CLOUD POINT MEASURMENTS OF β-D GALACTOSE PENTAACETATE IN SUPERCRITICAL CARBON DIOXIDE

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Sugar acetates such as β-D galactose pentaacetate are highly soluble in carbon dioxide, and form low-viscosity swollen liquids as transient phases in the dissolution process. These properties suggest possible applications of these compounds in molding operations and other processes, where a solid material removable by dissolution in carbon dioxide would be desirable. A variable-volume view cell is used to perform cloud point measurements on the β-D galactose pentaacetate-carbon dioxide system for evaluation of the solubility of that compound in an upper, carbon dioxide-rich phase within a range of conditions representative of prospective manufacturing processes. These measurements show that at temperatures of 34-50^{o}C, solubilities up to 18 wt% β-D galactose pentaacetate can be obtained with pressures ranging from 10-15 MPa.

Along with these cloud point data, we present results of a transient dissolution experiment, in which a 1 cm^3 plug of sand bound by β-D galactose pentaacetate is exposed to carbon dioxide at 40^{o}C and 15.2 MPa. This experiment shows that the β-D galactose pentaacetate is extracted rapidly from the plug, with complete dissolution occurring within 5 min. In contrast, extraction of β-D galactose pentaacetate from the plug required over 30 minutes in chloroform, indicating that extraction into supercritical carbon dioxide is potentially much faster than extraction into a liquid solvent.

INTRODUCTION

The high cost of organic solvents and the increasing stringent environmental regulations drive the development of newer clean technologies producing finer products without leaving toxic residues. Supercritical carbon dioxide with T_c of 31 ^{o}C and P_c of 73 atm is abundant, inexpensive, nonflammable, easily available and regenerated, nontoxic and environmentally benign [1]. It has a high solubility for nonpolar organic compounds. In extractions from porous media, the favorable transport properties of fluids near their critical points also allow deeper penetration into solid matrix and more efficient and faster extraction than with the conventional organic solvents, and selectivity can be modulated by varying the temperature or pressure within the supercritical range [2]. Although the ability of supercritical carbon dioxide to dissolve polar, ionic or polymeric compounds is exceedingly limited, small amounts of a polar entrainer or an appropriate surfactant dramatically change the microenvironment to increase the solubility of such substances.

In addition to many small molecules, polydimethylsiloxane, polyphenylmethylsilicone, polyethercarbonates, fluoropolymers and copolymers of fluoroethers such as perfluoroalkylpolyethers and chloro- and boromotrifluoroethylene are some of the polymers have been shown to be CO_2 soluble at or near room temperature and at pressures under 600 bar [3,4,5,6]. In recent studies, the addition of acetate side chains to silicone dramatically increased its CO_2 solubility. The remarkable solubility of polyvinylacetate in CO_2 has been examined with cloud point measurements [7]. Some sugar acetates in equilibrium with supercritical CO_2 have been studied by Potluri et al, Raveendran and Wallen [8,9]. In this paper the cloud point measurements of β-D-galactose pentaacetate in supercritical CO_2 are presented.

EXPERIMENTAL

β-D galactose pentaacetate (Figure 1), 98 % ($C_{16}H_{22}O_{11}$, Aldrich) with the melting point 139-142 ^{o} C is used. Since the sugar exist in very fine powder form, thin plates of the sugar acetate are prepared by solution casting for avoiding sealing problems caused by the fine powder getting entrapped between the piston, o-rings and the cell. The powder form β-D galactose pentaacetate is dissolved in chloroform. The solution is left at room conditions for the preliminary evaporation of the chloroform. This is followed by further evaporation in a vacuum oven at a temperature between 40-50 ^{o}C. The final sugar acetate cast is obtained with a wt % of chloroform less than 0.25%.

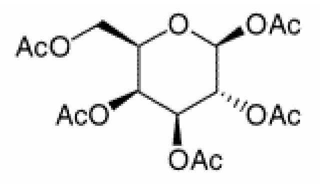

Figure 1: β-D galactose pentaacetate

The cloud points of sugar acetate (β-D Galactose Pentaacetate) - CO_2 system are conducted in a high-pressure, variable volume sapphire cell kept in a temperature constant air chamber. The main part of the set up is a visible cell with 1 in inner diameter and a sufficient height allowing an approximate sample volume of 60 cc, containing a floating piston between the working fluid and the sample fluid. The cell is loaded with CO_2 from a deep tube CO_2 cylinder with an estimated mass accuracy of 1 %. For a typical loading of 10.16 gr CO_2 the estimated error is ± 0.105 gr. The accuracy of sugar acetate concentrations is within 0.86 % of the values associated with the estimated accuracies of temperature, pressure and volume of the system. The upper part of the cell is equipped with a thermocouple and a pressure transducer to measure the temperature and pressure of the sample directly. The cell is completely enclosed in an air bath for temperature control. A positive displacement pump connected to a working fluid reservoir is employed to compress and to depressurize the system. To facilitate the slow decompression of the system needed for accurate cloud point measurements, a needle valve was added to the system.

