

BUTANOL STRUCTURE-SOLUBILITY RELATIONSHIP IN SUPERCRITICAL CARBON DIOXIDE

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By using a continuous flow apparatus, binary solubility of n-butanol, 2-butanol, iso and tert-butanol in supercritical carbon dioxide (SC-CO₂) have been measured at constant temperature of 323 K and at flow rate of 140±10 mL/min in the pressure range of (70 to 140) bar. Different binary solubilities in SC-CO₂ were observed for various structural isomers despite their similar molecular weight (74.12 g/mol) and functional group (OH). The different vapor pressure, dipole moment, and solute-solute interactions lead to the difference in their solubility in SC-CO₂. Tert-butanol has the highest solubility in SC-CO₂ in comparison with 2-butanol, iso-butanol and 1-butanol that may be related to its higher vapor pressure and lower solute-solute intermolecular hydrogen bonding due to steric hindrance. Despite higher vapor pressure of iso-butanol comparing with 1-butanol, solubility of iso-butanol is smaller that is related to its high dipole moment. The solubility order of these isomers were as tert-butanol > 2-butanol > 1-butanol > iso butanol.

Introduction

Supercritical fluids have been used as useful solvent for chemical reaction and extraction. Applications range from extraction in food industries, production of calorie-reduced nuts [1], isolation of volatile materials from raw beef [2], producing micron and sub micron particles and controlling of crystal growth [3,4]. Moreover, the solubility of solids and liquids in supercritical fluids has frequently been measured to establish the technical and economic feasibility of any supercritical fluid extraction and reaction.

The solute melting point, volatility, polarity and type of solute-solute and solute-solvent interactions affect their solubility in SC-CO₂. The binary solubility of p-hydroxybenzoic acid (p-HBA) in SC-CO₂ is two orders of magnitude lower than the binary solubility of o-hydroxybenzoic acid (o-HBA) [5]. The solubility of o-amino benzoic acid (O-ABA) is higher than that of p-amino benzoic acid (P-ABA) [6]. The differences in their structure make them behave differently. O-ABA can form intermolecular hydrogen bonding, which makes it more soluble in ethane. Furthermore, Suzuki et al. reported the solubility of 1-propanol and 2-propanol in SC-CO₂. Their results show that the solubility of 2-propanol is greater than that of 1-propanol. Also Iwai et al. studied the extent of the intermolecular interactions for propanol-d isomers (1- and 2-propanol-d) or xylenol isomers (2,5- and 2,6- and 3,4-xylenol) with acetone in SC-CO₂ by FT-IR spectroscopy [7].

In the present work, we report the binary solubility data for butanol structural isomers of 1-butanol, 2-butanol, iso-butanol and tert-butanol in SC-CO₂. The effect of intermolecular hydrogen bonding, dipole moment and vapor pressure, which are related to solute structure, on their solubility has also been discussed.

2. Experimental

2.1. Reagents: Carbon dioxide with purity of 99.5 mass% was purchased from Zam Zam Co. Ltd. (Isfahan, Iran). 1-Butanol (purity>98%) and iso-butanol (purity>99%) were purchased from Riedel-deHaën Co. 2-Butanol (purity>99%) and tert-butanol (purity>99%) were purchased from Merck Chemical Co. and Fluka, respectively. All of reagents were used without further purification.

2.2. Apparatus and Procedure: The solubility measurement was carried out using a continuous flow apparatus that is explained elsewhere [8]. In each experiment 2.0 ± 0.1 g of solute (1-butanol, 2-butanol, iso-butanol, tert-butanol) and glass beads (o.d.=3-4 mm) to lower dead volume and to increase the contact surface, was placed in the cylindrical equilibrium cell of solute. Then the outlet of the 1st cell was connected to the 2nd cell that was filled with 3 g of glass wool. This arrangement not only prevents physical transfer of solutes to the trap but also increases the reproducibility of solubility measurements. The cylindrical equilibrium cells are similar with a volume of 10 mL.

At the beginning of each experiment, the system was maintained at the desired temperature and pressure for 45 min (static condition) to reach equilibrium. The saturated SC-CO₂ was depressurized through a back-pressure regulator (BPR). Using the constant flow rate mode of the pump, constant pressure (± 1 bar) was maintained by the BPR. The dissolved solutes were trapped and collected in a vial, which was filled with glass wool and cooled in the table salt-ice slurry after exiting from the BPR. The volume of CO₂ was determined using a wet gas meter. The trapped solute was weighed with an analytical balance (± 0.1 mg). The solubility was defined as the mole fraction of the solutes in the expanded CO₂.

3. Results and Discussion

The binary solubility of 1-butanol, 2-butanol, iso-butanol and tert-butanol in SC-CO₂ were measured at constant temperature of 323 K and flow rate of 140 ± 5 mL/min. The results are listed in Table 1 and shown in Figure 1. Generally raising the pressure at constant temperature increases the density of SC-CO₂ and enhances the interaction between the solute and SC-CO₂ [9]. Therefore the solubility of each alcohol in SC-CO₂ is increased with the pressure. Since all of the solutes have similar functional group and molecular weights the differences in solubility maybe related to factors such as vapor pressure, solute-solute and solute-solvent interactions and their dipole moments. Some useful physical properties of each of the alcohols are listed in Table 2.

Chylinski et al. reported that solubility of n-alcohols have been increased as function of logarithm of the vapor pressure of the pure solute [10]. However, for 1-butanol and iso-butanol the same trend were not observed as shown in Table 2 and Figure 2. Perhaps this deviation from above mentioned trend is related to their difference in their dipole moments. Iso-butanol has greater dipole moment than 1-butanol (Table 2) therefore has less solubility in SC-CO₂. Moreover, the intermolecular hydrogen bonding and their steric hindrance are different in these structural isomers.

