extensively studied in the literature.

Hildebrand solubility parameter theory defines a solubility parameter as the square root of the ratio of cohesive energy density to the molar volume of the compound.[8] The basic principle of this theory is that the closer the solubility parameter of the solute is to the solvent, the greater the solubility of the solute in the solvent. However, solubility parameters of many structurally complex biological and organic compounds cannot be easily determined by direct experimental measurement. The solubility parameters of such compounds are traditionally determined using functional group contribution methods,[9] inverse gas chromatography (IGC),[10] micro-calorimetric measurements,[11] sessile drop evaporation[12] and evaporative light scattering detection.[13]

The use of the inverse gas chromatographic technique as a source of physicochemical data has been widely applied to polymers,[14] liquid crystals,[15] organic pollutants,[16] pharmaceutical products[17] and vegetable oils.[18] A concise review on the use of the inverse gas chromatographic technique for calculating the physicochemical properties of compounds has been provided by Voelkel *et al.*[19] This technique involves the preparation of a chromatographic column containing the solvent (*i.e.*, stationary phase) under study. Known test solute probes and temperatures are selected and their retention volume data used to quantify the interaction of these test probes with the stationary phase column packing.

The above-mentioned technique can also be extended to calculate the Hansen three dimensional solubility parameters of the solvent.[20] The basic tenet of the Hansen solubility parameter theory is that the total solubility parameter of a compound is dependent on the contribution of the dispersive, polar and hydrogen bonding forces contributing to the total solubility parameter. This theory was traditionally used to study the interactions of polymeric and biological compounds with a variety of solvents.[21] Knowing the interactions of the selected compounds with a range of chemicals, whose solubility parameters can be obtained from literature,[9] it is possible to plot Hansen spheres that depict the miscibility range of the compound under study. The center of the mass of the sphere in the three dimensional space with the dispersive, polar and

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Table 1 Specific retention volumes (mL g^{-1}) for solute/methyl soyate systems at selected experimental temperatures

	Temperature/°C							
	49.9		59.8		75.2		85.1	
Solute	Mean	SD[a]	Mean	SD[a]	Mean	SD[a]	Mean	SD[a]
Methanol	50.7	12.2	36.7	7.10	22.6	2.20	16.4	1.90
Ethanol	96.1	22.8	68.0	12.0	40.4	1.50	28.6	2.50
2-Propanol	144	30.0	99.6	19.0	57.6	4.30	39.9	3.90
1-Propanol	268	40.0	182	22.0	102	5.00	68.9	5.00
1-Butanol	753	152	485	79.0	251	10.0	161	12.0
n-Hexane	130	8.00	95.0	8.90	59.4	6.30	43.4	6.40
n-Heptane	343	23.0	239	21.0	139	15.0	96.7	15.3
n-Octane	882	67.0	591	54.0	324	37.0	217	35.0
n-Decane	5190	—[b]	3370	—[b]	1770	219	1150	143
Cyclohexane	241	24.0	176	110	110	11.0	80.0	11.2
Benzene	349	26.0	251	28.0	153	9.00	110	12.0
Toluene	968	80.0	661	77.0	373	23.0	255	29.0
Ethylbenzene	2230	193	1470	173	784	62.0	516	64.0
Acetone	79.0	9.90	59.5	9.20	38.9	1.20	29.3	2.00
Methyl ethyl ketone	206	24.0	148	21.0	90.8	3.00	65.4	4.80
Methyl isobutyl ketone	801	101	547	44.0	309	12.0	211	13.0
Furfural	2680	132	1790	253	969	31.0	645	30.0
Dichloromethane	128	8.00	94.3	7.30	59.9	6.90	44.3	7.00
Trichloroethylene	545	24.0	379	28.0	220	14.0	154	15.0

[a] Standard deviation (SD) calculated using eqn (2). [b] No value due to a very small number of samples.

hydrogen bonding axes is the Hansen solubility parameter of the compound under study.

In this study, the inverse gas chromatographic technique has been used to determine the solubility parameter of methyl soyate as a function of temperature and the solubility parameter values are verified using the Hansen three dimensional solubility parameter approach. The knowledge of the interaction and solubility parameters of methyl soyate at the selected temperatures can assist in explaining the solution and solvent behavior exhibited by methyl soyate and, thereby, optimizing its application as a renewable and sustainable solvent or fuel.