After loading, the desired temperature is set and the system is pressurized enough so all sugar is completely dissolved. During the dissolution, β-D Galactose Pentaacetate transforms into a sugar- acetate-rich liquid phase swollen by CO_2. While sugar acetate rich phase swells by absorbing CO_2, it also dissolves into the upper CO_2 rich phase. This process continues until all of the β-D Galactose Pentaacetate is dissolved in CO_2, and a single-phase solution is obtained. When the single-phase system is stabilized, the needle valve connected to the working fluid side of the cell below the piston is opened slightly. Depressurization is started and kept at a slow and steady rate, thereby avoiding temperature changes in the system due to the Joule-Thompson effect. For an accurate determination of the onset of turbidity, a sheet of laser light is transmitted through the cell for better visualization of the cloud point. The pressure and the temperature data of the cloud point are recorded, and the system is then repressurized and equilibrated at the next desired temperature to get the cloud point at the new conditions for the same composition. The reproducibility of the measurements is confirmed by the repeating selected cloud point data.

RESULTS and DISCUSSION

β-D galactose pentaacetate has substantial solubility in supercritical CO_2. The cloud point measurements were obtained for the concentration range between 2 and 18 wt % of β-D Galactose Pentaacetate in supercritical CO_2 at the temperature and pressure ranges of 34.5 - 49.5 ^{o}C and 8.7 – 15.6 Mpa. The cloud point data, system pressure versus temperature at various weight compositions, are displayed in Figure 2 along lines of constant β-D Galactose Pentaacetate concentration.

In Figure 2, the region below the curves represents the conditions at which at least two phases exist, whereas the region above the curves representing a single-phase solution for that sugar acetate composition, thereby corresponding to conditions in which complete solubility of the sugar acetate in supercritical carbondioxide is achieved. The cloud point curves are highly linear, and the slopes of the cloud point curves increase with increasing concentration of tsugar acetate. At constant temperature, higher pressures are required to achieve a single phase solution as the amount of dsugar acetate increases. At a constant sugar acetate composition, the pressure required to achieve complete dissolution of sugar acetate increases with increasing temperature.

The reproducibility of the system and the experimental procedure are checked by the repeated runs. In Figure 2, repeated measurements are identified by the points enclosed in the large circles. The cloud points of the repeated experiments are in very close agreement in every case.

The solvent power of a supercritical fluid is expected to be directly related to its density. Therefore, the cloud point data shown in Figure 2 have been consolidated in Figure 3 as a plot of the pure CO_2 density at the cloud point temperature and pressure, plotted as a function of composition. The pure CO_2 densities were calculated using with REFPROP algorithm developed by the National Institute of Standards and Technology.

The pure CO_2 densities at the cloud points obtained in this study are collapse onto each other, forming a master curve that is independent of temperature, and weakly dependent on sugar acetate concentration. The β-D Galactose Pentaacetate cloud point data of other researchers are shown for comparison. These data are in general agreement with the new measurements reported here, but appear to exhibit somewhat lower cloud point pressure values. These differences may be due to the method of pressure measurement and the speed of the depressurization.

