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Experimental solubilities of two lipid derivatives in supercritical carbon dioxide and new correlations based on activity coefficient models

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Abstract:

The solubilities of two lipid derivatives, geranyl butyrate and 10-undecen-1-ol, in SCCO₂ (supercritical carbon dioxide) were measured at different operating conditions of temperature (308.15 to 333.15 K) and pressure (10 to 18 MPa). The solubilities (in mole fraction) ranged from 2.1×10^{-3} to 23.2×10^{-3} for geranyl butyrate and 2.2×10^{-3} to 25.0×10^{-3} for 10-undecen-1-ol, respectively. The solubility data showed a retrograde behavior in the pressure and temperature range investigated. Various combinations of association and solution theory along with the different activity coefficient models were developed. The experimental data for the solubilities of 21 liquid solutes along with geranyl butyrate and 10-undecen-1-ol were correlated using both the newly derived models and the existing models. The average deviation of the correlation of the new models was below 15%.

Keywords: Solubilities; Association theory; Solution theory; Activity coefficient models.

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1. Introduction

A fluid, whose temperature and pressure has been raised above the critical point is called as a supercritical fluid (SCF). These fluids have properties intermediate of gases and liquids and find a number of applications in chemical engineering and biotechnology¹⁻⁷. In particular, carbon dioxide as a supercritical fluid has been investigated extensively as it is non-flammable as compared to other fluids such as hydrocarbon gases and fluorine based compounds. As the critical temperature of supercritical carbon dioxide is 304.25 K, it has been extensively utilized in processing biological materials, many of which are heat-labile⁸. Numerous studies pertaining to extraction and reaction of non-polar lipids (like vegetable oils, algal oil, animal fat and fatty acids) indicate the applicability of supercritical carbon dioxide⁹⁻¹².

With advances in oleochemistry, chemical derivatives of naturally occurring fatty acids and triglycerides are gaining immense importance in the areas of surfactants, perfumes, flavors, lubricants and reaction precursors. Supercritical carbon dioxide could be potentially used in many of these reactions and separations¹³⁻¹⁵. In this context, the importance of solubility data in designing such unit operations/ processes cannot be undermined. The solubilities of many solids are reported in the literature but the solubilities of liquids in SCFs are relatively scarce. The solubilities of fatty acids and triglycerides in supercritical fluids have been reported in literature¹⁶⁻¹⁹. The solubilities of geraniol and 10-undecenoic acid has been reported²⁰. The chemical derivatives of these compounds will find applicability in food, flavors and pharmaceutical industries but the solubilities of these compounds have not been reported.

In this work, the solubilities of two lipid derivatives, geranyl butyrate and 10-undecen-1-ol, have been reported. Geranyl butyrate (synthesized by esterification of naturally occurring geraniol and

butyric acid^{21, 22}) is used as a plasticizer and as a flavoring substance. The synthesis of geranyl butyrate in supercritical carbon dioxide has been reported earlier²³. The fatty alcohol, 10-undecen-1-ol is derived by reduction of 10-undecen-1-oic acid (obtained from the alkaline pyrolysis of castor oil²⁴) and it has been used in synthesizing several biodegradable polymers²⁵. Further, it could also be used as a surfactant and emulsifier like many other fatty alcohols. To the best of our knowledge, this is the first report on the solubilities of these compounds in supercritical carbon dioxide.

The semi-empirical models are known for their simplicity in correlating solubility data^{19, 26-30}. Models such as MT model³¹, Chrastil model³² and association model²⁸ have been used to correlate the experimental data. However, these correlations are empirical and may not provide insights into the nature of interactions between the solute and the SCF phase. Recently, new models based on solution and association theories^{29, 33} have been developed. However, a comprehensive survey and comparison of various models is lacking.

The objectives of this study are two-fold. Firstly: determining the solubilities of 10-undecen-1-ol and geranyl butyrate in a wide range of temperatures and pressures. Secondly: deriving several new models based on combinations of solution/association theory and activity coefficients. Thus, this work makes an earnest attempt to compare, evaluate and draw parallels among various combinations of models in their ability to correlate the experimental data of geranyl butyrate, 10-undecen-1-ol and several other liquid solutes reported in literature.

2. Materials:

Geranyl butyrate (CAS no. 106-29-6) with purity > 95%, having 4% geraniol and 1% nerol as impurities and 10-undecen-1-ol (CAS no. 112-43-6) with purity >98% were supplied by TCI chemicals, Japan. Carbon dioxide with 99% purity was purchased from Noble Gases, (Bangalore, India). Chemical structures of the compounds used in the study are shown in Figure 1.

3. Experiment and Procedure:

A detailed description and procedure along with the flow diagram of the experimental setup has already been reported in our earlier study¹⁵. Flow saturation technique was used in this study to determine the solubilities of the solutes in supercritical carbon dioxide (SCCO₂). CO₂ from the cylinder was passed through the silica gel bed to increase its purity to 0.999 mass fraction. A chiller maintained at 263 K followed by a HPLC pump (PU-2080-CO₂, Jasco International Company, Japan) was used to deliver CO₂ at a flow rate of 0.1 ml/min. This flow rate was optimized after conducting a number of experiments at different flow rates to ensure saturation¹⁵. A liquid column of volume 50 ml (EV-3-50-2, Jasco) was placed inside the thermostat, pre-filled with 30 ml of the liquid solute. After passing through the chiller, CO₂ was pumped to the 50 ml liquid column. The operating conditions of temperature and pressure were maintained by the thermostat and the back pressure regulator (BP-1580-81, Jasco), respectively. A six way Rheodyne valve was used to switch the flow between the online and offline modes. After the complete saturation of the solvent (CO₂) stream, the liquid solute depressurizes into a collection trap at regular intervals. The equilibrium solubility was then calculated using the amount collected. All the experiments were repeated in triplicate and the uncertainty was within $\pm 5\%$.