Results and discussion

Retention volumes

The experimental procedure followed in this study is very similar to that described by King.[22] Here, the interaction between the test probe solutes and the solvent (methyl soyate) are studied using the solute retention volumes ($V_g°$) and derived Flory–Huggins interaction parameter (χ). Retention volumes were calculated from eqn (1) as:

$$V_g^{\circ} = \frac{(t_r - t_a)(273.16/T_o)(760/P_o)(1 - P_w/P_o)(j)(F_o)}{w_2} \tag{1}$$

where t_r, t_a = retention time of solute (r) and nonsorbed solute (a) (methane in this study), respectively; F_o = flow rate at ambient conditions; P_o = atmospheric pressure under ambient conditions; P_w = vapor pressure of water; j = James–Martin compressibility factor; T_o = temperature at ambient conditions; and w_2 = weight of the stationary phase.

The retention volume data for all five columns used in this study are shown in Table 1. The error in the retention volumes was found to be 2.5% for slow eluting solutes and 3.3–5% for the faster eluting solutes. The specific retention volumes for the four higher loading columns revealed an excellent agreement between the values for all solutes while a 15% loading column resulted in lower values. This variation in $V_g°$ was a result of an error in the column preparation and hence the values were not used further in this study. The standard deviation (SD) of the sample retention volumes at the different temperatures was calculated using eqn (2) as follows:

$$\mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{n}\left(V_{g,i} - \bar{V}_g\right)^2}{(n-1)}} \tag{2}$$

where $V_{g,i}$ = specific retention volume (g mL^{-1}) for an i^th sample at a particular temperature for a selected solute; $\bar{V}_g$ = average specific retention volume (g mL^{-1}) for a selected solute at a particular temperature and n = number of samples.

Interaction parameters

The specific retention volume data was used in calculating the Flory–Huggins interaction parameter given by eqn (3) as:

$$\chi = \ln\left(\frac{273.16 \times R}{V_g^{\circ} M_1 P_1^{\circ}}\right) - \frac{p_1^{\circ}(B_{11} - \bar{V}_1)}{RT} - \ln\left(\frac{v_1}{v_2}\right) - 1 + \frac{\bar{V}_1}{M_2 v_2} \tag{3}$$

where R = universal gas constant; M_1, M_2 = molecular weight of the solute and solvent respectively; $p_1°$ = vapor pressure of the solute at the column temperature (T); B_{11} = second pure virial coefficient of solute at T; v_1, v_2 = specific volumes of the solute and solvent at T; and $\overline{V_1}$ = molar volume of the solute at T. The pure second virial coefficient was found using eqn (4) as:

$$B_{11} = a + \frac{b}{T} + \frac{c}{T^3} + \frac{d}{T^8} + \frac{e}{T^9} \qquad (4)$$

where constants a, b, c, d and e for the solutes were found using the Yaws compendium.[23] The second virial coefficients of the solutes calculated from the above equation were consistent with the literature.[22] The vapor pressure of the solutes was obtained using an Antoine equation using constants given in the Yaws compendium.[23] The average molecular weight of methyl soyate was 292.2 g gmol^{-1} as derived from literature,[24] while the molar volume of methyl soyate at different temperatures was calculated from methyl soyate density data given in the correlation of Tate *et al.*[25] The standard deviation in the interaction parameters of the selected solutes with methyl soyate at the experimental temperatures are proportional to those reported for the retention volumes.

The calculated interaction parameters for the 19 solutes at the four different temperatures are presented in Table 2. It can be seen from the table that the interaction parameter values for the aromatic and the chlorinated hydrocarbons are negative, indicating that the interaction between these particular solutes and the solvent is exothermic while the other solutes showed an endothermic mixing with the solvent. Also, there is a consistent decrease in the interaction parameters between the solute and the solvent indicating a greater solute–solvent miscibility with increasing temperature. However, this was not found to be the case for all of the solute–solvent interactions. The three lower alkanes (C6–C8) showed an increase in the interaction parameter with an increase in temperature, indicative of a decrease in their miscibility with methyl soyate at higher temperatures. Despite having a negative χ value, the interaction parameters of the aromatic and the chlorinated hydrocarbons (with the exception of benzene) also displayed a decreasing χ trend with increasing temperature, *i.e.*, an increase in solubility with temperature. From Table 2, the mixing process between *n*-decane and methyl soyate changed from an endothermic mixing to an exothermic one with an increase in temperature.

