SOLUBILITY BEHAVIOR OF TERNARY SYSTEMS OF LIPIDS, COSOLVENTS AND SUPERCRITICAL CARBON DIOXIDE

Özlem Güçlü-Üstündag and Feral Temelli*
Department of Agricultural Food and Nutritional Science, University of Alberta,
Edmonton, Alberta, Canada T6G 2P5
feral.temelli@ualberta.ca, Fax: 780-492-8914

In addition to changing temperature and pressure, the solvent strength of supercritical fluids can be fine-tuned according to the separation problem at hand by the use of small amounts of cosolvents. The addition of a cosolvent may increase solubility selectively or non-selectively. Ethanol is the cosolvent of choice for food applications. Solubility behavior of ternary systems of lipid components (fatty acids (palmitic, stearic and behenic acids), ß-carotene, squalene, stigmasterol), cosolvents and $SCCO_2$ was analyzed to determine the effect of operating conditions, cosolvent concentration, as well as cosolvent and solute properties on the cosolvent effect, which was quantified as solubility enhancement (ratio of solubility obtained with cosolvent addition to that without a cosolvent). Cosolvent effects for these solutes were compared and implications for fractionation noted. Solubility enhancement was observed for all systems studied but to different extents. Cosolvent effect was dependent on cosolvent concentration and pressure. It increased with cosolvent concentration for all systems, whereas pressure effect was system dependent. Cosolvent effect of ethanol for fatty acids decreased with pressure. This pressure effect was dependent on cosolvent concentration and pressure such that it increased with concentration and decreased with pressure. Specific intermolecular interactions, such as H-bonding between the fatty acids and ethanol contribute significantly to the cosolvent effect and can be exploited to increase the selectivity of a fractionation process. Benefits of cosolvent addition must be balanced against its disadvantages for a specific application, since the cosolvent has to be removed from the final product.

1. INTRODUCTION

Choice of cosolvent for a specific application requires a good understanding of the effect of cosolvent addition on the solubility behavior, mass transfer and economics of the process. Ethanol is the preferred cosolvent for food applications due to its GRAS (Generally Recognized As Safe) status. Cosolvent effect on solubility, extraction or fractionation behavior of selected lipids has been investigated, however a systematic investigation of the cosolvent effect on the solubility behavior of minor and major lipid components in supercritical CO_2 ($SCCO_2$) and the implications for extraction and fractionation processes has not been carried out. Therefore, the objectives of this study were: 1) to review the effect of cosolvent addition on solubility behavior with special emphasis on lipids, 2) to correlate and interpret the cosolvent effects observed for lipid components with a special focus on ethanol, and 3) to assess the implications of the findings for processing of fats and oils.

2. MATERIALS AND METHODS

Literature solubility data of ternary systems of minor and major lipids, cosolvents and $SCCO_2$ have been compiled. The effect of cosolvent addition on the solubility behavior of fatty acids (stearic, palmitic and behenic acids), squalene and β-carotene was studied by calculating the cosolvent effect (solubility enhancement = ratio of solubility obtained with cosolvent addition to that without a cosolvent) for these systems and plotting solubility enhancement versus cosolvent concentration graphs. Binary solubility data of stigmasterol and CO_2 and ternary solubility data of stigmasterol + CO_2 and cosolvents (ethanol, methanol and acetone) at 308 K [1] were correlated using Chrastil's model [2] using densities of solvent and solvent+cosolvent mixture to determine the density contribution to the cosolvent effect. Chrastil's model establishes a linear relationship between ln solubility and ln density as follows:

$$\ln c = k \ln d + a/T + b \quad (1)$$

where c is the solubility of the solute in the supercritical solvent (g/L), d is the density of the pure solvent (g/L) and a, b and k (association number) are model parameters. The model parameters were estimated using a multivariate regression analysis of the SAS statistical software package [3].

3. RESULTS AND DISCUSSION

The addition of cosolvents resulted in solubility enhancement in all the lipid systems investigated but to different extents. The magnitude of the cosolvent effect was dependent on the cosolvent, solute, pressure and cosolvent concentration. The effect of ethanol addition on the solubility of lipids has been summarized in Table 1. Increase in solvent density and specific intermolecular interactions are the major factors that contribute to the cosolvent effect.

Table 1. Cosolvent effect (solubility enhancement) of ethanol in lipid systems.