4. Models & Correlations:

4.1 Existing Models:

4.1.1. Mendez-Santiago and Teja (MT) model:

This model is an empirical model which relates the solubility of the solute to the operating temperature, pressure and the solvent density. This was derived on the basis of dilute solution theory that relates the enhancement factor and the density of the solvent to the solubility of solute³¹. The simplified form for the liquid solutes is,

$$T \ln(Py_2) = A_1 + B_1 \rho + C_1 T \quad (1)$$

In Eq. (1), T is the temperature in K, P is pressure in MPa, y_2 is solubility and ρ is density of solvent in kg.m^{-3} . A_1 (K), B_1 ($\text{K.m}^3/\text{kg}$) and C_1 are the temperature independent constants. This model can be used to check the consistency of the solubility data by plotting the variation of $T \ln(Py_2) - C_1 T$ with ρ . All points at different temperatures and pressure fall on to a straight line.

4.1.2. Solution theory plus Wilson activity coefficient model:

This model was derived for correlating the solubility of liquid solutes using the solution theory by comparing the fugacity of solute in both the liquid and the supercritical fluid (SCF) phase at equilibrium¹⁵. Wilson activity coefficient model at infinite dilution was used to correlate activity coefficient for the solute in SCF phase. The simplified expression for the solubility is

$$\ln(\Phi y_2) = A_2 + B_2 \Phi + \frac{C_2}{T} \quad (2)$$

In Eq. (2), Φ is the pure component molar volume ratio of solvent to solute, y_2 is solubility, T is temperature in K and A_2 , B_2 and C_2 (K) are temperature independent constants.

4.1.3. Association Model:

This model was derived using the association theory (similar to solids²⁸), where a molecule of solute associates with 'k' molecules of solvent to form a solvato complex at equilibrium with the SCF phase. This is a simple four parameter model relating the solubility of solute in SCF phase to the system pressure, temperature, solvent density and the association number^{20, 28},

$$y = \left(\frac{P}{P^*} \right)^{k_3-1} \exp \left(\frac{A_3}{T} + B_3 \frac{\rho_B}{\rho_A} + C_3 \right) \quad (3)$$

4.1.4. Association theory plus van Laar activity coefficient model²⁰:

This is based on the association theory i.e., formation of a solvato complex that is in equilibrium with the SCF phase. Further, van Laar activity coefficient model was used to correlate the activity coefficient of liquid solute in the liquid phase. A five parameter model for solubility was obtained,

$$y_2 = \left(\frac{P}{P^*} \right)^{k_4-1} \exp \left[\frac{1}{T} \left\{ A_4 + C_4 \left(\frac{\rho_B}{\rho_A} \right) \right\} + E_4 \left(\frac{\rho_B}{\rho_A} \right) + F_4 \right] \quad (4)$$

In Eqs. (3) and (4), P is pressure in MPa, P^* is the reference pressure, T is temperature in K, $\frac{\rho_B}{\rho_A}$ is the ratio of pure component molar density of the solvent (B) to solute (A) in kg.m^{-3} , k_3 and k_4 are the association numbers. A_3 (K), B_3 and C_3 and A_4 (K), C_4 (K), E_4 and F_4 are temperature independent constants in Eq. (3) and Eq. (4), respectively.

4.2 New Models:

4.2.1. Association theory plus Wilson activity coefficient model:

In accordance with the association theory, if a solute molecule 'A' associates with 'k' molecules of solvent 'B' and forms 'AB_k' solvato complex then at equilibrium,



The equilibrium constant (K) for Eq. (5) can be written as

$$K = \frac{\left(\frac{\hat{f}_{AB_k}}{f_{AB_k}^*} \right)_{SCF}}{\left(\frac{\hat{f}_A}{f_A^*} \right)_S \left(\frac{\hat{f}_B}{f_B^*} \right)_{SCF}^k} \quad (6)$$

In Eq. (5), \hat{f}_{AB_k} is the fugacity of the solvato complex in SCF phase ($\hat{f}_{AB_k} = y_A \gamma_A^\infty f_{AB_k}$), \hat{f}_A is the fugacity of solute in liquid phase ($\hat{f}_A = x_A \gamma_A f_A$) and \hat{f}_B is the fugacity of solvent in SCF phase ($\hat{f}_B = \hat{\phi}_B P y_B$). f^* represents the reference fugacities. The subscripts, 'SCF' and 'S' represent the supercritical and the solute phase, respectively.

Eq. (6) can be rewritten by expanding the individual terms of the equation as ²⁰,

$$K = \frac{\left(\frac{y_A \gamma_A^\infty f_{AB_k}}{\phi_{AB_k}^* P^*} \right)_{SCF}}{\left(\frac{x_A \gamma_A f_A}{\phi_A^* P^*} \right)_S \left(\frac{\hat{\phi}_B P y_B}{\phi_B^* P^*} \right)_{SCF}^k} \quad (7)$$

In Eq. (7), f_{AB_k} is the pure component fugacity of the solvato complex in SCF phase and f_A is the pure component fugacity of solute in liquid phase. P^* and ϕ^* are the reference pressure and reference fugacity. $\hat{\phi}_B$ is the fugacity of solvent in SCF phase. y_A and x_A are

the solubilities of the liquid solute in SCF and liquid phase, respectively. In SCF phase, ($\gamma_A = \gamma_A^\infty$ as y_A is order of 10^{-3}) γ_A^∞ is the infinite dilution activity coefficient of solute in SCF phase and γ_A is the activity coefficient of solute in liquid phase.

$$f_A = P_A^{vap} \phi_{sat} \exp\left(\frac{V_A(P - P_A^{vap})}{RT}\right) \quad (7a)$$

$$f_{AB_k} = \phi_{AB_k} P \quad (7b)$$

$$\ln P_A^{vap} = A_v - \frac{B_v}{T} \quad (7c)$$

$$\ln K = \frac{\Delta H_s}{RT} - q_s \quad (7d)$$

$$\frac{PV_A}{RT} = \frac{\rho_B M_B}{\rho_A M_A} \quad (7e)$$

In above equations, M_A and M_B are the molecular weights of the solute and solvent, respectively. P_A^{vap} is the vapor pressure of liquid solute. ρ_A and ρ_B are the densities of solute and solvent respectively. V_A is the molar volume of solute, K is the equilibrium constant, ΔH_s is heat of solvation and A_v , B_v (K) and q_s are constants. ϕ_{AB_k} is the fugacity coefficient of the solvato complex.