The critical interaction parameter (χ_C), as defined in the literature,[26,27] can be calculated using eqn (5) as:

$$\chi_C = \frac{\left(1 + x^{1/2}\right)^2}{2x} \qquad (5)$$

where, x = ratio of the molar volume of the solvent (methyl soyate) and that of the solute. The critical chi interaction parameters, χ_C, calculated by eqn (5), have been tabulated in the last column in Table 2 for comparison with the χ values determined by IGC. In general, the χ_C values in Table 2 are relatively independent of the temperature, since the change in molar volume with temperature for both solute and solvent are of similar magnitude over the given experimental temperature range. In all cases, χ for the various solute–methyl soyate pairs are less than χ_C except for methanol and ethanol and are very close for the propanol isomers. This implies that the lower *n*-alkanols are either not miscible or very soluble in methyl soyate, whereas the other solute–solvent pairs have lower χ_C values than their calculated χ_C values, thereby showing varying degrees of solubility-miscibility for methyl soyate as a solvent—in fact, the aromatic and chlorinated solutes have negative χ values as noted previously. Similar miscibility trends were observed for soybean

Table 2 Flory–Huggins interaction parameters and critical interaction parameters (χ_C) for solute/methyl soyate systems at selected experimental temperatures

	Temperature/°C				
Solute	49.9	59.8	75.2	85.1	χ_C
Methanol	1.80	1.75	1.67	1.62	0.900–0.901
Ethanol	1.80	1.74	1.66	1.60	0.994–0.995
2-Propanol	1.12	1.06	0.968	0.907	1.08
1-Propanol	0.966	0.953	0.935	0.923	1.07
1-Butanol	0.770	0.744	0.705	0.679	1.15
n-Hexane	0.341	0.342	0.344	0.345	1.31
n-Heptane	0.261	0.264	0.268	0.270	1.36
n-Octane	0.184	0.186	0.190	0.192	1.42
n-Decane	0.0622	0.0357	−0.00399	−0.0305	1.53
Cyclohexane	0.129	0.119	0.105	0.0950	1.22
Benzene	−0.165	−0.167	−0.169	−0.170	1.13–1.14
Toluene	−0.178	−0.175	−0.170	−0.166	1.20–1.21
Ethylbenzene	−0.338	−0.326	−0.308	−0.296	1.26–1.27
Acetone	0.830	0.806	0.771	0.747	1.07
Methyl ethyl ketone	0.457	0.448	0.434	0.425	1.14
Methyl isobutyl ketone	0.175	0.153	0.120	0.097	1.28
Furfural	0.499	0.466	0.416	0.382	1.01
Dichloromethane	−0.608	−0.591	−0.564	−0.547	1.03
Trichloroethylene	−0.689	−0.668	−0.637	−0.616	1.14

oil–organic solvent systems.[22] As indicated in the literature,[22,26,27] it should be noted that the χ values are also dependent on the solution composition and, hence, χ values at infinite dilution might not be applicable with an increase in the mole fraction of the solutes in the methyl soyate stationary phase.

In studying the effect of solute molecular structure on the interaction between the solute and the solvent, the total interaction parameter is assumed to be a sum of its enthalpic and entropic contributions.[28] The total interaction parameter can be expressed mathematically by eqn (6), where the enthalpy term can be calculated from the Hildebrand–Scatchard regular solution theory[8] as:

$$\chi = \chi_H + \chi_S = \frac{v_1(\delta_1 - \delta_2)^2}{\mathrm{R}T} + \chi_S \tag{6}$$

where, δ_1 and δ_2 are the solubility parameters of the solvent, respectively, and v_1 refers to the molar volume of the solute at the column temperature, T. The Hildebrand solubility parameter can be given by eqn (7) as:

$$\delta = \mathrm{CED}^{1/2} = \left[\frac{\Delta H_{\mathrm{vap}} - \mathrm{R}T}{V_{\mathrm{m}}}\right]^{1/2} = \left[\frac{\Delta E}{V_{\mathrm{m}}}\right]^{1/2} \tag{7}$$

where, CED = cohesive energy density of the compound; ΔH_{vap} = molar heat of vaporization of the compound; V_{m} = molar volume of the compound; and ΔE = energy of vaporization of the compound. The solubility parameters of the test solutes at room temperature conditions were obtained from the literature[9] and the temperature dependence of the solubility parameter of the solute was obtained from the Jayasri and Yaseen correlation[29] given in eqn (8) as:

$$\delta_{1,T_2} = \delta_{1,T_1}\left(\frac{1-T_2}{1-T_1}\right)^{0.34} \tag{8}$$

where, δ_{1,T_1} = solubility parameter of the solute at the reference reduced temperature (T_1) and δ_{1,T_2} = solubility parameter of the solute at the reduced temperature (T_2). This correlation indicates that the solubility parameters of the solutes decrease with an increase in temperature, consistent with their loss of cohesional energy per unit volume. It can also be shown from eqn (6) that the χ values are dependent on the difference in the solubility parameters of the solute and the solvent.[22] A negative χ value between methyl soyate and moderately polar compounds like the aromatic and the chlorinated hydrocarbons indicate that methyl soyate is slightly polar in nature. However, the greater positive χ values between methyl soyate and polar compounds (the alcohols) verify that the solvent is moderately polar.