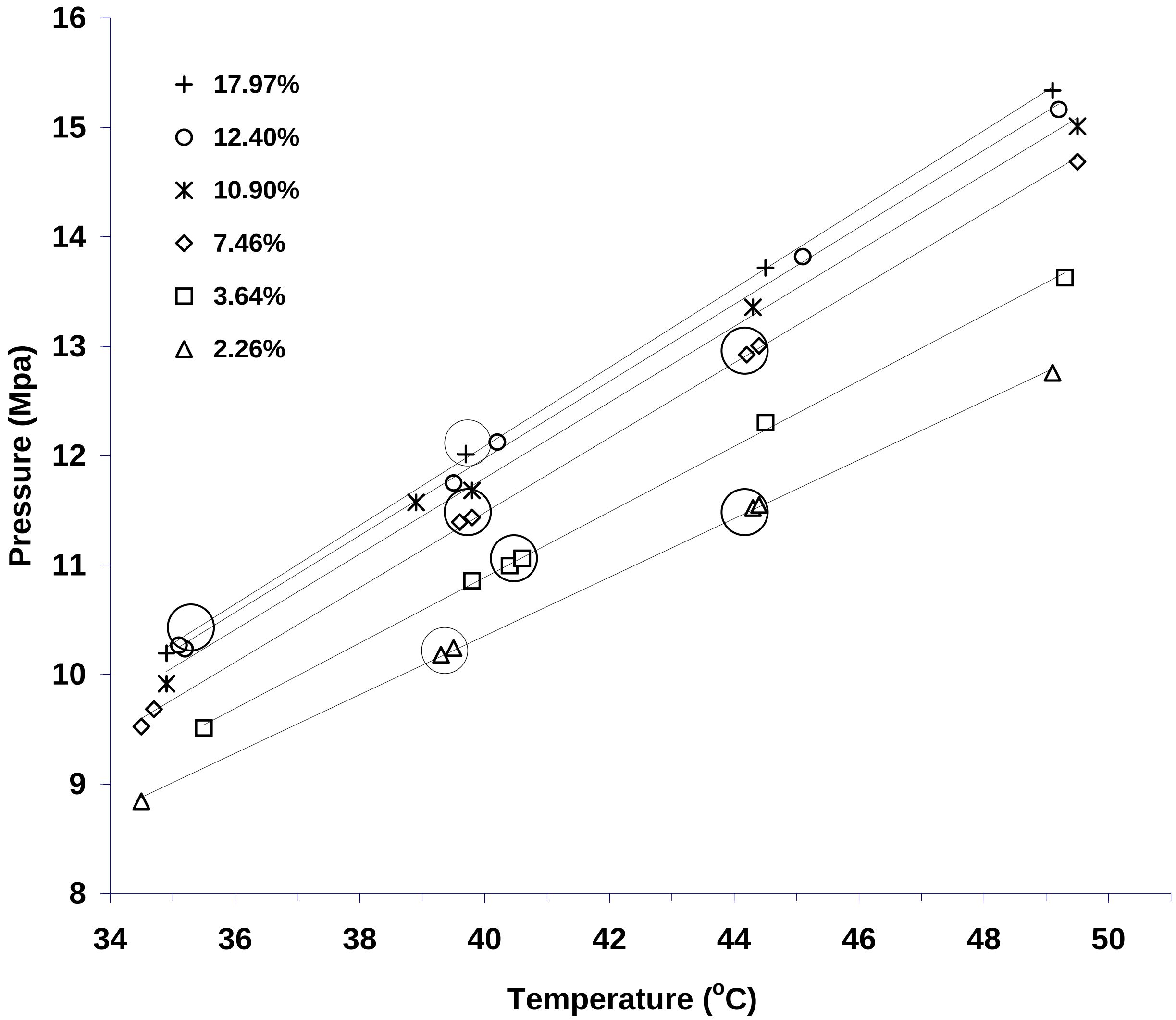

Figure 2: Temperature vs. pressure curves of the cloud points at various weight compositions.

CONCLUSIONS

New cloud point measurements have been performed for solutions of β-D Galactose Pentaacetate in carbon dioxide. These measurements employ direct measurement of the temperature and pressure of the sample, and slow depressurization to insure accuracy and reproducibility. The cloud point measurements confirm that β-D Galactose Pentaacetate exhibits high solubility in carbon dioxide in a relatively moderate temperatures and pressures, which may facilitate its use as a convenient and inexpensive CO_2-soluble material in industrial processes.

