



Solubility of 2-methyl-2-propyl-1,3-propanediol and its derivatives in supercritical carbon dioxide: measurement and mathematical modeling



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ABSTRACT

The modifications for the end group of 2-methyl-2-propyl-1,3-propanediol (compound 1) were achieved by reacting with methyl oxalyl chloride and methyl malonyl chloride to generate two new CO₂-philic compounds: bis(methoxyoxalic)-2-methyl-2-propyl propylene glycol ester (compound 2) and bis(methoxymalonic)-2-methyl-2-propyl propylene glycol ester (compound 3). After that, the solubilities of these three compounds were tested and compared in supercritical carbon dioxide (scCO₂) within the temperature range of (313 to 353) K and in the pressure range of (9.3 to 19.0) MPa. The influence of molar mass and end group on the solubility of compound was also studied. In addition, the experimental solubility data were correlated according to Bartle, Chrastil and JCF model, and good consistencies were obtained. The average absolute relative deviation (AARD) of the measured values were (5.83, 8.98, 8.77)% when using Bartle's method, (10.95, 7.53, 7.55)% for Chrastil's method, and (6.89, 4.10, 4.19)% for the JCF method, respectively. It is obvious that the JCF model was proven to be the best model because it had more adjustable parameters of temperature and pressure. Finally, the partial molar volumes \bar{V}_2 for each compound in the supercritical phase were estimated in accordance with Kumar and Johnston's theory.

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1. Introduction

In the past decades, the technology of supercritical fluids (SCFs) has been widely applied in natural product extraction, chemical reactions, dyeing, cleaning, drying, replacement to volatile organic solvents, food and pharmaceutical industries [1–7]. Among those fluids, supercritical carbon dioxide (scCO₂) has inarguably become the most prevalent supercritical fluid that has ever been researched and employed, which could be mainly ascribed to its relatively low critical temperature and critical pressure ($T_c = 304.15$ K, $P_c = 7.38$ MPa), as well as other versatile properties such as non-toxicity, non-flammability, high mass, heat transfer rates and low cost [8–14]. No matter how many useful functions scCO₂ may have, the solubility determination of various compounds in supercritical solvents continuously plays a leading role. Solubility information of the compound is essential for effective synthesis and access to any practical super-critical separation processes [15–18]. Although carbon dioxide has numerous advantages due to its inherent physical properties, it is a non-polar molecule with low polarizability

and low dielectric constant and unable to dissolve many polar compounds such as amides, ureas, water, ionic species, proteins, sugars, and so on [19–22]. To overcome the shortcoming, CO₂-philic moieties are embedded into compounds which are insoluble or show low solubility in scCO₂ [23–26].

It is generally acknowledged that hydrocarbons substituted with fluorine are the most effective CO₂-philic groups. However, fluorinated compounds are usually considered expensive and hardly available. Therefore, finding some cheap, easily available CO₂-philic groups has significant meaning. According to literatures and based on our research results [27–30], suitable length hydrocarbons, ether or carbonyl groups have been proven to be good CO₂-philic moieties. Therefore, in present study, the hydroxyl end groups of 2-methyl-2-propyl-1,3-propanediol were modified with methyl oxalyl chloride and methyl malonyl chloride, respectively, to obtain two new CO₂-philic compounds, which were subsequently exposed to solubility test in scCO₂ over the pressure range of (9.3 to 19.0) MPa and temperatures from (313 to 353) K. The effect of the compound's structure on solubility was discussed and the tested results were correlated by the Bartle model, Chrastil model and JCF model. Furthermore, the partial molar volumes of three compounds were estimated according to the theory proposed by Kumar and Johnston.

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Table 1
Provenance and mass fraction purity of the materials.

| Materials | Mass fraction purity | CAS | Provenance |
|-----------------------------------------------|----------------------|------------|-----------------|
| Methyl oxalyl chloride | 0.98 | 5781-53-3 | J&K Chem. Co. |
| Methyl malonyl chloride | 0.97 | 37517-81-0 | J&K Chem. Co. |
| 2-Methyl-2-propyl-1,3-propanediol(compound 1) | 0.99 | 78-26-2 | J&K Chem. Co. |
| Carbon dioxide | 0.9999 | 124-38-9 | Wuhan Steel Co. |
| Compound 2 | 0.99 | | |
| Compound 3 | 0.99 | | |

2. Materials and methods

2.1. Chemicals and Experimental Apparatus

Carbon dioxide was purchased from Wuhan Steel Co. (mass fraction purity 0.9999). The 2-methyl-2-propyl-1,3-propanediol (mass fraction purity 0.99), methyl oxalyl chloride (mass fraction purity 0.98), methyl malonyl chloride (mass fraction purity 0.97), triethylamine (mass fraction purity 0.99) were bought from J&K Chem. Co. and used without further purification (table 1). Dichloromethane (CH_2Cl_2) was obtained from Tianjin Kemel Co. Ltd. (China) and distilled before utilization.

NMR experiments were performed on a JEOL AI-400 MHz instrument using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. Elemental analysis was conducted on a PE 2400 series II CHNS/O elemental analyzer. The apparatus of supercritical carbon dioxide was bought from JASCO Corporation (Japan): “PU-1580- CO_2 ” CO_2 Delivery Pump, “PU-2080 Plus” intelligent HPLC Pump, and “BP-1580-81” Back Pressure Regulator.

2.2. Modification

Methyl oxalyl acid esters and methyl malonyl acid esters were synthesized according to a generally synthetic procedure shown in scheme 1. The structures of two newly-synthesized compounds 2–3 were fully confirmed by ^1H NMR, ^{13}C NMR, IR, and elemental analysis.