Solubility parameters

Guillet and others[30,31] have modified the eqn (6) to permit the determination of the solubility parameter of the solvent (methyl soyate) from IGC retention data as:

$$\left(\frac{\delta_1^2}{\mathrm{R}T} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{\mathrm{R}T}\right)\delta_1 - \left(\frac{\delta_2^2}{\mathrm{R}T} + \frac{\chi_S}{V_1}\right) \tag{9}$$

From eqn 8, it can be seen that by plotting $\left(\frac{\delta_1^2}{\mathrm{R}T} - \frac{\chi}{V_1}\right)$ *vs.* δ_1 (solubility parameter of the solute), the slope of the linear regression is given by $\left(\frac{2\delta_2}{\mathrm{R}T}\right)$ and, thereby, can yield the solubility parameter of methyl soyate as a function of the temperature. This process can be repeated for all the temperatures and extrapolated to yield the solubility parameter of methyl soyate at room temperature for comparison purposes.

Fig. 1 shows a plot of eqn (9) for one of the four experimental temperatures (49.9 °C) used in this study. Approximately 255 data points (including all of the column loadings) were used in plotting eqn (9) at each of the four experimental temperatures. Fig. 1 shows an excellent correlation coefficient of 0.988 for 49.9 °C. Similarly, correlation coefficients of 0.986, 0.986 and 0.984 were obtained at the experimental temperatures of 59.8, 75.2 and 85.1 °C, respectively. The solubility parameter of methyl soyate at room temperature obtained from a linear extrapolation of the values was found to be 8.49 cal$^{1/2}$cm$^{-3/2}$.

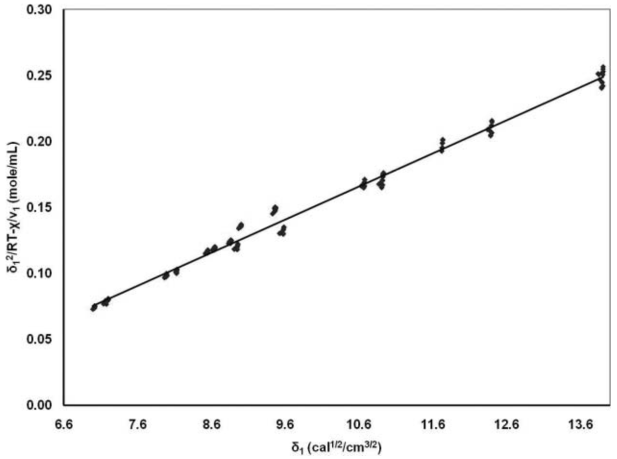

Fig. 1 Determination of the solubility parameter of methyl soyate at 49.9 °C according to eqn (9).

The solubility parameter of methyl soyate at the four experimental temperatures and the error (in cal$^{1/2}$cm$^{-3/2}$ units) associated with the different column loadings at each temperature are presented in Table 3. The solubility parameter values reported in Table 3 can be converted from cal$^{1/2}$cm$^{-3/2}$ to MPa$^{1/2}$ by using a factor of 2.0455 to aid in comparison with those estimated by the Hansen three-dimensional solubility parameter approach to be discussed in the latter part of this study.

It is evident from eqn (7) that the entropic contribution to the χ values is dependent on the size and shape of the solute molecules and the specific interactions between the solute and the solvent. Studies have indicated that an increase in the molecular weight of the solute increases the free volume contribution to χ_s, thereby, resulting in greater positive values of χ_s, indicative of an increase in the order of interaction between the solvent and the solute.[32] Using the experimentally determined solubility parameter value of methyl soyate and the interaction parameters presented in Table 2, the χ_s values for the solute–solvent interactions at four different temperatures were calculated. The χ_s values for compounds varied from −0.7 to 1.4 depending on the various solutes and their interaction with the solvent. It was found that

Table 3 Comparison between the solubility parameter of methyl soyate with that of methyl oleate, methyl stearate and methyl linoleate