The fugacity coefficient of solvent in SCF phase can be written as³⁴,

$$\ln \hat{\phi}_B = 2\rho_B(y_B B_{BB} + y_{AB_k} B_{AB_k B} + B) \quad (7f)$$

B_{ij} is the second virial coefficient of the pair i-j, B is the second virial coefficient of the mixture in the SCF phase and k_s is the association number. The activity coefficient for the solute in SCF phase is given by Wilson activity coefficient model as,

$$\ln \gamma_A^\infty = 1 + \ln \frac{\rho_B}{\rho_A} + \frac{a_{AB}}{RT} - \frac{\rho_B}{\rho_A} \exp\left(\frac{-a_{BA}}{RT}\right) \quad (7g)$$

a_{AB} and a_{BA} represent the interaction potential between solute (A) and solvent (B).

Combining all the equations from Eq. (7a) to Eq. (7g) and assuming that the contribution of higher powers in density is negligible^{15, 20}, Eq. (7) can be rewritten as a four parameter model,

$$\rho' y = \left(\frac{P}{P^*}\right)^{k_5-1} \exp\left(\frac{A_5}{T} + B_5 \rho' + C_5\right) \quad (8)$$

In Eq. (8), ρ' is the ratio of pure component molar density of the solvent (B) to solute (A) in $\text{kg}\cdot\text{m}^{-3}$, y is solubility, P is pressure in MPa, P^* is the reference pressure, T is temperature in K, k_5 is the association number and A_5 (K), B_5 and C_5 are temperature independent constants.

In Eq. (8),

$$\rho' = \frac{\rho_B}{\rho_A} \quad (8a)$$

$$A_5 = \frac{\Delta H_s}{R} - \frac{a_{AB}}{R} - B_v \quad (8b)$$

$$B_5 = \frac{M_B}{M_A} \left(1 + \exp\left(\frac{-a_{BA}}{RT}\right) + 2k_5 \rho_A (y_B B_{BB} + y_{AB_k} B_{AB_k} + B) \right) \quad (8c)$$

$$C_5 = A_v - 1 - q_s - \ln \left(\frac{\phi_{AB_k} \phi_A^* (\phi_B^*)^{k_5} P^*}{\phi_{AB_k}^* \phi_{sat} \gamma_A x_A} \right) \quad (8d)$$

4.2.2. Association theory plus van Laar plus Wilson activity coefficient model:

For Eq. (5), the equilibrium constant can be written in terms of ratio of fugacities (Eq. (6)) and further expanded in terms of activity coefficients, as discussed in the previous section,

$$K = \frac{\left(\frac{y_A \gamma_A^\infty f_{AB_k}}{\phi_{AB_k}^* P^*} \right)_{SCF}}{\left(\frac{x_A \gamma_A f_A}{\phi_A^* P^*} \right)_S \left(\frac{\hat{\phi}_B P y_B}{\phi_B^* P^*} \right)^k} \quad (9)$$

\hat{f}_{AB} can be expanded in terms of activity coefficient of solute in SCF phase using the Wilson activity coefficient model at infinite dilution as given in Eq. (7g). \hat{f}_A is also written in terms of activity coefficient for the solute in liquid phase expanded using van Laar activity coefficient model as ²⁰,

$$\ln \gamma_A = \frac{1}{RT} \left[\left(a_{BB} \frac{\rho_B}{\rho_A} \right) + a_{AA} - \left(2\sqrt{a_{BB} a_{AA}} \left(\frac{\rho_B}{\rho_A} \right)^{0.5} \right) - \left(2a_{AA} \frac{x_A \rho_B}{x_B \rho_A} \right) + \left(4\sqrt{a_{BB} a_{AA}} \frac{x_A}{x_B} \left(\frac{\rho_B}{\rho_A} \right)^{1.5} \right) - \left(2a_{BB} \frac{x_A}{x_B} \left(\frac{\rho_B}{\rho_A} \right)^2 \right) \right] \quad (10)$$

In Eq. (10), a_{BB} and a_{AA} are the interaction potentials between solvent-solvent and solute-solute molecules, respectively. x_A and x_B are the solubilities of solute (A) and solvent (B), respectively in liquid phase. Using all the equations from Eq. (7a) to Eq. (7g) and Eq. (10), a simplified expression for solubility is obtained,

$$\rho' y = \left(\frac{P}{P^*} \right)^{k_6-1} \exp \left[\left(\frac{1}{T} \right) \left\{ A_6 + B_6 \left((\rho')^{0.5} - 2 \frac{x_A M_B}{x_B M_A} (\rho')^{1.5} \right) + C_6 (\rho') + D_6 (\rho')^2 \right\} + E_6 (\rho') + F_6 \right] \quad (11)$$

In Eq. (11),

$$\rho' = \frac{\rho_B}{\rho_A} \quad (11a)$$

$$A_6 = \frac{\Delta H_s}{R} + \frac{a_{AA}}{R} - B_v - \frac{a_{AB}}{R} \quad (11b)$$

$$B_6 = \frac{-2\sqrt{a_{BB}a_{AA}}\sqrt{M_B/M_A}}{R} \quad (11c)$$

$$C_6 = \frac{1}{R} \left(\frac{M_B}{M_A} \right) \left(a_{BB} - 2a_{AA} \frac{x_A}{x_B} \right) \quad (11d)$$

$$D_6 = -\frac{2a_{BB}}{R} \frac{x_A}{x_B} \left(\frac{M_B}{M_A} \right)^2 \quad (11e)$$

$$E_6 = \frac{M_B}{M_A} \left(1 + 2\rho_A k_6 (y_{AB_k} B_{AB_k B} + y_B B_{BB} + B) + \exp\left(\frac{-a_{BA}}{RT}\right) \right) \quad (11f)$$

$$F_6 = A_v - q_s - 1 - \ln \left(\frac{\phi_A^* P^* \phi_{AB_k}}{\phi_{sat} x_A \phi_{AB_k}^*} (\phi_B^*)^{k_6} \right) \quad (11g)$$

Eq. (11) simplifies to a 5 parameter model,

$$\rho' y = \left(\frac{P}{P^*} \right)^{k_6 - 1} \exp \left[\left(\frac{1}{T} \right) \{ A_6 + C_6 \rho' \} + E_6 \rho' + F_6 \right] \quad (12)$$

In Eq. (12), k_6 is the association number and A_6 (K), C_6 (K), E_6 and F_6 are constants.

