Supporting Information

Heterogeneous palladium-catalyzed telomerization of myrcene with glycerol derivatives in supercritical carbon dioxide: a facile route to new building blocks

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Solubility of CO₂ in β -myrcene at 9 MPa and 353.15 K

The literature data for system consisting of β -myrcene and CO₂ at 353.15 K does not exist, however the only available literature data¹ allows predicting the phase envelope for the system mentioned at the telomerization reaction temperature. The phase envelope was predicted by PE Software² using Peng-Robinson EOS³ and Mathias-Klotz-Prausnitz mixing rule⁴ using the methods described elsewhere.¹ The phase envelope for CO₂ + β -myrcene at 353.15 K is presented in Figure 1 and obtained results showed that at 9 MPa the CO₂ expanded liquid phase contains up to 0.92 mole fraction of CO₂.



Figure 1. The phase diagram of the system containing $CO_2 + \beta$ -myrcene and 353.15 K.

Solubility of CO₂ in glycerol at 9 MPa and 353.15 K

Only a few authors presented data about the phase diagram for the system containing CO_2 and glycerol.^{5,6,7} Data available in the literature do not cover the range of our interest. Francis⁵ presented only one pair of data for LLE for system consisting of CO_2 and glycerol (for 298.15 K and 65 bar), while Sovova gave solubility of glycerol in CO_2 without information about the composition of the liquid phase for investigated pressure and temperature.⁶

The base for the prediction and correlation of the solubility of CO_2 in glycerol-rich phase was derived from data presented by Sovova and Francis. Parameters (critical pressure (p_c) and temperature (T_c) and ω) for glycerol⁸ and carbon dioxide⁹ were taken from literature and are collected in Table 1.

Predictions for system CO_2 + glycerol were performed using Peng-Robinson³ equation of state with Mathias-Copeman alpha function.⁴ The modified Huron-Vidal 1 - UNIFAC (Table 2) mixing rule was used for the prediction also.¹⁰

Table 2. UNIFAC parameters for CO₂ and



Data presented by Francis⁵ allows performing calculations to determine the solubility of CO_2 in glycerol-rich phase. However, to carry out calculations some assumptions have to be done: (i) compositions of the CO_2 -rich phase for 296.2 K and 298.15 K are equal; (ii) the k_{ij} parameter (one of the parameter from the binary interaction parameters) is temperature independent.

Considering assumptions it can be concluded that at 298.15 K and 65 bar the composition of the vapor phase is presented in Sovova's work (296.2 K an 99 bar)⁶ while the composition of the liquid phase is taken from Francis.⁵ Data received due to assumptions were correlated using the Peng-Robinson equation of state³ and Mathias-Klotz-Prausnitz mixing rule.⁴ Ten

series of the optimized binary interaction parameters (k_{ij} , l_{ij} , λ_{ij}) which gave the lowest deviation of the correlated data were determined and are presented in Table 3.

Taking into account the assumption about the temperature independence of k_{ij} parameter, the optimized binary interaction parameters ($k_{ij} = 1.003$, $l_{ij} = 0.6019$, $\lambda_{ij} = 0.6061$) were used for predictions of CO₂ solubility in glycerol-rich phase at 383.15 K and 9 MPa. The predicted phase envelope for system CO₂ + glycerol is presented in Figure 2. The solubility of CO₂ in glycerol rich phase at 353.15 K at 9 MPa is $x_{CO2}=0.108$.



Figure 2. The phase diagram of the system containing CO_2 + glycerol and 353.15 K.

Experimental

Reagents and solvents

Table 3. Reagents and solvents used in reactions

| Chemical | Supplier | Purity |
|------------------------------|--------------------------------|-----------|
| argon | Air Liquid | 99.9% |
| acetonitrile | Sigma Aldrich | 99.8% |
| 1-butanol | Merck | min 99.5% |
| carbon dioxide | Air Liquid | 99.9% |
| cyclohexanone | Fluka | ≥99.5% |
| deuterated chloroform | Cambridge Isotope Laboratories | 99.8% |
| dimethylformamide | Sigma Aldrich | 99.8% |
| ethylene glycol | Sigma Aldrich | 99.8% |
| glycerol | Sigma Aldrich | ≥99.5% |
| β-myrcene | Fluka | 90% |
| Pd/Al_2O_3 (5wt%Pd) powder | Sigma Aldrich | - |
| tridecane | Sigma Aldrich | ≥99% |
| toluene | Sigma Aldrich | ≥99.5% |
| tungstophosphoric acid | Merck | 99% |