Solute	Solubility enhancement	Ethanol concentration	T (K)	P (MPa)	Data from Ref
Fatty acids					
palmitic acid	1.5-63.7[a]	0.99-8.83[c]	308	9.9, 19.7	4
stearic acid	1.2-63.2[a]	0.47-8.75[c]	308, 318	8-19.7	4, 5, 6
behenic acid	2.0-29.2[a]	1.21-6.67[c]	308, 318	8-16	7
Minor lipid components					
? -carotene	2.2-9.8[a]	0.30-2.37[d]	313-333	15-28	8
stigmasterol	4.0[a]	3.5[e]	308	15.2	1
squalene	1.8-5.9[b]	4.07-12.04[d]	333	20-27.5	9

[a] calculations based on solubility in mole fraction, [b] solubility in w/w
[c] mole % (solute inclusive), [d] wt % (solute free), [e] mole % (solute free)

3.1. Density Effect

The addition of a cosolvent generally increases the bulk density of the supercritical fluid (SCF) mixture. A comparison of the density isotherms of binary mixtures of CO_2 and cosolvents, acetone, ethanol and pentane at 323 K is presented in Figure 1. Density of CO_2 + cosolvent was higher than pure CO_2 density at lower pressures, however a crossover of density isotherms was observed at approximately 23 MPa for acetone and ethanol, and at 15 MPa for pentane such that at lower pressures the density of solvent mixture was higher than pure CO_2 density whereas at higher pressures density of CO_2 was higher. Estimated Chrastil's

model parameters were used to plot solubility isotherms for stigmasterol+cosolvent systems (Fig. 2). As the measured densities of CO_2 and CO_2 + cosolvent mixtures were used in the correlation, the effect of cosolvent addition on solvent density is removed and therefore the difference in the isotherms reflect the differences in specific intermolecular interactions. The difference in cosolvent effects of methanol and ethanol is due to the difference in the stoichiometry of the stigmasterol-alcohol complexes formed in the solid phase [1].

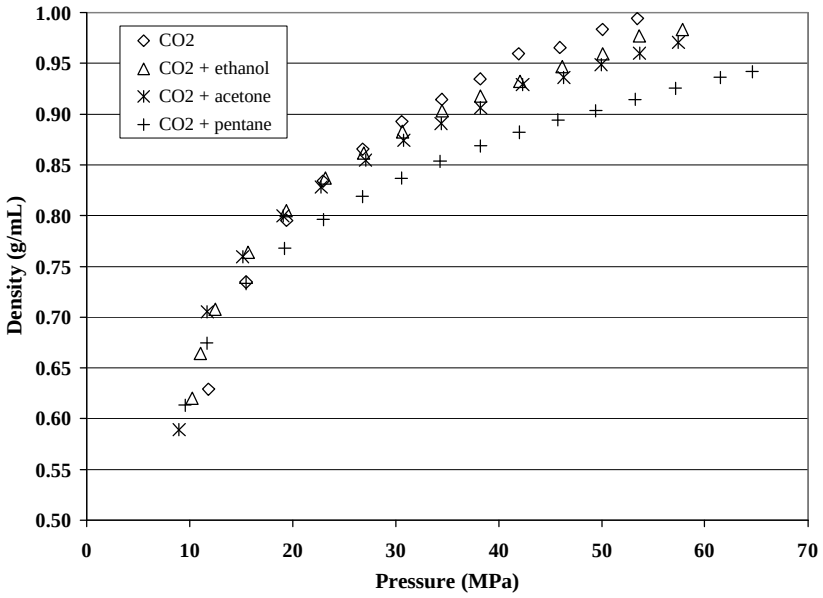

Figure 1. Density isotherms of binary mixtures of CO_2 + cosolvents (10% w/w ethanol, 12 % w/w pentane and 10 % w/w acetone) at 323 K (Data from Refs. 10-12).