4.2.3. Solution theory plus Wilson plus van Laar activity coefficient model:

At equilibrium, the fugacity of solute in liquid and SCF phase can be equated as ¹⁵,

$$\hat{f}_A^{lp} = \hat{f}_A^{SCF} \quad (13)$$

In Eq. (13), 'A' is the solute and 'lp' and 'SCF' represent the liquid and the supercritical phase respectively. Eq. (13) can be rewritten in terms of the activity coefficients as,

$$\hat{f}_A^{lp} = \gamma_A^{lp} x_A f_A^{lp} \quad (13a)$$

$$\hat{f}_A^{SCF} = \gamma_A^{SCF} y_A f_A^l \quad (13b)$$

γ_A^{lp} and γ_A^{SCF} are the activity coefficients of solute in liquid and SCCO₂ phase. x_A and y_A are the mole fractions of solute in the liquid and the SCF phase, respectively. f_A^{lp} and f_A^l are the pure component fugacity of solute in the respective phases. For the supercritical fluid-liquid equilibria, the logarithm of fugacity ratio can be related as ¹⁵,

$$\ln\left(\frac{\hat{f}_A^{lp}}{f_A^l}\right) = A_7 - \frac{B_7}{T} \quad (14)$$

Using Eq. (13a) and Eq. (13b) in Eq. (14),

$$\ln\left(\frac{\gamma_A^{SCF} y_A}{\gamma_A^{lp} x_A}\right) = A_7 - \frac{B_7}{T} \quad (14a)$$

In Eq. (14a), x_A and y_A are the mole fractions of solute in the liquid and the SCF phase, respectively. A_7 and B_7 are constants and T is temperature in K. The solute forms a dilute solution in the SCF phase. Therefore, the activity coefficient of solute in SCF phase (γ_A^{SCF}) can be expanded using Wilson activity coefficient model at infinite dilution as,

$$\ln \gamma_A^\infty = 1 + \ln \frac{\rho_B}{\rho_A} + \frac{a_{AB}}{RT} - \frac{\rho_B}{\rho_A} \exp\left(\frac{-a_{BA}}{RT}\right) \quad (14b)$$

The activity coefficient of solute in liquid phase (γ_A^{lp}) can be expressed using the van Laar activity coefficient model as ²⁰,

$$\ln \gamma_A^{lp} = \frac{1}{RT} \left[\left(a_{BB} \frac{\rho_B}{\rho_A} \right) + a_{AA} - \left(2\sqrt{a_{BB} a_{AA}} \left(\frac{\rho_B}{\rho_A} \right)^{0.5} \right) - \left(2a_{AA} \frac{x_A}{x_B} \frac{\rho_B}{\rho_A} \right) + \left(4\sqrt{a_{BB} a_{AA}} \frac{x_A}{x_B} \left(\frac{\rho_B}{\rho_A} \right)^{1.5} \right) - \left(2a_{BB} \frac{x_A}{x_B} \left(\frac{\rho_B}{\rho_A} \right)^2 \right) \right] \quad (14c)$$

From Eq. (14a), (14b) and (14c),

$$\ln(\rho' y_A) = \frac{1}{T} \left(A_8 + B_8 \left[(\rho')^{0.5} - 2 \frac{x_A}{x_B} \frac{M_B}{M_A} (\rho')^{1.5} \right] + C_8 \rho' + D_8 (\rho')^2 \right) + E_8 \rho' + F_8 \quad (15)$$

In Eq. (15),

$$\rho' = \frac{\rho_B}{\rho_A} \quad (15a)$$

$$A_8 = \frac{a_{AA}}{R} - B_7 - \frac{a_{AB}}{R} \quad (15b)$$

$$B_8 = \frac{-2\sqrt{a_{BB}a_{AA}}\sqrt{M_B/M_A}}{R} \quad (15c)$$

$$C_8 = \frac{1}{R} \left(\frac{M_B}{M_A} \right) \left(a_{BB} - 2a_{AA} \frac{x_A}{x_B} \right) \quad (15d)$$

$$D_8 = -\frac{2a_{BB}}{R} \frac{x_A}{x_B} \left(\frac{M_B}{M_A} \right)^2 \quad (15e)$$

$$E_8 = \frac{M_B}{M_A} \exp\left(\frac{-a_{BA}}{RT}\right) \quad (15f)$$

$$F_8 = A_7 - 1 - \ln x_A \quad (15g)$$

As solubility cannot depend on fractional powers of density, Eq. (15) reduces to a four parameter model,

$$\ln(\rho' y_A) = \frac{1}{T} (A_8 + C_8 \rho') + E_8 \rho' + F_8 \quad (16)$$

In Eq. (16), A_8 (K), C_8 (K), E_8 and F_8 are constants.

5. Results and discussion:

5.1 Experimental data:

The solubilities of geranyl butyrate and 10-undecen-1-ol in SCCO₂ were measured from 308.15 to 333.15 K and at pressures varying from 10 to 18 MPa. At temperatures above 333.15 K, solubilities are normally very low. Similarly, there is no significant difference in solubilities at higher pressures (above 18 MPa). Therefore, the solubilities of the compounds studied are determined in the range of T_c to $1.1 T_c$ and P_c to $3 P_c$ as there is significant change of densities (and solubilities) only in these regions. In order to verify the internal consistency of the experimental data, MT model (Eq. (1)) was used. The term $T \ln(Py_2) - C_1 T$ was plotted against ρ , the density of SCCO₂ as shown in Fig. (1). It can be observed from Fig. (1) that different isotherms fall onto a single straight line indicating self consistency of the experimental data obtained in this study.

Figures 2(a) and 2(b) show the variation of solubilities of 10-undecen-1-ol and geranyl butyrate as a function of pressure. It was observed that solubility increases with pressure along an isotherm. This is due to increase in density of the supercritical carbon dioxide with pressure, when the temperature and thereby the vapor pressure is constant³⁵. This has been observed for all solid and liquid solutes analyzed in literature. However, the variation of solubility with temperature is not straightforward. This is due to the interplay of two variables: density and vapor pressure, both of which vary with temperature. In case of experimental data reported in this work, at a constant pressure, increase in solubility was observed with decrease in temperature (in the given pressure and temperature range). This phenomenon is called retrograde

behavior, where the density plays a dominant role as compared to the vapor pressure³⁶. In other words, the operating pressures seem to be lower than the cross over pressure³⁷. This can be attributed to the low vapor pressures of the compounds in the given range of temperatures.

