TERNARY SOLUBILITY OF BUTANOL STRUCTURAL ISOMERS IN SUPERCRITICAL CARBON DIOXIDE: INTERNAL HYDROGEN BONDING AND SELECTIVITY

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Abstract

Ternary solubility of 1-butanol/2-butanol, i-butanol/2-butanol, and i-butanol/t-butanol in supercritical carbon dioxide (SC-CO_2) have been measured, using a continuous flow apparatus, at a temperature and a pressure range of (40-60) ^{o}C and (80-140) bar respectively and at a flow rate of 140 ± 5 mL/min. The ternary solubilities of the pairs were increased with pressure at constant temperature and they were reduced with temperature at constant pressure of 100 bar. Despite their different binary solubility in SC-CO_2 at pressure of 100 bar [1], their ternary solubility in SC-CO_2 were similar for the pairs of the structural isomers. The selectivity of SC-CO_2 for each pair of isomers were reported.

The observed solubility of alcohols in SC-CO_2 were affected by intermolecular hydrogen bonding. FT-IR spectra of neat and mixed liquid solutes were used to explain the effect of the intermolecular hydrogen bonding on the solubility of butanol structural isomers. The ternary solubilities of the butanol structural isomers were also compared with their binary solubilities and several conclusions were made regarding the structure-solubility relationship.

The ternary solubilities of the butanol structural isomers were also measured at the different solute molar ratio of 0.33, 0.50, 1.0, and 2.0 in the equilibrium cell at 50 ^{o}C and 100 bar. The results show that the solubilities of each solute are depended on their molar ratio in the equilibrium cell. But, the total solubilities remain constant, indicating that the saturation condition has been established.

INTRODUCTION

The solute melting point, volatility, polarity and type of solute-solute and solute-solvent interactions affect their solubility in SC-CO_2 and the selectivity of reactions under SC-CO_2. There are several reports on the use of vibration spectroscopy in supercritical fluid science and especially investigation of the effect of hydrogen bonding on the solubility in SC-CO_2 [2-4]. However, due to lack of proper instrumentation in our research laboratory, we are trying to relate the vibration frequencies of species in liquid phase to their solubilities in SC-CO_2. In this work the solubility of butanol structural isomers were measured and some conclusions regarding the structure-solubility relationship were made. The solubility data are useful in various applications of SC-CO_2 on the horizon [5-12].

EXPERIMENTAL

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 (= i-butanol) with purity>99% were purchased from Riedel-deHaën Co. 2-Butanol (purity>99%) and tertiary-butanol (= t-butanol) with purity>99% were purchased from Merck Chemical Co. and Fluka, respectively. All of reagents were used without further purification.

Apparatus and Procedure: The solubility measurement was carried out using a continuous flow apparatus that is explained elsewhere [12]. Due to high solubility of the isomers in SC-CO_2, two equilibrium cells (8 mL volume each containing 5.0 g of species) were used before the 3rd one that was filled with Pyrex wool. Then, the outlet of the 1st cell was connected to the 2nd and the 3rd cell. This arrangement not only prevents physical transfer of solutes to the trap but also increases the reproducibility of solubility measurements.

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-CO_2 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 CO_2 was determined using a wet gas meter. The trapped solutes were analyzed by GC-FID and the solubilities were calculated as the mole of the solutes in the mole of expanded CO_2. The uncertainty of all the solubility measurements including GC analysis is below 10%.

RESULTS AND DISCUSSION

The ternary solubility of 1-butanol/2-butanol, i-butanol/2-butanol, and i-butanol/t-butanol in SC-CO_2 were measured at the pressure range of (80-140) bar, at constant temperature of 50°C, and flow rate of 140±5 mL/min. The results are listed in Table 1-3. Generally raising the pressure at constant temperature increases the density of SC-CO_2 and enhances the interaction between the solute and SC-CO_2. Therefore, the ternary solubility of each alcohol in SC-CO_2 is increased with the pressure.

The ternary solubility of 1-butanol/2-butanol, i-butanol/2-butanol, and i-butanol/t-butanol in SC-CO_2 at the temperature range of (40-60) °C were measured at constant pressure of 100 bar and flow rate of 140±5 mL/min. With increasing the temperature, the solubilities have been diminished. This is related to the lower density of SC-CO_2 at higher temperatures. The data are given in Tables 4-6.

