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Quaternary solubility of acetic acid, diacetin and triacetin in supercritical carbon dioxide

Hassan S. Ghaziaskar*, Sepideh Afsari, Marzieh Rezayat, Hajar Rastegari

Department of Chemistry, Isfahan University of Technology, Isfahan, 84156-83111, Islamic Republic of Iran

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ABSTRACT

By a continuous-flow apparatus, quaternary solubility of acetic acid, diacetin, and triacetin in supercritical CO_2 was measured at constant flow rate of 180 mL min^{-1} and temperatures of 313 K, 333 K and 348 K in a pressure range of 70–180 bar. Acetic acid had the highest solubility in $scCO_2$. The binary solubility of acetic acid was also investigated at temperature of 333 k in the pressure range of 70–180 bar. With going from binary to quaternary, acetic acid solubility decreased in the range of 85–90% at different pressures. The quaternary solubility of acetic acid was decreased in the presence of diacetin and triacetin, due to more effective hydrogen bonds with acetic acid and supercritical CO_2. In addition, it was observed that the solubility of polar diacetin molecules in non-polar CO_2 solvent increased by increasing temperature.

1. Introduction

Over the past decade, it has been imperious to find new applications for glycerol (the major by-product of biodiesel) or convert it to the more applicable or expensive chemicals, due to the introduction of large amounts of it. Esterification of glycerol with acetic acid using catalyst to get mono, di and tri esters of glycerol acetates is one of the proposed solutions for conversion of relatively low-priced glycerol to valuable products. Glycerol acetates named monoacetin (MA), diacetin (DA) and triacetin (TA) have great industrial applications. They can be used as food additive, in the manufacturing of explosives and smokeless powder, as a cocoa butter blooming, as an intermediate in the synthesis of structural lipids, for plasticizer coating and foodstuffs, in cryogenics and biodegradable polyesters, chemical products in the food and cosmetic industries, in cigarette filters, as gelatinizing agent, as fuel additive, solvents for printing inks and dyestuffs, and softening agents [1].

These derivatives of glycerol are synthesized via esterification of glycerol with acetic acid or acetic anhydride with or without a homogeneous or heterogeneous catalyst using an organic solvent in both batch and continuous processes [2]. The three consecutive reversible steps of glycerol esterification with acetic acid is shown in Fig. 1. As it can be seen, all three-glycerol acetates are synthesized simultaneously through the reaction process. Whereas the reaction products is usually accompanied with some by-products that cause a change in the color or the odor. To this end, a purification process is needed that would be difficult and costly. As a result, selective synthesis of esters with high purity has been a great challenge for some researchers [3–9].

It should be noted that the boiling points of MA (282 °C), DA (260 °C) and TA (259 °C) are close to each other [10]. Especially the close boiling points of DA and TA, make their separation very difficult and costly, using conventional separation methods [11]. Also excess acetic acid remains in the mixture of the products. Therefore, separation of acetic acid for reusing and making the process economical is necessary. Supercritical fluid extraction, compared to conventional extraction methods, has a great potential as an efficient and clean alternative. Supercritical carbon dioxide ($scCO_2$) is known as the most intensively used solvent due to its low critical point (Pc = 73 bar, Tc = 304 K), non-toxicity, inertness, and non-flammability, while remaining an inexpensive and environmentally acceptable substance [12]. The solubility information for the chemicals can provide data applicable for possible tailoring of the abovementioned reaction toward a specific product or higher efficiency including possible separation of mixture components of the products during the continuous synthesis, in $scCO_2$ [13]. Most of the experimental solubility measurements in $scCO_2$ deal with binary systems [14–16]. However, to the best of our knowledge, quaternary solubility measurements for acetic acid/DA/TA mixture in $scCO_2$ is not reported yet. The main goal of this study was to find

* Corresponding author.
E-mail addresses: ghazi@cc.iut.ac.ir, Hassanghaziaskar@gmail.com (H.S. Ghaziaskar).