Temperature/°C	Solubility parameter of methyl soyate/$cal^{1/2}cm^{-3/2}$ [a]	Solubility parameter of methyl oleate/$cal^{1/2}cm^{-3/2}$ [b]	Solubility parameter of methyl stearate/$cal^{1/2}cm^{-3/2}$ [c]	Solubility parameter of methyl linoleate/$cal^{1/2}cm^{-3/2}$ [c]
49.9	8.03 ± 0.2	8.13	8.63	8.67
59.8	7.85 ± 0.2	8.07	8.58	8.62
75.1	7.57 ± 0.1	7.97	8.49	8.54
85.2	7.39 ± 0.1	7.90	8.44	8.48

[a] From inverse gas chromatography. [b] From Yaws.[23] [c] From group contribution method.[33,29]

the χ_s values for acetone and ethanol were very high while those for methyl isobutyl ketone, cyclohexane and *n*-propanol were low.

Comparison of the solubility parameters of methyl soyate with that of model esters of fatty acids

Compositional studies indicate that soybean oil fatty acid methyl esters mainly consist of about 53% linoleic acid, 22% oleic acid and a mixture of palmitic, stearic and linolenic acids.[33] Comparison of the experimentally determined solubility parameters with those calculated for methyl oleate, methyl stearate and methyl linoleate are given in Table 3. The solubility parameters of methyl oleate were obtained from Yaws[23] while the solubility parameters of methyl stearate and methyl linoleate were calculated using the Fedors group contribution method,[34] their temperature dependence was estimated using the Jayasri and Yaseen correlation.[29] The graph in Fig. 2 compares the Hildebrand solubility parameters of the calculated methyl oleate, methyl stearate and methyl linoleate with the IGC experimentally-determined solubility parameters for methyl soyate. It can be seen from Fig. 2 that the solubility parameter of methyl soyate is only slightly lower than that estimated for the constituent individual fatty acid methyl esters. There is also a greater decrease in the experimentally-determined solubility parameter of methyl soyate in contrast with the trend shown for the other compounds. This difference in the temperature dependence of the solubility parameter of methyl soyate with that of the model esters can be primarily due to the linearity of the temperature dependence of model esters predicted using the Jayasri and Yaseen equation which maybe slightly inaccurate. This comparison of the solubility parameter values determined *via* IGC with calculated values illustrates the value of IGC as a versatile technique in computing the values of solubility parameters as a function of the temperature. It should be noted that the solubility parameter determined using IGC is the total solubility parameter. However, recently, a number of studies have been focused on calculating the Hansen three dimensional solubility parameters of polymers using inverse gas chromatography.[19,20,32,35]

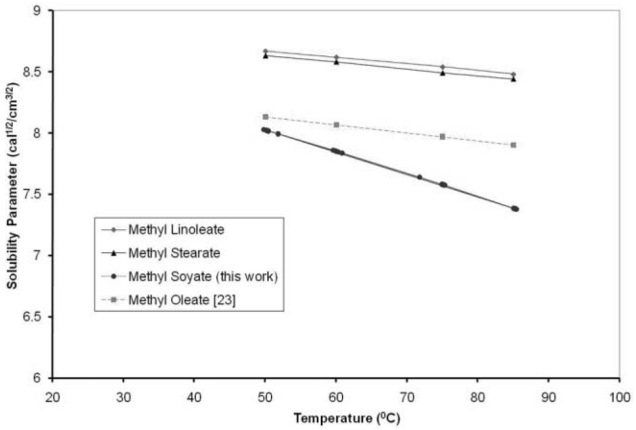

Fig. 2 Comparison of solubility parameter of methyl soyate with methyl oleate, methyl stearate and methyl linoleate over the selected experimental temperature range.

Hansen spheres

The principle behind the Hansen three-dimensional solubility parameter concept can be given by eqn (10) as:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{10}$$

where, δ_d, δ_p and δ_h are the solubility parameters of the compound due to dispersion, polar and hydrogen intermolecular forces contributions to the solubility parameter, respectively; and δ_T is the total solubility parameter of the compound.