Selectivities of SC-CO_2 in ternary systems of 2-butanol/isobutanol, i-butanol/t-butanol, and 2-butanol/1-butanol at different pressures at temperature of 50 °C and expanded gas flow rate of 140 ± 5 mL/min are calculated and given in Table 7. The selectivity for each pair was defined as the ratio of the solubility of highly soluble solute to the solubility of the less soluble solute. The selectivity for the 2-butanol/i-butanol is highest at 80 bar while it is the lowest for the i-butanol/t-butanol pair, and it remains almost constant for the 2-butanol/1-butanol pair. Addition of 2-butanol or t-butanol to i-butanol breaks down the strong hydrogen bonding cluster in neat i-butanol.

Selectivities of SC-CO_2 for ternary systems of 2-butanol/i-butanol, i-butanol/t-butanol, and 2-butanol/1-butanol at the temperature range of (40-60) °C at pressure of 100 bar and expanded gas flow rate of 140 ± 5 mL/min are calculated and given in Table 8. Higher selectivities were observed for each pair at higher temperatures implying that their solubilities are different at higher temperatures.

The ternary solubilities of the butanol structural isomers were also measured at the different solute molar ratios of 0.33, 0.50, 1.0, and 2.0 in the equilibrium cell at 50 °C and 100 bar. The results, listed in Tables 9-11, show that the solubilities of each solute are depended on their molar ratio in the equilibrium cell. But, the total solubilities remain constant, indicating that the saturation condition has been established with respect to the concentration of both solutes.

The total ternary solubility of 1-butanol/2-butanol, i-butanol/t-butanol, i-butanol/2-butanol were increased as much as 17, 7, and 7 times in comparison with binary solubilities at 100 bar and 50 °C as shown in Table 12. This increase indicates that 2-btanol and t-butanol are acting as modifiers and increasing the ternary solubilities. This may happen via reducing the strength of the hydrogen-bonding of neat 1-butanol and i-butanol.

The observed solubility of alcohols in SC-CO_2 were affected by the strength of intermolecular hydrogen bonding in liquid solutes. FT-IR spectra of neat and mixed liquid solutes were used to explain the effect of the intermolecular hydrogen bonding on the solubility of butanol structural isomers. The data are reported in Table 13. The frequency of OH vibration for both 1-butanol and i-butanol is the same (3337.2 cm^{-1}) implying that the intermolecular-hydrogen-bonding strength is about the same and stronger than the other two isomers. This trend is exactly matching the order of their binary solubility of these isomers that is reported elsewhere [1]. When the isomers are mixed, the strength of the intermolecular hydrogen bonding is reduced and their total solubility is increased. In the mixture of i-butanol/2-butanol or i-butanol/ t-butanol, the intermolecular hydrogen-bonding strength are the same therefore they experience the same extent of increase in their ternary and total solubility.

CONCLUSIONS

The ternary solubility of 1-butanol/2-butanol, i-butanol/2-butanol, and i-butanol/t-butanol in SC-CO_2 at (80-140) bar and temperature range of (40-60) °C were measured and their selectivities were calculated. FT-IR spectra of neat and mixed species were used to show the strength of intermolecular hydrogen bonding and their effect on their solubility measurements. Increasing temperature increased the selectivity of SC-CO_2 for all pairs of structural isomers studied.

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Table 1: Ternary solubility of 1-butanol/2-butanol in SC-CO_2 versus pressure at temperature of 50 ^{o}C and expanded gas flow rate of 140 ± 5 mL/min.

Pressure (bar)	1-Butanol solubility (X)	2-Butanol solubility (X)
80	0.072	0.074
100	0.161	0.171
120	0.182	0.183
140	0.196	0.191

Table 2: Ternary solubility of isobutanol/2-butanol in SC-CO_2 versus pressure at temperature of 50 ^{o}C and expanded gas flow rate of 140 ± 5 mL/min.

Pressure (bar)	I-butanol solubility (X)	2-Butanol solubility (X)
80	0.003	0.004
100	0.101	0.099
120	0.119	0.121
140	0.134	0.134

Table 3: Ternary solubility of i-butanol/t-butanol in SC-CO_2 versus pressure at temperature of 50 ^{o}C and expanded gas flow rate of 140 ± 5 mL/min.

Pressure (bar)	I-butanol solubility (X)	T-butanol solubility (X)
80	0.005	0.005
100	0.107	0.094
120	0.145	0.115
140	0.173	0.135

Table 4: Ternary solubility of 1-butanol/2-butanol in SC-CO_2 versus temperature at pressure of 100 bar and expanded gas flow rate of 140 ± 5 mL/min.

