ANALYSIS OF MIXING AND CRYSTALLIZATION IN SUPERCRITICAL FLUIDS USING SMALL ANGLE X-RAY SCATTERING

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Small angle X-ray scattering (SAXS) was successfully applied for *in situ* analysis of solution structure, fluid mixing and particle nucleation in supercritical CO_2 using a through-flow crystallisation system. The dependencies of the Ornstein-Zernike correlation length, ξ, and density fluctuation, $\langle (\Delta N)^2 \rangle / \langle N \rangle$, in ethanol-$CO_2$ solvent mixtures were obtained as functions of the thermodynamic parameters and in relation to the nozzle mixing. It is shown that supercritical properties of solution are important in the vicinity of the CO_2 – ethanol mixture critical curve and have a pronounced effect on the mixing phenomena and particle formation.

1. INTRODUCTION

Supercritical fluids (SCF) have become a viable alternative to chlorinated and non-chlorinated solvents in many industrial processes. They offer many advantages for crystallisation of fine chemicals and pharmaceuticals including enhanced mixing and solvent extraction, adjustable solvent properties, efficient separation of solvents and impurities and recyclable process engineering [1]. Although the applications of SCF are rapidly growing, there is a considerable knowledge gap in understanding of the fundamental properties of supercritical mixtures. For example, supercritical CO_2 is miscible (or partly miscible below the critical mixture point) with most organic solvents, forming binary and ternary solvent-CO_2 systems. The ability to form such mixtures greatly increases the solvating power and polarity range of supercritical CO_2 and strongly affects the supersaturation profile during precipitation. During antisolvent precipitation, macro- and micro-mixing are followed by the non-equilibrium molecular-level processes of nucleation and growth [2]. Although in the macro-mixing stage, SCF can be characterised by being somewhat between "liquid-like" and "gas-like" in terms of their viscosity and density, on the characteristic microscale between 10 and 100 Å the supercritical state exhibits unique properties associated with solvent clustering and density fluctuations. Therefore it is important to identify, in quantitative terms, the boundaries of processing conditions where the critical phenomena are taken place. SAXS technique has been previously applied, both experimentally and theoretically, to study pure SCF such as CO_2, CHF_3 and water [3-5]. However, no data is available on the structure of supercritical mixtures. "Chemical engineering applications" of SAXS, for example, observation of mixing and crystallization processes, have not been investigated. The present work explores SAXS possibilities in these research areas.

2. EXPERIMENTAL METHOD

SAXS measurements were carried out at station 16.1 of the synchrotron radiation source at the CLRC Daresbury Laboratory, Warrington, UK. A fixed wavelength of $\lambda = 1.41\text{Å}$ was used in all experiments. A movable camera equipped with an area detector was positioned at 2 m from the optical cell for solution scattering measurements or at 5 m for particle size measurements. The scattering intensity, $I(s)$, corrected for adsorption and beam decay, was measured as a function of the scattering vector, $s = 2sin\Theta/\lambda$, where 2Θ is the scattering angle. The principal scheme of high-pressure flow system is shown in Fig. 1. The stainless steel optical cell (about 3 cm^3 volume, 5 mm pass-length) was provided with two 0.5 mm thick, parallel widows made of natural diamonds giving unsupported view area about 3.2 mm and aperture 15°. Single-crystal diamond is the only material transparent at the wavelength used and strong enough to withstand the maximum working pressure 30 MPa. A coaxial nozzle of diameter $a = 0.35$ mm with internal mixing chamber length $D = 9$ mm was positioned in such a way that X-ray beam was centered within 2 mm distance (i.e. about $5a$) from the nozzle orifice. This position corresponded to the most important mixing and nucleation area [2]. The other components included thermostats, pumps and system of valves for flow control and which also allowed for preparation of completely pre-mixed CO_2 – ethanol fluids to obtain the background for mixing and nucleation measurements.
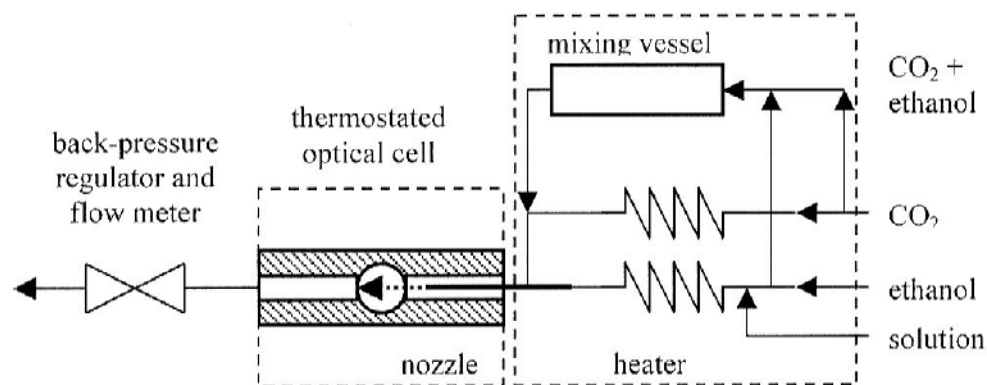

Fig. 1: Diagram of through-flow system.