Compounds 2: bis(methoxyoxalic)-2-methyl-2-propyl propylene glycol ester. Methyl oxalyl chloride (50 mmol, 4.6 mL) was added drop wise into a CH_2Cl_2 solution (40 mL) of 2-methyl-2-propyl-1,3-propanediol (25 mmol, 3.3065 mg) and triethylamine (50 mmol) under a nitrogen atmosphere at 0°C within 2 h. Then, the reaction mixture was warmed to room temperature and stirred for 12 h. After that, the reaction mixture was washed with 1% HCl aq, saturated NaHCO_3 aq, and water for three times, respectively. The organic phase was collected and dried over anhydrous Na_2SO_4 for a whole night. After filtration and evaporation, the residue was purified by a silica gel column chromatography (ethyl acetate: petroleum ether = 1:6) to obtain a light yellow oil with 86% yield (GC purity > 99%). FT-IR (KBr, cm^{-1}) 1742.6 (C=O), 1162.46 (C–O–C); ^1H NMR (CDCl_3) δ_{H} = 0.947 (s, 3H, CH_3), 4.076 (s, 4H,

$2 \times \text{CH}_2$), 1.267 (s, 2H, CH_2), 1.290 (s, 2H, CH_2), 0.842–0.858 (d, J = 6.4, 3H, CH_3), 3.812 (s, 6H, $2 \times \text{CH}_3$); ^{13}C NMR (CDCl_3) δ_{C} = 14.64 (s, C), 16.26 (s, C), 18.42 (d, C), 36.48 (s, C), 37.50 (s, C), 53.43 (s, C), 53.53 (s, C), 69.90 (s, C), 70.88 (s, C), 157.08 (s, C), 157.39 (s, C), 157.82 (s, C), 158.06 (s, C). Elemental Anal.: $\text{C}_{13}\text{H}_{20}\text{O}_8$. Found: (C, 51.33; H, 6.60; O, 42.07)%. Required: (C, 51.31; H, 6.63; O, 42.06)%.

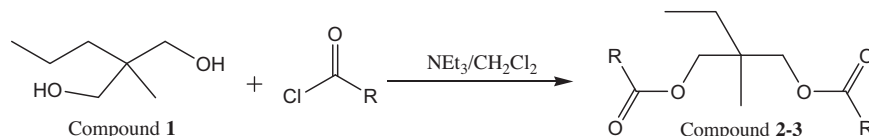
Compounds 3 has been synthesized with the same procedure.

Compounds 3: bis(methoxymalonic)-2-methyl-2-propyl propylene glycol ester.

A light yellow oil with 84% yield (GC purity > 99%). FT-IR (KBr, cm^{-1}) 1735.15 (C=O), 1147.69(C–O–C); ^1H NMR (CDCl_3) δ_{H} = 3.631 (s, 6H, $2 \times \text{CH}_3$), 3.295 (s, 4H, $2 \times \text{O}=\text{CCH}_2\text{C}=\text{O}$), 3.867 (s, 4H, $2 \times \text{CH}_2$), 1.187 (s, 4H, $2 \times \text{CH}_2$), 0.804 (s, 3H, CH_3), 0.832 (s, 3H, CH_3); ^{13}C NMR (CDCl_3): δ_{C} = 14.70 (s, C), 16.24 (s, C), 18.79 (s, C), 36.67 (s, C), 37.22 (s, C), 41.19 (s, 2C), 52.36 (s, C), 52.43 (s, C), 68.54 (s, 2C), 166.18 (s, C), 166.25 (s, C), 166.74 (s, C), 166.80 (s, C). Elemental Anal.: $\text{C}_{15}\text{H}_{24}\text{O}_{18}$. Found: (C, 48.70; H, 6.70; O, 44.60)%. Required: (C, 54.21; H, 7.28; O, 38.51)%.

2.3. Solubility test

The solubility measurements were carried out in a stainless steel view cell (7.11 mL) with two sapphire windows, which permit visual observation of the phase behavior. A suitable amount of solute was loaded into the high-pressure view cell, and the stainless steel cell was then sealed. The compound in the cell was stirred by a magnetic stirrer, and the temperature was controlled using a temperature controller jacket with a circulator. A “BP-1580-81” Back Pressure Regulator was used to maintain a stable and accurate pressure. The system was heated to the desired temperature and pressurized with CO_2 from a syringe pump. The pressure was increased gradually by adding CO_2 with a flow rate of $0.15 \text{ mL} \cdot \text{min}^{-1}$ until the compound disappeared and the fluid in the cell became transparent single phase: this pressure was defined as the dissolution pressure. At each condition, the experiment was repeated at least three times. The uncertainties of the dissolution pressure and temperature are $\pm 0.5 \text{ MPa}$ and $\pm 0.1^\circ\text{C}$, respectively [31–35]. The dissolution pressure and temperature were recorded to obtain the density of CO_2 from the web site page [36].



| Compound | R | Full name |
|----------|-------------------------------------|---------------------------------------------------------------|
| 1 | | 2-Methyl-2-propyl-1,3-propanediol |
| 2 | -COOCH ₃ | Bis (methoxyoxalic)-2-methyl-2-propyl propylene glycol ester |
| 3 | -CH ₂ COOCH ₃ | Bis (methoxymalonic)-2-methyl-2-propyl propylene glycol ester |

Scheme 1. synthetic procedure of compounds 2 and 3.

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