The solubility of geranyl butyrate was higher than 10-undecen-1-ol, although the former has a higher molecular weight. The solubility data of geranyl butyrate was compared with geraniol and myristic acid and the solubilities of 10-undecen-1-ol can be compared to 10-undecenoic acid. The solubility of geraniol, 10-undecenoic acid and myristic acid has been reported earlier^{20, 38}. The solubility of geranyl butyrate was found to be comparable to geraniol²⁰. The solubility of 10-undecen-1-ol (C11 alcohol with single double bond) was lower than the solubility of geraniol (C10 alcohol with 2 double bonds). This indicates, solubility decreases with increase in molecular weight, and it increases with an increase in unsaturation^{16, 17, 39}. Further, the solubility of 10-undecen-1-ol was higher than the solubility of 10-undecenoic acid²⁰. The solubility of geranyl butyrate was higher than the solubility of myristic acid (a fatty acid with the 14 carbon atoms as geranyl butyrate) and geraniol. As carbon dioxide is non-polar, it is expected that non-polar compounds will have higher solubilities than polar solutes in SCCO₂.

5.2 Models:

Many empirical and semi empirical models have been reported in the literature⁴⁰. These models relate the solubility of solute in SCF (solvent) with temperature, pressure or density of solvent (Eq. (1), Eq. (2), Eq. (3) and Eq. (4)). The SCF phase or liquid phase non-ideality is expressed

using either of the expressions for the activity coefficient. Different possible combinations of solution or association theory with activity coefficient models were tried, as shown in Table 2.

Among the various combinations, some of them are either redundant or lead to a highly complex non-linear expression. Three such cases are possible,

Case A: When Wilson activity coefficient model was used for the liquid phase was coupled with association theory or solution theory, the final expression becomes non-linear and complex.

Case B: When van Laar model was used to express the activity coefficient in the SCF phase or when solution model is used as a stand-alone model, expressions of the form $\left(\ln y_2 = A_9 - \frac{B_9}{T}\right)$ were obtained. This expression is trivial as it does not account the effect of pressure or density.

Case C: These combinations of solution model are not possible as they do not account for non-ideality in the SCF phase.

In another case when van Laar is used in the SCF phase along with association model, a similar expression like Eq. (3) was obtained. Hence, all the possible combinations of association or solution theory with different activity coefficients (Eq. (2), Eq. (3), Eq. (4), Eq. (8), Eq. (12) and Eq. (16)) were considered. Thus, in this study, three new models (Eq. (8), Eq. (12) and eq. (16)) have been derived for correlating the solubilities of various compounds at different temperatures and pressures. These models have been derived by considering liquid-SCF phase equilibria by using association theory and solution theory along with the van Laar and Wilson activity coefficient models for the solute.

In the first case, association theory was used along with the Wilson activity coefficient model for solute in SCF, resulting in a four parameter model (Eq. (8)). The experimental data were fitted to the model using multiple linear regression using Origin[®] 8.5. In Eq. (8b), A_5 can either be positive and negative depending on the interaction potential between solute and solvent and the Clausius Clapeyron equation's constant. A_5 can be positive or negative depending on whether $\Delta H_s / (a_{AB} + B_v R)$ is greater than or less than unity, respectively. B_5 in Eq. (8c) accounting for the virial coefficients, interaction potential and association number was always found to be positive. Similarly, C_5 in Eq. (8d) having activity coefficient of the solvate complex and the reference activity coefficients along with the Clausius Clapeyron equation's constant can be either positive or negative depending on whether A_v is greater than or less than the quantity,

$1 + q_s + \ln \left(\frac{\phi_{AB_k} \phi_A^* (\phi_B^*)^{k_s} P^*}{\phi_{AB_k}^* \phi_{sat} \gamma_A x_A} \right)$, respectively. Thus, two parameters (k_5 , B_5) need to be always positive and two parameters (A_5 , C_5) can be either positive or negative.

In the second case, association theory was used along with the van Laar (for solute in liquid phase) and Wilson (for solute in SCF phase) activity coefficient models and a model with five parameters was obtained (Eq. (12)). The constants were obtained by the multiple linear regression. A_6 in Eq. (11b) is similar to A_5 and can be positive or negative depending upon the value of interaction potentials, heat of solvation and the Clausius Clapeyron equation's constant. Positive value of A_6 implies that $\Delta H_s > (a_{AA} - a_{AB} - B_v R)$. In Eq. (11d), C_6 accounts for the interaction potential between the solute-solute and the solvent-solvent molecules, respectively. This can have positive or negative values depending upon which type of interactions are

dominant. C_6 will be positive if $a_{BB} > (2x_A / x_B)a_{AA}$ and negative when $a_{BB} < (2x_A / x_B)a_{AA}$. E_6 in Eq. (11f) is similar to B_5 (Eq. (8c)) and also accounts for the virial coefficients and the intermolecular interaction between solute and the solvent particles. F_6 (Eq. (11g)) similar to C_5 (Eq. (8d)) can be positive or negative depending on whether A_v is greater or less than the

quantity, $1 + q_s + \ln \left(\frac{\phi_A^* P^* \phi_{AB_k}}{\phi_{sat} x_A \phi_{AB_k}^*} (\phi_B^*)^{k_6} \right)$. Thus, in this model, among the five parameters, only k_6

needs to be positive.

In the last case, the model was derived using solution theory (instead of association theory) along with the van Laar and Wilson activity coefficient models and a four parameter model (Eq. (16)) was obtained. Eq. (16) differs from Eq. (12) due to the absence of the term $(k_6 - 1)\ln(P/P^*)$, thereby reducing a parameter in Eq. (16). In Eq. (15b), A_8 accounts for the interactions between solute-solvent and solute-solute interactions. The value of E_8 in Eq. (15f) will depend upon the interaction potential of solute-solvent pair. F_8 in Eq. (15g) will have either positive or negative value depending upon the constant A_7 . There are no constraints on the parameters in this model.