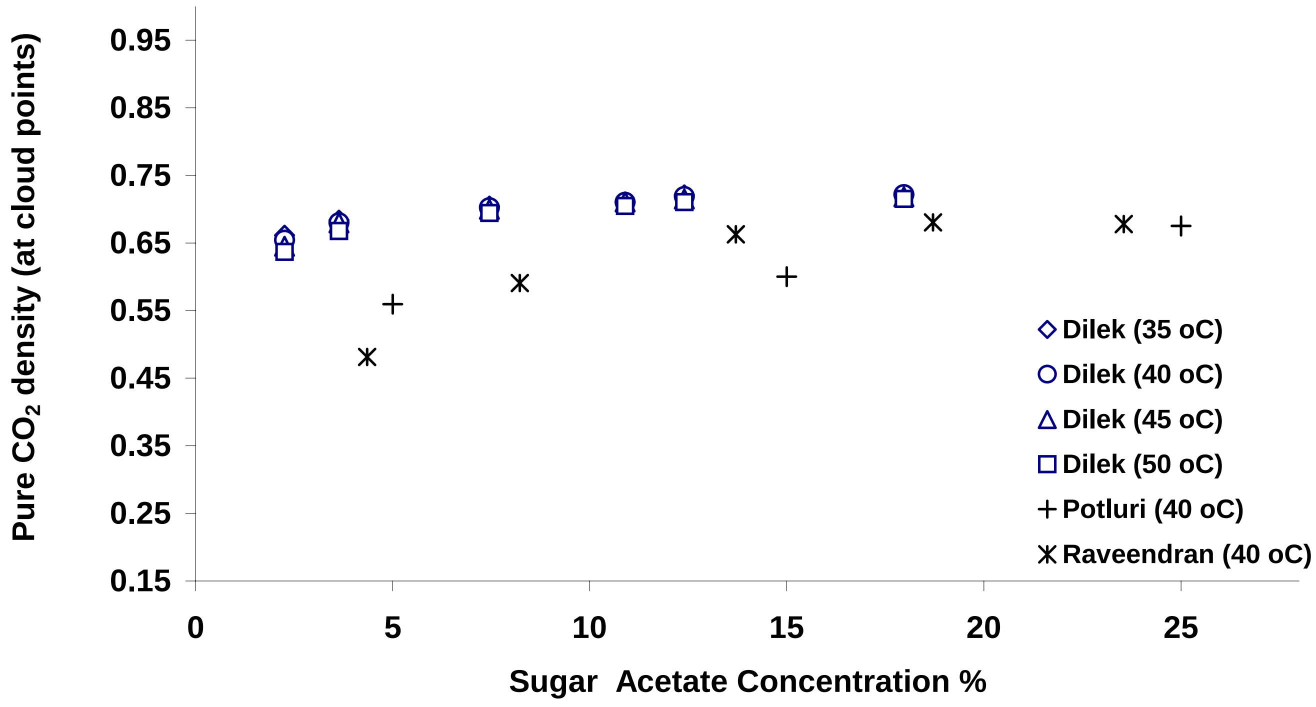

Figure 3: Density of the pure CO_2 at the cloud point conditions of various β-D Galactose Pentaacetate compositions

REFERENCES:

1. Noyori, R. *Supercritical Fluids: Introduction*, Chemical Reviews, **1999**, 99 (2), 353-354.
2. Mohamed, R. S.; Mansoori, G. A.; *The Use of Supercritical Fluid Extraction Technology in Food Processing*, Food Technology, WMRC, June **2002**.
3. Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. *Solubility of Polymers and Copolymers in Supercritical CO_2*, Journal of Physical Chemistry, **1996**, 100, 15581-15587.
4. Lousenberg, R.; Shoichet, M. S. *Synthesis of Linear Poly(tetrafluoroethylene-co-vinyl acetate) in Carbon Dioxide*, Macromolecules, **2000**, 33, 1682-1685.
5. Sarbu, T.; Styranec, T.; Beckman, E. *Non-fluorous Polymers with Very High Solubility in Supercritical CO_2 Down to Low Pressures*, Letters to Nature, **2000**, 405,165-168.

6. Baradie, B.; Shoichet, M. *Synthesis of Fluorocarbon-Vinyl Acetate Copolymers in Supercritical Carbon Dioxide: Insight into Bulk Properties*, Macromolecules, **2002**, 35, 3569-3575.
7. Shen, Z.; McHugh, M. A.; Xu, J.; Belardi, J.; Kilic, S.; Mesiano, A.; Bane, S.; Karnikas, C.; Beckman, E.; Enick, R. *CO_2 –Solubility of Oligomers and Polymers That Contain the Carbonyl Group*, Polymer, **2003**, 1491-1498.
8. Potluri, V. K.; Xu, J.; Enick, R.; Beckman, E.; Hamilton, A. D. *Peracetylated Sugar Derivatives Show High Solubility in Liquid and Supercritical Carbon Dioxide*, Organic Letters, **2002**, *4*, 2333-2335.
9. Raveendran, P.; Wallen, S. L.; *Sugar Acetates as Novel, Renewable CO_2-philes*, J. Am. Chem. Soc., **2002**, *124*, 7274-7275.