Temperature (^{o}C)	1-Butanol solubility (X)	2-Butanol solubility (X)
40	0.212	0.208
50	0.164	0.171
60	0.040	0.046

Table 5: Ternary solubility of isobutanol/2-butanol in SC-CO_2 versus temperature at pressure of 100 bar and expanded gas flow rate of 140 ± 5 mL/min.

Temperature (^{o}C)	I-butanol solubility (X)	2-Butanol solubility (X)
40	0.203	0.195
50	0.101	0.099
60	0.016	0.018

Table 6: Ternary solubility of i-butanol/t-butanol in SC-CO_2 versus temperature at pressure of 100 bar and expanded gas flow rate of 140 ± 5 mL/min.

Temperature (^{o}C)	I-butanol solubility (X)	T-butanol solubility (X)
40	0.158	0.145
50	0.107	0.094
60	0.035	0.020

Table 7: Selectivities of SC-CO_2 for ternary systems of 2-butanol/isobutanol, i-butanol/t-butanol, and 2-butanol/1-butanol versus pressure at temperature of 50 ^{o}C and expanded gas flow rate of 140 ± 5 mL/min.

Pressure (bar)	$a_{\text{2-But/ Iso}}$	$a_{\text{Iso/Tert}}$	$a_{\text{2-But/1-But}}$
80	1.30	1.06	1.02
100	0.98	1.14	1.05
120	1.01	1.27	1.00
140	1.01	1.29	0.97

Table 8: Selectivities of SC-CO_2 for ternary systems of 2-butanol/isobutanol, i-butanol/t-butanol, and 2-butanol/1-butanol versus temperature at pressure of 100 bar and expanded gas flow rate of 140 ± 5 mL/min.

Temperature (^{o}C)	$a_{\text{2-But/Iso}}$	$a_{\text{Iso/Tert}}$	$a_{\text{2-But/1-But}}$
40	0.96	1.09	0.98
50	0.98	1.14	1.05
60	1.15	1.80	1.16

Table 9: Ternary solubilities of isobutanol/2-butanol in SC-CO_2 at different mole ratios in the equilibrium cell at 50 ^{o}C, 100 bar, and expanded gas flow rate of 140 ± 5 mL/min.

Isobutanol/2-butanol mole ratio	I-butanol solubility (X)	2-Butanol solubility (X)	Total solubility (X)
0.33	0.055	0.144	0.199
0.5	0.064	0.117	0.181
1.0	0.101	0.099	0.200
2.0	0.128	0.077	0.205

Table 10: Ternary solubilities of 1-butanol/2-butanol in SC-CO_2 at different mole ratios in the equilibrium cell at 50 ^{o}C, 100 bar, and expanded gas flow rate of 140 ± 5 mL/min.

1-Butanol/2-butanol mole ratio	1-Butanol solubility (X)	2-Butanol solubility (X)	Total solubility (X)
0.33	0.099	0.239	0.338
0.5	0.120	0.212	0.333
1	0.163	0.171	0.335
2	0.208	0.112	0.320

Table 11: Ternary solubilities of i-butanol/t-butanol in SC-CO_2 at different mole ratios in the equilibrium cell at 50 ^{o}C, 100 bar, and expanded gas flow rate of 140 ± 5 mL/min.

I-butanol/t-butanol mol ratio	I-butanol solubility (X)	T-butanol solubility (X)	Total solubility (X)
0.33	0.078	0.126	0.204
0.5	0.088	0.111	0.199
1	0.107	0.094	0.200
2	0.143	0.052	0.196

Table 12: The increase in total ternary (S_t) and ternary (S_T) solubilities of different solute pairs in SC-CO_2 comparing to their binary solubility (S_B) at mole ratio of one in the equilibrium cell at 50 ^oC, 100 bar, and expanded gas flow rate of 140 ± 5 mL/min.

Species	S_B (X)*	Ternary solubility			S_t (X)	S_t / S_B
		Species	(X)	S_T/S_t		
1-butanol	0.02	2-butanol	0.17	8.5	0.43	17
i-butanol	0.03	t-butanol	0.11	3.7	0.20	7
i-butanol	0.03	2-butanol	0.10	3.3	0.20	7

* Binary solubilities were taken from Ref. [1].

Table 13: Vibration frequencies of OH stretching mode from FT-IR spectra of neat and mixed isomers.

Neat and mixed isomers	OH vibration frequency (cm^{-1})
1-Butanol	3337.22
I-butanol	3337.22
2-Butanol	3356.23
T-butanol	3367.63
1-Butanol/2-butanol	3341.02
Isobutanol/2-butanol/	3348.62
I-butanol/t-butanol	3348.62