Synthesis of 1,4-dioxaspiro[4.5]decane-2-methanol

Herein, the highly regioselective catalytic process for synthesis of 1,4-dioxaspiro[4.5]decane-2-methanol from glycerol using tungstophosphoric acid instead of phosphomolybdic acid was performed. The tungstophosphoric acid is twice cheaper than phosphomolybdic acid and does not exhibit oxidative properties towards organic compounds.

The protected glycerol was obtained in the following way. To a two necked round bottomed flask fitted with a magnetic stirrer and Dean-Stark assembly commercial glycerol (100 mmol; 85 % purity), tungstophosphoric acid (0.5 mmol; 1.44 g; 0.5 eq), toluene (100 ml) were added and the mixture was refluxed with stirring until the residual water was removed (approximately 2 h). Cyclohexanone (100 mmol; 10.3 ml) was then added and the reaction

mixture was refluxed with stirring until water was formed (for 3 h). After complete conversion the reaction mixture was cooled to room temperature, concentrated and the cloudy residue filtered on celite and evaporated to provide pure 1,4-dioxaspiro[4.5]decane-2-methanol (Figure 3) with an 89% yield. The purity was confirmed by ¹H NMR and is in good agreement with presented elsewhere.¹¹

Figure 3. Structure of 1,4-dioxaspiro[4.5]decane-2-methanol.



Figure 4. The 1,4-dioxaspiro[4.5]decane-2-methanol

Methodology – Telomerization reaction

The telomerization reactions in the organic solvents were performed in the following way. The solution of β -myrcene (100 mmol), alcohol (100 mmol) in solvent (100 mmol) was prepared and transferred to previously evacuated 50 mL high pressure Parr reactor. Prior to introduction of the solution a 5 wt% Pd/Al₂O₃ (1.0 g, 9 mmol) solid powder catalyst was

placed in the reactor and then air was evacuated and reactor was flushed with argon. To start the reaction the reactor was pressurized with 0.5 MPa argon and the autoclave was thermostated at temperature below the boiling point of the solvent (353.15 K) using heating mantle. Mixture was stirred using the magnetic drive coupling and after 48 hours argon was vented out and the catalyst and reaction liquid were separated through decantation. The reaction mixture was analyzed by GC and GC-TOFMS.

The reaction under CO₂ pressure was performed in high pressure vessel. The core of the apparatus used in this work was a 3.5 cm³ cell with a sapphire window. The 7 mmol of each reagent and 1 mmol of a 5 wt% Pd/Al₂O₃ powder were placed inside the cell and cell was closed and situated in the thermostated bath. Next cell was carefully pressurized by adding CO₂ to achieve required pressure of 9 MPa. Reaction at 353.15 K was performed for 48 hours and next system was depressurized and the reaction mixture collected was analyzed by GC and GC-TOFMS.

Sample analysis

The qualitative analysis conditions were as follows: Mass Spectrometer: Gas Chromatography-Time of Flight (GC-TOF); Model: GCT from Micromass; Ionization method: Electronic Impact (EI); Column: DB-Wax (30 m; 0.32 I.D.; 0.25 µm film); Temperature program: 40°C (0min), 4°C/min (1min) to 220°C (5min); Injector: 240°C; Split: 1/40. The DB - Wax column has the polyethylene glycol stationary phase ideal for the separation of glycols. A tailing effect was obtained in the case of glycerol. The obtained spectra of the analyzed samples were compared with the individual spectra from NIST 2005 MS library using ChemStation software.

Next quantitative analysis was performed using classical GC. A DB-Wax column (30 m; 0.32 I.D.; 0.25 μ m film) was used in the following conditions: carrier flow 0.5 mL/min; injector temperature 240°C; split ratio 1/30. Temperature program: start temperature 40°C hold for one minute, rate 1: 4°C/min to 120°C, rate 2: 20°C/min to 220°C hold for 5 minutes.

References for supporting information

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