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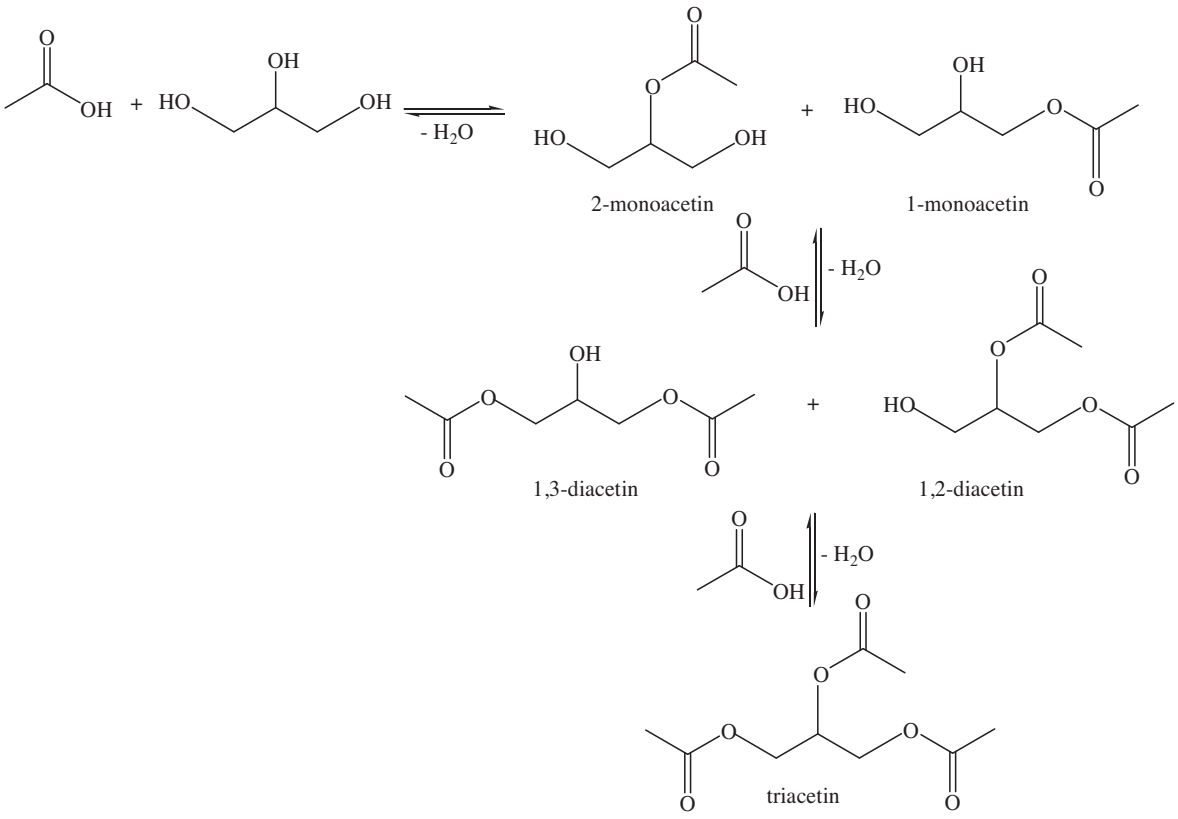

Fig. 1. Three consecutive reversible steps of glycerol esterification with acetic acid.

proper pressure and temperature in which $scCO_2$ dissolves acetic acid selectively and extract it from the mixture of acetic acid/DA/TA. In this way, it is possible to develop a new process for selective extraction of excess acetic acid during the continuous synthesis of the products.

2. Experimental section

2.1. Materials

CO_2 (purity > 99.95%) and ethanol (purity > 99%) were obtained from Zamzam Co. Ltd. (Isfahan, Iran) and Temad Co. (Tehran, Iran), respectively. Acetic acid (purity > 99%) and Pyrex wool were purchased from Merck Co. (Germany), DA (purity = 50% verified by GC-FID), TA (purity > 99%) were from Fluka Co. (Germany), 1-hexanol (purity > 98%) and 1-decanol (purity > 99%) were from Riedel-deHaën Co. (Germany). It must be noted that all the substances was used without further purification.

2.2. Procedure

The solubility measurements were carried out using a continuous-flow apparatus as shown in Fig. 2. In each experiment 1.5 g of sample mixture containing 89, 9 and 6 wt.% of acetic acid, DA and TA, respectively, was placed in a two port cylindrical equilibrium cell (1st cell), which was filled with Pyrex wool to lower the cell dead volume and to increase the contact surface. Second cell was packed by only Pyrex wool to lower the physical transfer of solutes to the trap. Both cells had an inner diameter and length of 1.0 and 10 cm, respectively. The first cell was connected to the top of the second cell and followed by a deep tube to the bottom of the second cell. To bypass the cells and direct the flow toward entering the back-pressure regulator (BPR), a two-way valve were used. Liquid CO_2 passed through a molecular sieve trap into a liquid CO_2 pump (PU-2080, JASCO, Japan). The liquid CO_2 was passed through a preheated coil in the oven and enabled CO_2 to reach oven temperature before it enters the cell. The accuracy of the oven (CO_2-2060 Plus, JASCO, Japan) temperature was within ±0.1 K. At the beginning of each experiment, the system was kept at the desired temperature and pressure for 30 min (i.e. static time) to reach equilibrium. Then at a constant flow rate, the saturated $scCO_2$ was depressurized via a BPR (BP 1580-81, JASCO, Japan). The volume of CO_2 was determined using a wet-gas meter (W-NK-1B, Shinagava Co., Japan).

For quaternary solubility measurements, the dissolved solutes after exiting from the BPR were trapped in a tube filled with glass beads and solvent of ethanol. The purge test were performed to assure negligible weight loss and at least 95% collection efficiency. Having the time of sample collection and the volume of CO_2 passed through the wet-gas meter, the expanded-gas flow rate (i.e. 180 mL min^{-1}) was determined. Collected mixtures of the solute in the trap was transferred to a volumetric flask after adding the proper internal standard and analyzed with the GC-FID to calculate the solubility of acetic acid, DA and TA.

In order to assess the reliability of the equipment and method used, 1-decanol solubility were measured in the range of 110–180 bar. The values obtained in our previous work [13] validated this continuous method for the solubility measurements. Moreover, the accuracy of the measurements of 1-decanol solubility in $scCO_2$ in comparison with the values found in the literature [17] was found to be higher than 10%.

2.3. Analysis method

The gas chromatographic analyses were conducted with an Agilent Technologies, 6890N gas chromatograph with a FID detector. Helium gas was used as the carrier. An HP-5 capillary column with