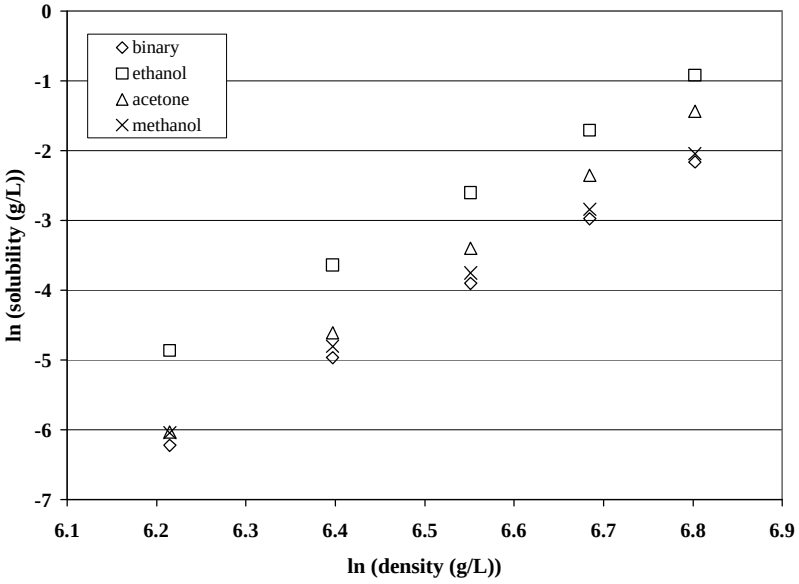

Figure 2. Solubility isotherms of stigmasterol at 308 K in pure CO_2, CO_2 + ethanol, CO_2 + methanol and CO_2 + acetone plotted using estimated model parameters.

3.2. Intermolecular interactions

Non-specific physical interactions between the solute and cosolvent such as dipole-dipole, dipole-induced dipole, or induced dipole-induced dipole interactions and specific chemical interactions such as hydrogen bonding and charge transfer complexes are important contributors to the cosolvent effect. Intermolecular interactions in the solid phase such as complex formation between sterols and organic solvents can also affect the solubility behavior, hence the cosolvent effect. Therefore, accurate interpretation of the cosolvent effect requires knowledge of the intermolecular interactions between the solutes and solvents of interest.

3.3. Effect of cosolvent

A comparison of the cosolvent effects of acetic acid, ethanol, acetonitrile, methyl acetate and octane on the solubility of stearic acid in $SCCO_2$ is given in Figure 3. Stearic acid is capable of participating in H-bonding interactions both as a hydrogen bond acceptor and as a donor due to its carboxyl group. Ethanol and acetic acid also have both hydrogen bond donor and acceptor properties, whereas methyl acetate and acetonitrile participate in H-bonding with stearic acid as hydrogen bond acceptors. Octane does not have any H-bond donor or acceptor properties but have the highest polarizability. Solubility enhancement of stearic acid was highest for acetic acid, which has the highest H-bond donor acidity followed by ethanol, suggesting that H-bonding interactions played a significant role in the observed cosolvent effects. Effect of octane was higher than those of methyl acetate and acetonitrile due to its higher polarizability. The solubility enhancement in the presence of octane was due to induced dipole-dipole and dispersion interactions.

3.4. Effect of solute

The highest enhancements were observed for stearic and palmitic acids at the highest cosolvent concentrations used, whereas lowest enhancement was observed for squalene (Table 1). Tocopherols (-OH and -O-), sterols (-OH), fatty acids (-COOH) and vegetable oils (-O-) have H-bonding ability; therefore, H-bonding between ethanol and these solutes contributes to the cosolvent effect, whereas squalene and β-carotene mainly interact through induced dipole-dipole and dispersion forces.

3.5. Effect of cosolvent concentration

The cosolvent effect increased with cosolvent concentration for all the investigated systems (Figs. 3, 4). A decrease in the cosolvent effect of self-associating cosolvents (cosolvents with both H-bond donor and acceptor properties like alcohols, acetic acid) may occur at high cosolvent concentrations. However, such a decrease was not observed in the cosolvent effect of ethanol and acetic acid on stearic acid, implying that self-association did not have a significant effect on the solubility enhancement in these systems at the concentrations and experimental conditions studied.

3.6. Effect of pressure

The pressure dependence of the cosolvent effect of ethanol on lipid systems was system dependent. No clear trend was observed with pressure for β-carotene, however solubility enhancement of squalene appeared to be independent of pressure in the pressure range investigated (20-27.5 MPa). A decrease in cosolvent effect with pressure was observed for palmitic and stearic acids (Fig. 4). Such a pressure effect has been reported for various solutes in cosolvent-CO_2 mixtures and has been attributed to the decrease in contribution of

density to the cosolvent effect with pressure [13] and the decrease in local composition enhancement with pressure [14]. The influence of pressure on the solubility enhancement of fatty acids was dependent on pressure and cosolvent concentration such that it increased with concentration and decreased with pressure. At 308 K (Fig. 4), the solubility enhancement of stearic acid in CO_2+ethanol decreased with increasing pressure in the pressure range of 8-16 MPa. The influence of pressure was more dominant at lower pressures, such that the highest decrease was observed from 8.5 to 8 MPa, whereas the enhancements were relatively constant in the range 11-16 MPa.