The effect of steric hindrance can be estimated by comparison of the number of alcohol molecules in an oligomer numbers. The oligomer numbers, for 1-butanol and tert-butanol are five and three respectively [11]. This means that, the extent of intermolecular hydrogen bonding for 1-butanol is more than tert-butanol.

In conclusion, solute-solute intermolecular interaction forces between 1-butanol molecules is more than tert-butanol, thus solubility of 1-butanol is less than the tert-butanol.

Suzuki et al reported similar conclusion about the solubility of propanol isomers [7]. Iwai et al. reported that the amount of the intermolecular hydrogen bonding between 1-propanol-d and acetone was larger than that between 2-propanol-d and acetone, also the amount of acetone interacting with OH group for 3,4-xyleneol was the largest among xyleneol isomers (2,5- and 2,6-xyleneol). They have concluded that the steric hindrance of methyl groups around hydroxyl group leads to these differences. It may be due to the fact that the solute-solute interaction hydrogen bonding in tert-butanol is weaker than 2-butanol. 2-Butanol has also less solute-solute intermolecular interaction in comparison with 1-butanol and iso-butanol.

Similar conclusions can be made by comparing the solubility of these alcohols in water. Tert-butanol has the highest solubility than 2-butanol and 2-butanol is more soluble in water than iso-butanol and 1-butanol (Table 2).

4. Conclusions

The binary solubility of 1-butanol, 2-butanol, iso-butanol and tert-butanol in SC-CO₂ at 75-140 bar and temperature of 323 K were measured. Despite of their similar molecular weight and functional group, they have different solubility. Solubility of tert-butanol in SC-CO₂ was found the highest that may be related to higher volatility and weak intermolecular interactions. Moreover, the solubility of 2-butanol was found higher than that of iso-butanol and 1-butanol due to higher vapor pressure and lower solute-solute intermolecular hydrogen bonding. Despite of the higher vapor pressure of iso-butanol in comparison with 1-butanol, the solubility of 1-butanol is higher due its lower dipole moment. Solute structure affects the solubility of butanol structural isomers in SC-CO₂

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Table 1: The binary solubility of 1-butanol, 2-butanol, iso and tert-butanol in SC-CO₂ at 323 K, and flow rate of 140 ± 5 mL/min.

Pressure (bar)	Solubility (mole fraction*100)			
	1- butanol	2- butanol	Isobutanol	Tert- butanol
75	0.39±0.01	0.54±0.05	0.15±0.01	0.15±0.01
85	0.65±0.01*	0.86±0.03	0.24±0.02	0.59±0.03
95	1.33±0.09	4.15±0.41	0.42±0.05	6.66±0.29
100	2.23±0.20	9.96±0.53	3.08±0.34	10.26±1.82
110	12.21±0.32	13.98±0.22	10.92±0.54	11.20±1.32
120	15.44±1.15	15.79±1.48	13.58±0.41	13.42±0.90
130	17.11±1.61	15.97±0.79	15.17±1.00	16.51±1.30
140	18.23±2.70	16.03±1.50	16.25±0.79	18.02±1.70

*The standard deviation of at least 3 measurements is given in parenthesis.

Table 2: Physical Properties of the Solutes Sorted by Their Boiling Points.^a

Solute	M. P. (°C)	B. P. (°C)	V. P. (bar)	D. M. (D)	S. ^c _w (g/L)
1-Butanol	-89	118	6.7 ^b	1.66	77
Iso-butanol	-108	108	10.6	1.79	80
2-Butanol	-114	99.5	16.5		245
Tert-butanol	25.3	82.5	40.7	1.7	Soluble

^aMerck Index; ^bCalculated; ^cSolubility in water

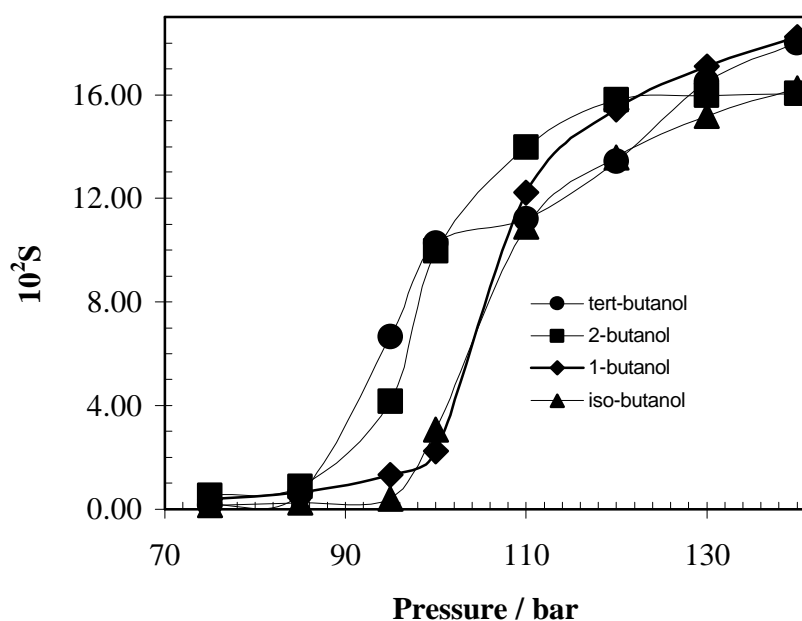


Figure 2: Binary solubility of 1-butanol, 2-butanol, iso and tert-butanol in SC-CO₂ at 323 K and different pressures.