In order to determine the Hansen solubility parameters of methyl soyate, the Hansen sphere approach was utilized. Here, the interaction of methyl soyate with 41 organic solutes reported in this work and other literature sources[5] were used to plot the Hansen spheres. The Hansen solubility parameters of the 41 solutes were obtained from the literature.[21] The Hansen spheres were plotted using a Hsp3D program kindly provided as a freeware by Dr Fred Turner (Western Research Institute, Laramie, WY, USA).[36] The center of mass of the sphere obtained from a computerized optimization method is assumed to be the Hansen three-dimensional solubility parameter of methyl soyate. The solubility parameter of methyl soyate obtained by this approach at room temperature was found to be $\delta_d = 7.53$ $cal^{1/2}cm^{-3/2}$, $\delta_p = 2.84$ $cal^{1/2}cm^{-3/2}$ and $\delta_h = 2.44$ $cal^{1/2}cm^{-3/2}$. The total solubility parameter of methyl soyate was calculated from eqn (9) as 8.41 $cal^{1/2}cm^{-3/2}$ or 17.2 $MPa^{1/2}$. The total solubility parameter of methyl soyate obtained by this method was consistent with that obtained from the inverse gas chromatographic technique (8.49 $cal^{1/2}cm^{-3/2}$).

The relative energy difference (RED) defined by eqn (11) can be used to determine the miscibility of methyl soyate with selected organic compounds as:

$$\text{RED} = \frac{R_a}{R_o} \tag{11}$$

Table 4 RED values of the selected solutes obtained by computerized optimization of their interaction with methyl soyate

Solute	RED	Solute	RED	Solute	RED
Methyl isobutyl ketone	0.31	Benzene	0.72	Isopropanol	1.42
Chloroform	0.48	Chlorobenzene	0.73	Propanol	1.54
Trichloroethylene	0.50	Butyric acid	0.78	Acetonitrile	1.63
Toluene	0.57	Methyl iodide	0.79	Dimethylsulfoxide	1.69
Decane	0.58	Acetone	0.84	Formic acid	1.73
Octane	0.59	1,4-Dichlorobenzene	0.89	Ethanol	1.82
Propylamine	0.59	Octanol	0.91	Salicylic acid	1.84
Heptane	0.60	Propionic acid	1.00	Pthalic acid	2.08
Cyclohexane	0.60	Carbon disulfide	1.00	Methanol	2.27
Ethylbenzene	0.61	Acetophenone	1.00	1,2 Dinitrobenzene	2.38
Hexane	0.62	Pentanol	1.14	Ethylene glycol	2.61
Methyl ethyl ketone	0.62	Acetic acid	1.22	Glycerol	3.00
1,2,4-Trichlorobenzene	0.68	Butanol	1.35	Water	4.49
Carbon tetrachloride	0.69	Furfural	1.41		

where, R_o = radius of the Hansen sphere obtained by a computerized optimization method as described above and R_a can be defined by eqn (12) as:

$$R_a^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2 \qquad (12)$$

In the above equation, the subscript "1" refers to the organic compound and "2" refers to methyl soyate. The RED values for the organic compounds obtained by the above method are given in Table 4. In principle, the mixture with the lowest RED value is considered the solvent exhibiting similar solvation properties with methyl soyate. The Hansen spheres plotted using three-dimensional axes consisting of dispersion, polar and hydrogen bonding solubility parameters (in $MPa^{1/2}$ units) is shown in Fig. 3(a). However, for a better understanding of the system, the dispersion and polar solubility parameters were plotted *vs.* the hydrogen bonding solubility parameter (in $MPa^{1/2}$ units) as shown in Fig. 3(b) and (c). It can be seen from the figures that the organic compounds having a RED value of 1.00 form the boundary of the Hansen sphere. Those solutes (solvents) indicating RED values greater than 1.00 show poor solute–solvent interactions and, hence, methyl soyate would not be a suitable substitute for these solvents. These RED values are consistent with the χ values shown in Table 2. However, the Hansen three-dimensional solubility parameter method does not fully account for the entropy of mixing (χ_S) effect to the relatively large size disparity between methyl soyate and the test probe molecules.

The plots in Fig. 3(b) and (c) also show certain immiscible solutes (indicated by darkened triangles) within the Hansen solvation sphere, which are actually outside the sphere on the other side related to the three-dimensional axes as shown in Fig. 3(a). It can be seen from the figures that the contribution of the polar and hydrogen bonding interactions towards the total solubility parameter of methyl soyate are very low. A similar result was seen in another study[37] using model fatty acid methyl esters varying in carbon number from C8 to C18, in which this result was attributed to the presence of oxygen atoms in the ester functional group and the absence of an electropositive hydrogen atom. It can be seen from Table 4 that the lowest RED value was obtained for methyl isobutyl ketone which also reported a low χ_s value (~0.2), as discussed previously. Also, the Hansen solubility parameters obtained by this approach is consistent with that available in the commercial datasheets[38] (δ_d = 7.9 $cal^{1/2}cm^{-3/2}$, δ_p = 2.9 $cal^{1/2}cm^{-3/2}$ and δ_h = 2.4 $cal^{1/2}cm^{-3/2}$) assumed to be determined from a group contribution method. Previous studies have indicated that a data fit of 1.0 obtained by the computerized optimization method using as few as 41 solutes is unlikely to yield highly accurate results and, hence, a further study of the interaction of methyl soyate with a wider range of solutes (solvents) could provide an accurate determination of the three-dimensional solubility parameter of methyl soyate using the Hansen sphere method.[21]