The deviation of experimental data from the model was quantified using AARD% (average absolute relative deviation) and given by,

$$AARD\% = \frac{1}{N} \left(\sum_{i=1}^N \frac{(y_2^{cal} - y_2^{exp})}{y_2^{exp}} \right) * 100 \quad (17)$$

In Eq. (17), y_2^{cal} is the solubility value calculated by the model and y_2^{exp} denotes the solubility obtained from experimental data and N is the number of data points. To determine the best model

among all the models, solubility data of geranyl butyrate and 10-undecen-1-ol were regressed using the various models ((Eq. (2), Eq. (3), Eq. (4), Eq. (8), Eq. (12) and Eq. (16))). In addition, the solubilities of 21 compounds were chosen based on their relevance in lipid processing and biodiesel/biolubricant production and correlated using the above models. Among the combinations discussed, all solution theory based models and the association + Wilson activity coefficient model resulted in one parameter less than the other association theory based models. The regression was performed using multiple linear regression routine in Origin[®] 8.5 and the AARD% values for all the compounds were calculated. The AARD (%) of all the six models are reported in Table 3.

Table 3 shows that for some systems such as geraniol, oleic acid and methyl linoleate, all the models showed AARDs less than 5%. Further systems such as nonanoic acid, styrene and methyl laurate have shown AARDs greater than or around 25% for the solution theory based models. The models that are derived using a particular theory have similar AARDs. Thus models based on association theory have similar AARDs (10-12 %) while the solution theory based models (14-16 %) have similar AARDs. However, there is a significant difference between these models and, generally, association theory based models (Eq. (3), Eq. (4) and Eq. (8), Eq. (12)) are superior to solution theory based models (Eq. (2) and Eq. (16)) as can be observed from the Table 3. Further, among the association theory based models, AARD (%) obtained for the association theory based model using van Laar and Wilson activity coefficient model (Eq. (12)) gave the least AARD for many compounds.

In the new models derived in the present work, the non ideality in both the phases was considered. Further, the non ideality of the liquid phase can be neglected for the higher

molecular weight lipids and lipid derivatives (liquid solutes) discussed in the present study, as it does not make any significant difference in the AARD values. Thus, the AARD values of the models discussed in this study are not significantly different. However, the AARD values for these models can be significantly different for lower molecular weight compounds, where the non ideality in the liquid phase cannot be neglected.

The experimental solubility data was fitted using Eq. (12) as shown in Figures 2(a) and 2(b) for the compounds investigated in this study (10-undecen-1-ol and geranyl butyrate). The parameters obtained from the model using Eq. (12) are reported in Table 4, and the physical interpretation of the parameters and an insight into the model has been discussed below.

It was found that A_ϕ and E_ϕ were positive and C_ϕ and F_ϕ were negative for both the compounds, as reported in Table 4. As discussed earlier the model has constraints that require k_ϕ to be positive while the other parameters (A_ϕ , C_ϕ , E_ϕ and F_ϕ) can be either positive or negative. Based on multiple linear regression, it was observed that F_ϕ was negative for most of the compounds. For nonanoic acid, it was observed that k_ϕ was negative when the solubility data was regressed using multiple linear regression (Case 1, Table 4). Therefore, the data was regressed using non linear regression with a constraint of $k_\phi > 0$. This resulted in similar values of A_ϕ and E_ϕ but a different value for F_ϕ (Case 2, Table 4) and also resulted in an increase of AARD % from 20.7 to 37.7 %. For all other compounds, k_ϕ was positive. Based on the phenomenon of association, k_ϕ can take values in two ranges, $0 < k_\phi < 1$ or $k_\phi > 1$. Association number in this range has also been reported in case of solubilities of solids in supercritical carbon dioxide²⁸. In the first condition, when $0 < k_\phi < 1$, the solvent molecule i.e., CO₂ is surrounded by the solute molecules.

When $k_c > 1$, the solute molecule is surrounded by the solvent molecules. Thus, the parameters in Table 4 provide physical insights into the solubilities of these compounds.

All the existing models based on association and solution theory for *liquids* have been selected for a comparative study. However, all these theories assume that the activity coefficient of the solute in liquid phase is constant. Therefore, in the newly developed correlations, the variation of the activity coefficient of the solute in both the phases was accounted. Different possible correlations were derived using van Laar and Wilson activity coefficient models to understand the non idealities present in both the phases. Further, one can understand the interaction potential between the like pairs of molecules from the interaction parameters present in the van Laar model (a_{AA} and a_{BB}) and similarly between the unlike pair of molecules from the Wilson model (a_{AB}). Different parameters of the models give the physical interpretations for these interactions. The new models have been fitted to lipids and lipid derivatives to indicate their applicability, as shown in Table 3 and various parameters have been discussed for the three new models with their physical insights. However, the models derived in this study are applicable to all the liquid solutes reported in the literature. Therefore, these new models are capable of correlating a wide variety of systems as well as providing insights into the molecular interactions of these compounds with SCCO_2 .

6. Conclusions:

The solubilities of two lipid derivatives, 10-undecen-1-ol and geranyl butyrate in SCCO_2 for a temperature range of 308.15 to 333.15 K and pressures from 10 to 18 MPa was experimentally determined and were in the order of 10^{-3} to 10^{-2} . The solubility of geranyl butyrate was similar to

10-undecen-1-ol. Three new models based on association and solution theories were derived. The models based on association theory were slightly more capable than the solution model in correlating experimental data. The association model plus van Laar activity plus Wilson activity coefficient model resulted in lower AARD (%) for many compounds compared to all the other models.

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Figure captions:

Figure 1: Solubility of (a) 10-undecen-1-ol & (b) geranyl butyrate at different temperatures, ■, 308.15 K; ●, 313.15 K; ▲, 323.15 K; ▼, 333.15 K. Solid line represents the MT model fit.

Figure 2: Variation of solubilities of (a) 10-undecen-1-ol & (b) geranyl butyrate with pressure at different temperatures, ■, 308.15 K; ●, 313.15 K; ▲, 323.15 K; ▼, 333.15 K. The solid line represents the correlation based on association + van Laar activity coefficient model Eq. (12).