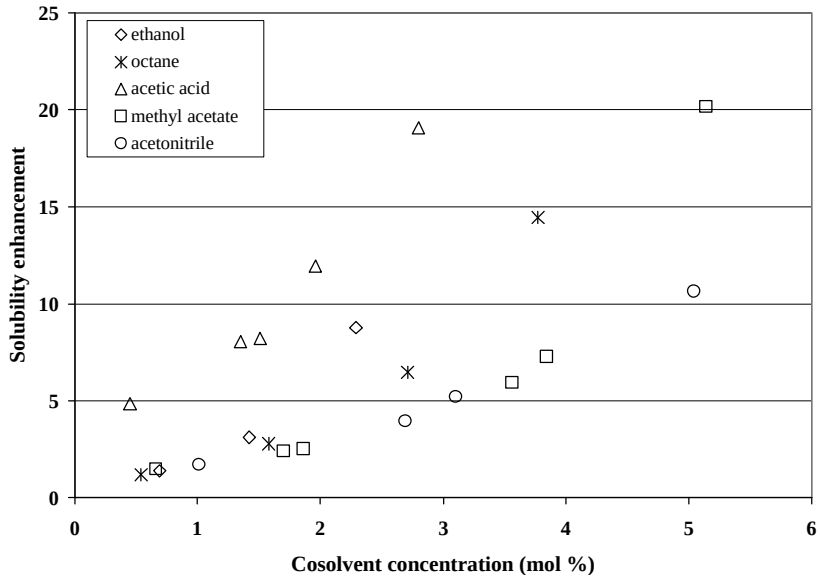

Figure 3. Solubility enhancement of stearic acid in cosolvent + CO_2 mixtures at 318 K and 9.5-9.8 MPa (Data from Refs. 6, 15, 16).

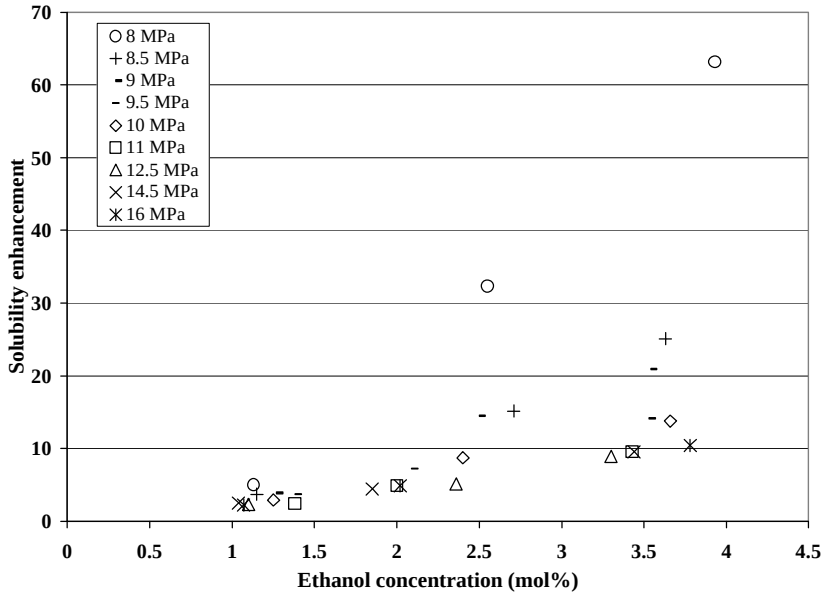

Figure 4. Solubility enhancement of stearic acid in ethanol + CO_2 mixtures at 308 K (Data from Ref. 5).

4. IMPLICATIONS

The addition of cosolvents may improve the feasibility of a process by increasing solvent loading and by improving the selectivity of a process. Due to the solubility enhancement obtained using a cosolvent, a required level of extraction yield can be obtained at a lower pressure. Such a pressure reduction makes extraction of solutes, which are sparingly soluble in $SCCO_2$ under practical conditions, such as phospholipids, possible. Addition of a cosolvent improves selectivity of a separation process if there are specific interactions between the cosolvent and one or more of the mixture components, such as H-bonding. Different cosolvent effects observed for lipids can be exploited for fractionation of fats and oils, such as deacidification of oils. Partitioning of the extract components between the cosolvent and extract-rich phase during solvent recovery can be exploited to achieve fractionation.

Benefits of cosolvent addition must be balanced against its disadvantages for a specific application. Solvent recovery (separation of the cosolvent from the extract, SCF and solids residue) and cosolvent introduction complicates process design. An increase in solvent loading may result in the co-extraction of undesirable compounds. The effect of cosolvent addition on the sample matrix should also be considered. For example, cosolvent addition for oil extraction from oilseeds may alter the functional properties of the proteins in the meal. Use of cosolvents overrides one of the major advantages offered by $SCCO_2$, namely the ability to produce "natural" products with no organic solvent residue.

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