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# The solubilities of xanthone and xanthene in supercritical carbon dioxide: Structure effect

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## Abstract

The equilibrium solubility of the two pesticides – xanthone and xanthene – in supercritical carbon dioxide was determined with a flow-type method. Measurements were performed at pressures ranging from 80 to 300 bar and temperatures from 308.15 to 328.15 K. The results show that xanthene was much more soluble in supercritical carbon dioxide than xanthone with its solubility being over 10-fold higher than that of xanthone due to their different volatility related to their chemical structures. The determined solubility data were well correlated by the Peng–Robinson equation of state and the empirical density-based Chrastil model with the average absolute relative deviation (AARD) less than 11.5% for two solutes investigated.
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## 1. Introduction

Supercritical carbon dioxide has received ever-increasing attention since it can be potentially used to replace conventional toxic liquid solvents in both analytical applications and engineering processes. In fact, supercritical fluid technology has been successfully commissioned for caffeine, tea, spices, hops and flavor extraction process on large commercial scale in USA and Europe [1]. Among the factors that affect the development of the SCF extraction processes and other SCF technologies, knowledge of supercritical solubility data has been frequently highlighted [1–3].

In this study, xanthone and xanthene with close chemical structures were selected to study. Xanthone and xanthene are two agricultural chemicals, where the former is a fungicide and the latter is a chemical agent to kill insect eggs. These two species are also important parent compounds whose derivatives, naturally occurring or synthesized, are extensively used for medical and dyeing purposes [4–6]. After reaction, xanthone and xanthene are required to separating from the synthetic products. Supercritical fluid extraction can be a potential alternative to extract and purify these compounds from their parent products. Information about solubility data of these species is essential for efficiently designing and better understanding any supercritical fluid extraction process and the others like particle formation for comminuting the pesticide particles to improve the dissolution properties and thus enhance the bioactivity [7–13]. Besides, the solubility behaviors of two chemically similar compounds (i.e., anthraquinone [14] and thioxanthone [15]) have previously been studied. Hence, it is very interesting to choose xanthone and xanthene for investigating the influence of the chemical structures on their solubilities in supercritical carbon dioxide among these compounds.

In this work, the solubilities of xanthone and xanthene in supercritical carbon dioxide were determined by using a dynamic flow method combined with gravimetric analysis over a wide range of pressures and temperature at 308.15 and

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328.15 K. Measured solubility data are discussed in terms of the chemical structure and related physical properties. The Peng–Robinson equation of state (PR EOS) is used to quantitatively correlate the solubility data of all the systems investigated, and the density-based model of Chrastil [16] has also been used to describe various binary systems.

## 2. Experimental

### 2.1. Materials

The compounds used in this study were purchased from commercial suppliers: xanthene (Aldrich Chemicals, USA, >99%), xanthone (MERK-Schuchardt, Germany, >98%) and carbon dioxide (Soxal Singapore, >99.8%). They were used as received without further purification.

### 2.2. Experimental procedure

The solubility of xanthone and xanthene in supercritical carbon dioxide was measured using a dynamic flow technique along with gravimetric analysis. A schematic of the experimental setup is shown in Fig. 1. The solubility determination system consisted of a $CO_2$ cylinder, a delivery pump, an extraction unit (two extraction vessels in series), an oven, a back-pressure regulator, a solute collector, a wet gas meter and tubings, valves and fittings of various types. Detailed description of the apparatus and experimental procedure is available elsewhere [17]. The experimental procedure is briefly described as follows. Carbon dioxide, after liquefied at $-10\,°C$ and 60 bar, was led into the liquid type pump with a precision of less than $\pm0.1\%$. Through the pump, the $CO_2$ was fed into the extraction vessels that were held inside the temperature-controlled oven ($\pm0.01\,°C$). The extraction vessels were loaded with alternate layers of solute powder (ca. 10 g) and 0.5–0.6 mm diameter glass beads. Downstream to the extraction vessels, the saturated $CO_2$/solute solution was depressurized to ambient conditions through a needle valve set in the back-pressure regulator with the pressure error no more than 0.2%. The precipitated solute was collected in a glass U-tube collector immersed in a salt–ice bath (at around

$-5$ to $0\,°C$). The gas released was led through a wet gas meter ($\pm0.2\%$) for atmospheric volume measurement. The precipitation line was flushed by carbon dioxide in order to thoroughly recover the solute at the end of each run. The collected solute (ca. 50 mg per run) was weighed by a balance ($\pm0.01$ mg). By means of the measured solute mass ($M_s$) and the solvent volume ($V$), the solubility value in terms of molar fraction was readily obtained from the following expression:

$$y = \frac{M_s/M_w}{(P_0 - P_{water})V/RT} \tag{1}$$

where $M_w$ is the solute molecular weight, $P_0$, $R$ and $T$ are the atmospheric pressure, the universal gas constant and the temperature of the released gas flowing through the wet gas meter, respectively. $P_{water}$ is the vapor pressure of water at $T$, which can be found from a well-documented literature [18]. The subtraction of the water partial pressure from the atmospheric pressure was considered so as to remove the influence arising from vaporized water.

## 3. Results and discussion

The technique used in this study is a dynamic flow method that has been shown to produce reliable solubility measurements in supercritical fluids [17,19–22]. Measurements were carried out at carbon dioxide (liquid-based) flow rates ranging from 0.4 to 1.0 ml/min. The equilibrium between the solid phase and the fluid phase was assumed since no effect was found on the obtained solubilities through varying carbon dioxide (liquid-based) flow rates within this range. Hence, the supercritical carbon dioxide solvent leaving the extraction vessel was saturated with the solute and equilibrium between the solid and supercritical phase was achieved. In our study, naphthalene solubilities obtained have been found to be consistent with those data previously reported in the literatures [23–25]. The measurements were repeated at least twice with an error within 5.0%, indicative of the reliability of the method used and the expected accuracy of experimental results obtained.

The solubility isotherms of xanthone and xanthene in supercritical $CO_2$ at 308.15 and 328.15 K were measured at pressures ranging from 80 to 300 bar. The solubility results obtained are presented in Tables 1 and 2 and shown graphically in Fig. 2. From the data given in Table 1, it is readily observed that the xanthene solubility increases with increasing pressure at constant temperature, following expected trends. As pressure was increases, carbon dioxide density increases and so did the solubility. At higher temperature, the solubility increases much more rapidly with increasing pressure. Temperature affects the solubility through two competing factors: solute sublimation (i.e., vapor pressure) and SCF solvent density [1,17,19]. These two temperature-dependent factors lead to the crossover pressure of around 170 bar between solubility isotherms as shown in Fig. 2. At pressures lower than 170 bar, the density effect, sensitive to
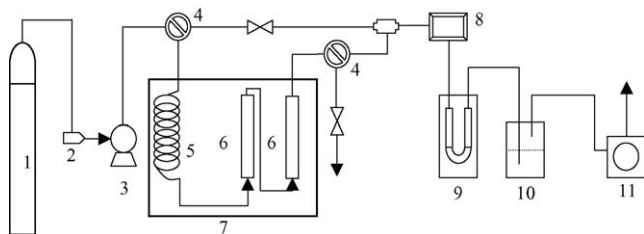


Fig. 1. Schematic of the experimental apparatus used in the study: (1) $CO_2$ cylinder, (2) circulating freezer, (3) HPLC pump, (4) switching valve, (5) premixing coil, (6) equilibrium vessel, (7) oven, (8) back-pressure regulator, (9) collection U-tube, (10) saturator and (11) wet gas meter.