Table 1: Experimental Solubilities ($y_2/\text{mol.mol}^{-1}$) for the liquid solutes 10-undecen-1-ol and geranyl butyrate at temperature T (K) and pressure P (MPa).

Table 2: Possible combinations of the association and solution theory with different activity coefficient models.

Table 3: Solubility data and AARD% values from all the models of all the compounds reported.

Table 4: Model parameters of Eq. (12) obtained using multiple linear regression.

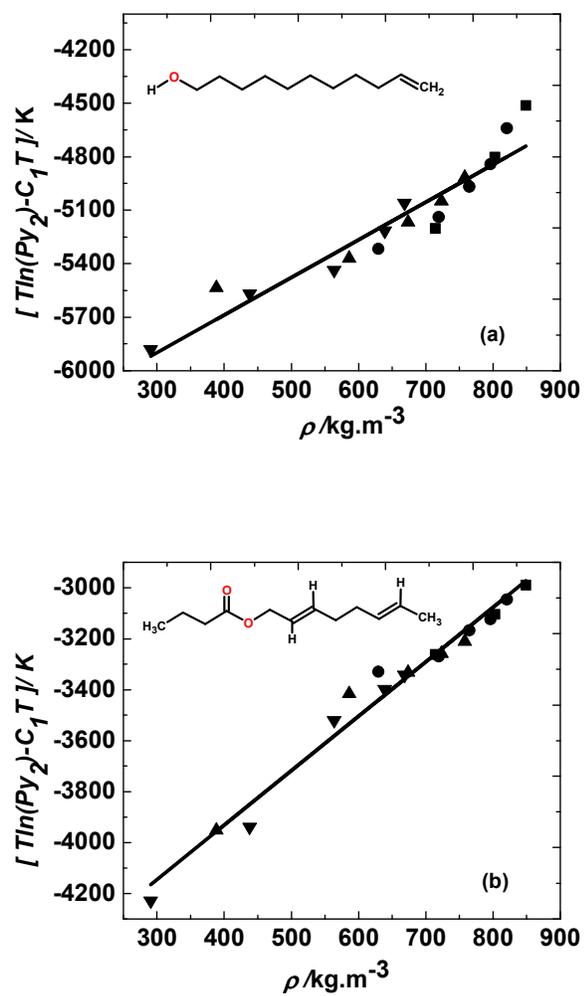


Figure 1: Solubility of (a) 10-undecen-1-ol & (b) geranyl butyrate at different temperatures, \blacksquare , 308.15 K; \bullet , 313.15 K; \blacktriangle , 323.15 K; \blacktriangledown , 333.15 K. Solid line represents the MT model fit.

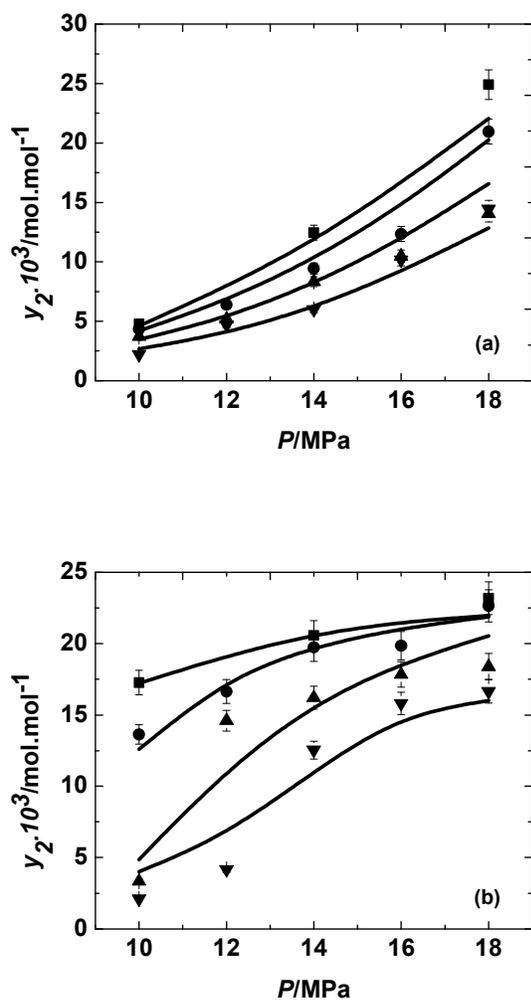


Figure 2: Variation of solubilities of (a) 10-undecen-1-ol & (b) geranyl butyrate with pressure at different temperatures, ■, 308.15 K; ●, 313.15 K; ▲, 323.15 K; ▼, 333.15 K. The solid line represents the correlation based on association + van Laar + Wilson activity coefficient model Eq. (12).

Table 1: Experimental solubilities ($y_2/\text{mol.mol}^{-1}$) for the liquid solutes, 10-undecen-1-ol and geranyl butyrate, at temperature T (K) and pressure P (MPa).

T/K	P/MPa	geranyl butyrate	10-undecen-1-ol
		($y_2 \times 10^3$)	($y_2 \times 10^3$)
308.15	10	17.3	4.8
	14	20.6	12.5
	18	23.2	25.0
313.15	10	16.5	4.3
	12	16.7	6.4
	14	19.7	9.4
	16	19.9	12.4
	18	22.7	21.0
323.15	10	3.3	3.7
	12	14.6	5.2
	14	16.2	8.3
	16	17.8	10.5
	18	18.4	14.1
333.15	10	2.1	2.2
	12	4.2	4.7
	14	12.5	6.0
	16	15.8	10.2
	18	16.7	14.4

Standard uncertainties (u) are $u(T) = 0.1$ K, $u(P) = 0.2$ MPa and relative uncertainty (u_r), $u_r(y_2) = 0.05$.

Theory	Activity coefficient model for solute in SCF phase	Activity coefficient model for solute in liquid phase	Correlation
Association	constant	constant	Eq. (3)
	Wilson	constant	Eq. (8)
	Wilson	van Laar	Eq. (12)
	constant	van Laar	Eq. (4)
	van Laar	constant	Eq. (3)
	van Laar	Wilson	Case A
	constant	Wilson	Case A
Solution	van Laar	Wilson	Case A

Table 2: All possible combinations of the association and solution theory with different activity coefficient models.

	van Laar	constant	Case B
	constant	van Laar	Case C
	constant	Wilson	Case C
	constant	constant	Case C
	Wilson	van Laar	Eq. (16)
	Wilson	constant	Eq. (2)

Table 3: Solubility data and AARD% values from all the models of all the compounds reported.