Experimental

Chemicals and materials

Methyl soyate was obtained as gratis samples from Cargill Industrial Oil & Lubricants (Chicago, IL, USA) and AG Environmental Products (Omaha, NE, USA). The methyl soyate specifications are shown in Table 5. All the test solutes (reagent grade) and reagents were obtained from VWR (Batavia, IL, USA). Chromasorb G (size: 45/60 mesh, acid washed and silanized) was obtained from Restek Corporation (Bellefonte, PA, USA). The helium, hydrogen and compressed air used in this study were obtained from Airgas products (Tulsa, OK, USA). Chromatographic injections were made using GC syringes obtained from Hamilton Company (Reno, NV, USA).

Table 5 Specifications of methyl soyate used in the IGC columns

Specifications	Soygold 1100[a]	Cargill[b]
CAS or Lot #	67784-80-9	17932
Methyl esters	>90%	99.2%
Color (Gardner)	3	2
Appearance	Light amber liquid	Light yellow liquid
Volatile organic matter, wt%	11.1	3.84
Flash point/°F	302	425
Kauri-butanol number	56	58
Specific gravity	0.88	0.88
Boiling point/°F	400 @ 1 atm	600 @ 1 atm
Additives	None	None

[a] Compiled from the literature.[38] [b] Compiled from the literature.[39]

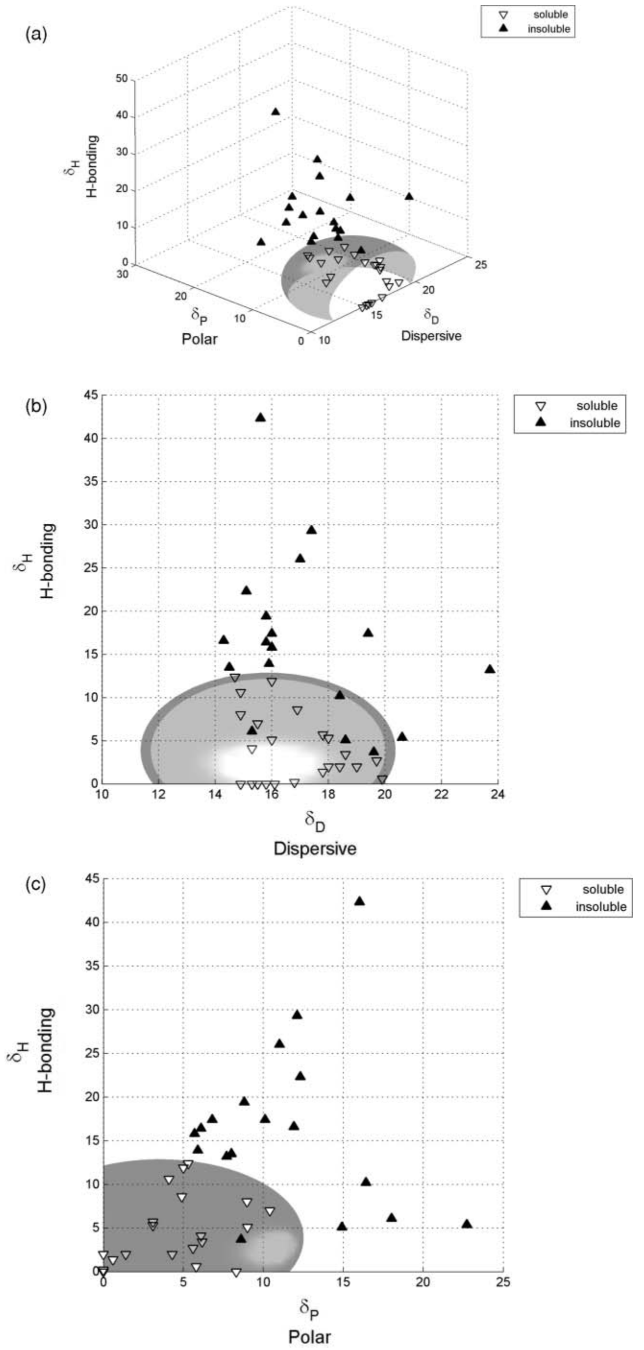

Fig. 3 (a) Three-dimensional solubility sphere of methyl soyate using computer program Hsp3D; (b) two-dimensional plot δ_h *vs.* δ_d of the solubility data for methyl soyate; (c) two-dimensional plot δ_h *vs.* δ_p of the solubility data for methyl soyate.