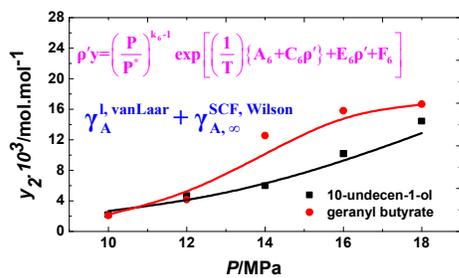
Compound	Temperature (K)	Pressure (MPa)	Solubility ($y_2 \times 10^3$)	AARD%						References
				Associati on	Association + van Laar	Association + Wilson	Association + van Laar + Wilson	Solution + Wilson	Solution + van Laar + Wilson	
10-undecenoic	308-333	10-18	0.38-17.4	9.8	10	10	9.1	11.5	11.7	²⁰
geraniol	308-333	10-18	2.74-25.15	4.8	4.8	4.2	4.4	4.4	4.5	²⁰
butyl-stearate	308-323	10-16	0.31-5.54	9.8	8.3	9.4	8.1	9.9	8.7	⁴¹
butyl laurate	313-328	10-16	1.3-23	12.1	9.3	13.1	9.9	22.0	12.3	⁴¹
dimethyl sebacate	308-328	10-18	4.5-11.8	5.8	5.8	5.9	5.9	7.7	6.1	¹⁵
bis-2-ethylhexyl-	308-328	10-18	0.08-5.5	11.8	10.8	11.7	11.1	14.4	11.9	¹⁵
ethyl stearate	313-333	8.94-18.26	1-15	12.4	12.2	12.3	12.2	17.1	19.4	⁴²
ethyl oleate	313-333	9.54-18.62	1-23	12.3	11.9	12.0	11.8	12.7	12.7	⁴²
ethyl linoleate	313-333	9.30-16.97	1-19	13.4	13.4	13.3	13.2	14.5	13.7	⁴²
methyl stearate	313-343	9.08-20.42	0.2-25	20.3	22.6	20.4	22.3	15.1	23.3	⁴³

methyl oleate	313-333	9.55-18.12	3-33	11.4	10.6	11.4	10.5	26.8	14.7	⁴⁴
methyl palmitate	313-343	6.72-18.29	0.1-27	13.0	10.7	13.3	9.4	16.5	16.4	⁴⁵
Nonanoic acid	313-333	10-30	0.13-7.82	19.0	19.1	20.5	20.7	35.9	26.1	¹⁹
Ethyl ester-EPA	313-333	9.03-21.07	0.2-19.4	12.9	12.4	13.0	12.5	13.0	12.9	⁴²
Ethyl ester-DHA	313-333	9.03-21.07	0.6-12.9	8.3	7.0	8.4	7.0	10.2	9.1	⁴²
1-octanol	313-348	7-19	0.39-80.8	13.1	10.9	16.7	13.5	18.2	14.2	⁴⁶
oleic acid	308-318	9.6-18.62	0.48-2.57	4.9	3.6	5.0	3.8	5.0	4.4	⁴⁷
Styrene	323-333	8-24	4.95-170.24	14.3	14.2	17.3	17.3	22.9	22.8	³⁴
methyl laurate	313-333	8-12	0.2-5.2	19.9	19.9	19.7	19.7	24.3	24.0	⁴⁸
Methyl linoleate	313-333	10.44-18.03	4.1-19.4	2.0	2.0	2.0	2.0	9.6	7.6	⁴⁹
methyl myristate	313-343	7.87-15.97	0.3-13	14.2	11.5	14.8	11.3	14.9	14.8	⁵⁰
Geranyl butyrate	308-333	10-18	2.1-23.19	11.0	10.1	12.4	9.0	19.0	12.9	Present work
10-undecen-1-	308-333	10-18	2.2-24.9	8.7	8.5	9.7	9.3	19.0	16.3	Present work
Average AARD%				11.5	10.9	12.0	11.0	15.9	13.9	

Table 4: Model parameters of Eq. (12) obtained using multiple linear regression.

Compound		Parameters				
		k_6	A_6	C_6	E_6	F_6
10-undecenoic acid		2.42	7656	-7140	27.78	-37.36
geraniol		0.91	-690	-863	8.62	-6.79
butyl-stearate		0.51	-11896	11228	-26.11	25.12
butyl laurate		0.20	9624	-14900	52.41	-36.95
dimethyl sebacate		0.58	6093	-10457	37.51	-26.34
bis-2-ethylhexyl-ethyl stearate		1.92	-4723	6641	-12.74	-0.80
ethyl oleate		5.23	5255	1058	0.43	-35.53
ethyl oleate		2.35	-1354	2140	3.69	-12.24
ethyl linoleate		2.81	2626	-2607	17.44	-24.92
methyl stearate		2.38	-4869	-0.06	30.26	-1.50
methyl oleate		10.21	31786	-17314	56.79	-129.71
methyl palmitate		7.52	4525	10730	-28.23	-38.93
nonanoic acid	Case 1	-2.6	-5099	-3288	24.70	9.04
	Case 2	0.69	-5099	330948	24.70	-0.92
ethyl ester-EPA		1.87	-850	3481	0.52	-13.83
ethyl ester-DHA		2.53	8024	-9100	37.00	-41.52
1-octanol		0.29	-2679	-4804	25.05	-1.31
oleic acid		0.23	-25993	22068	-58.85	68.20
styrene		3.62	275	-3998	14.72	-13.39

methyl laurate	10.01	5302	-1397	5.01	-44.78
methyl linoleate	11.52	22563	751	-9.72	-96.55
methyl myristate	13.03	2664	30633	-92.24	-44.38
geranyl butyrate	0.18	30	-3544	17.29	-7.10
10-undecen-1- ol	3.73	5517	-3897	13.51	-30.47



Solubilities of 10-undecen-1-ol and geranyl butyrate were determined and correlated based on new models by combinations of solution/association theories.