Preparation of the column

Chromatographic column packing was prepared by initially coating the methyl soyate on Chromasorb G followed by concentrating the mixture in dimethyl chloride using a Rotavapor R110 (Buchi Laboratechnik AG, Flawil, Switzerland). The amount of methyl soyate on the packing was measured by determining the relative weight loss *via* high temperature pyrolysis. Triplicate samples of the dried packing were weighed into ceramic crucibles and pyrolyzed in a bench top muffle furnace (Omegalux LMF A550, Omega Engineering Inc., Stamford, CT, USA) at 1200 °C overnight. The weight difference before and after pyrolysis was assumed to be the weight of the methyl soyate coated on the inert diatomaceous earth. The percentage liquid loading factor was calculated by dividing the amount of methyl soyate lost relative to the initial weight of the dry packing. The methyl soyate coated mixture was then packed in 50 cm, 1/4 in. O. D. solvent-rinsed copper tubing, inserting silanized glass wool on either end of the column. Columns consisting of methyl soyate loadings of approximately 15%, 20% and 25% were prepared and equilibrated in the gas chromatographic oven at 85 °C overnight.

Inverse gas chromatography

A modified Varian 1400 gas chromatograph with a flame ionization detector (Varian Inc., Pal Alto, CA, USA) was used for determining the retention volumes of the various probe chemicals. The experimental procedure followed in this study was previously described in King.[22] Helium was used as the carrier gas and its flow rate was measured with a soap bubble flow meter at the head of the column. The calculated flow rate was corrected for compressibility, temperature, pressure drop, and the pressure of the water in the flow meter by the method described by Laub and Pecsok.[40] The temperatures at the soap bubble flow meter, the gas chromatograph oven, the injector end of the column, and the detector end of the column were measured using iron-constantan (copper/nickel) thermocouples (J-Type thermocouples). The column temperatures were maintained at approximately 50, 60, 75 and 85 °C. The pressure drop across the column was measured with a mercury filled U-tube manometer. These probes were selected to consist of five chemical types, *n*-alkanes, aromatics, chlorinated hydrocarbons, ketones, and alcohols. Infinite dilution injections were made by extracting a very small concentration of the solute followed by constant pumping of the syringe to retain only a small saturated vapor pressure of the solute in the GC syringe. 5 μL of methane (used as nonsorbed solute) was then drawn in the GC syringe before injecting through the column. The atmospheric pressure was read from a mercury barometer (Fisher Scientific, Pittsburgh, PA, USA) at four-hour intervals. The thermocouple signals were translated to digital signals using a Cole-Parmer 18200–040 thermocouple module (Vernon Hills, IL, USA). The FID signal and a battery powered injection marker signal were translated to a digital signal using a Cole-Parmer 18200–00 analog input module. The digital signals from both modules were then used for data reduction and analysis. Statistical analysis was performed over all the column loadings to calculate the standard error in the measurements.

Conclusions

This study has focused on determining the solubility parameter of methyl soyate and its interaction with a select range of test solutes. Determination of such data will aid in assessing the substitution solvent properties of methyl soyate as a "green" solvent replacement for the test solutes. The Hansen three-dimensional solubility parameter concept and the Hansen spheres approach were used in coordination with the data obtained from this study to estimate the three-dimensional solubility parameter of methyl soyate. From the data presented in the study, it can be seen that the solvent properties of methyl soyate are consistent with those of several test solutes, *i.e.*, methyl isobutyl ketone, trichloroethylene and toluene. This knowledge can be used to further characterize methyl soyate as a substitute "green" solvent.

It was also found that the extrapolated total solubility parameter of methyl soyate at room temperature is very similar to that reported for soybean oil,[22] which is consistent with the observation that the solubility parameters of oleochemical derivatives increase for the alcohol, ester, acid and nitrile derivatives and decreased for the ether and amine derivatives with increasing carbon number, until reaching a limiting solubility parameter value of ~8.5 Hildebrand units (cal$^{1/2}$cm$^{-3/2}$).[11]

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