3. RESULTS AND DISCUSION

3.1 CORRELATION LENGTH AND DENSITY FLUCTUATIONS IN SUPERCRITICAL MIXTURES

It is well known that in the vicinity of the critical point, the scattering profile conforms the Ornstein-Zernike relation:

$$I(s) = \frac{I(0)}{1 + \xi^2 (2\pi s)^2} \tag{1}$$

where ξ is the correlation length which characterizes the volume dimension of fluctuations and $I(0)$ is the zero-angle scattering intensity. In addition, the mean-square density fluctuation, $\langle (\Delta N)^2 \rangle / \langle N \rangle$ is related to the zero-angle intensity per molecule as:

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} \cong \frac{1}{x(Z_1 - Z_2) + Z_2} \frac{I(0)}{N} \tag{2}$$

where x is the mole fraction of co-solvent (ethanol) in solvent (CO_2), and Z_1 and Z_2 are the number of electrons in ethanol and CO_2 molecules correspondingly. Although the magnitude of ξ can be determined directly from the scattering intensities using eq. (1), the fundamental quantity $I(0)$ is always measured in arbitrary units and therefore has to be recalculated into the absolute quantities using the thermodynamic definition of the density fluctuations:

$$\frac{\langle (\Delta N)^2 \rangle}{\langle N \rangle} = \frac{N}{V} \kappa_T kT \tag{3}$$

where κ_T is the isothermal compressibility of pure solvent, k is the Boltzmann constant, N is the number of molecules in the sample volume V. In this work, the calibration was done using the compressibility and density data for pure CO_2 modeled from the Peng-Robinson EOS. The density of binary mixtures, required to calculate $\langle (\Delta N)^2 \rangle / \langle N \rangle$ in eq. (2) for ethanol-CO_2 was approximated using experimental data obtained by Guan et al [6]. In Fig. 2 the results are plotted as a function of x.
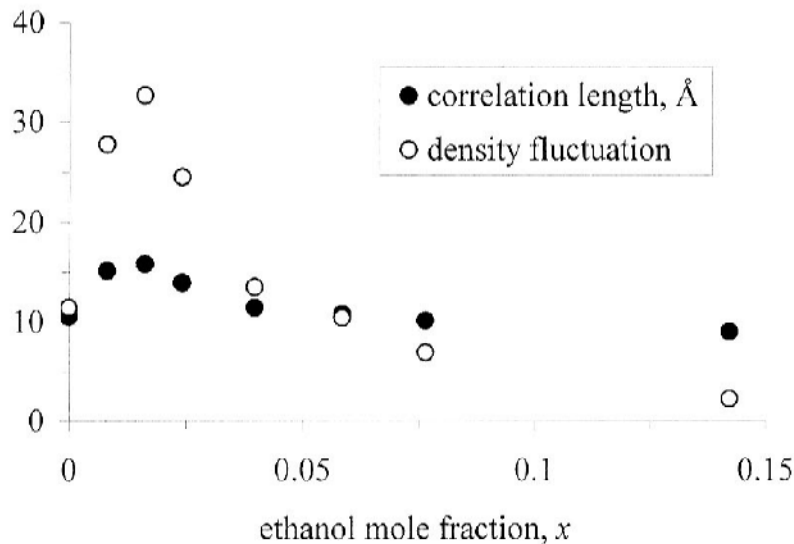

Fig. 2. Correlation length and density fluctuation at $T = 313.15K$, $P = 8.5$ MPa.

Both functions correlate with each other and strongly depend on the fluid composition. In general, the maximum is observed in the vicinity of the P-T mixture critical curve (Fig.3). This curve is formed by the mixture critical points (mcp) modeled from the Peng-Robinson EOS with the mixing rules suggested by Reid et al [7] and binary interaction parameter $K_{i,j} =$

1.372×10^{-2}. Along the curve the mixture becomes supercritical, whereas a single phase exists for all compositions above it. The "liquid-like" supercritical state SCF(L) lies above the curve whereas the vapour-like state SCF(V) belongs to the lower-P, higher-T range of conditions. The data obtained at different temperatures indicate that the peak of ξ and $\langle(\Delta N)^2\rangle/\langle N\rangle$ has a different shape and reaches its maximum at a lower pressure than correspondent functions in pure CO_2. It was shown by Nishikawa et al [4], that the density fluctuation in pure CO_2 forms a ridge along the extension of the gas-liquid co-existence curve on which the critical point (cp) corresponds to the second-order phase transition (Fig. 3). This ridge is also very close to the critical isohore (i.e. SCF density equals the critical density). However, for the solvent mixtures studied in this work, the critical behaviour became more complex dependently on the co-solvent mole fraction. Both parameters, ξ and $\langle(\Delta N)^2\rangle/\langle N\rangle$, had a maximum along the mixture critical curve at the mixture critical composition. However for points outside this curve, the ethanol mole fraction required to produce the maximum fluctuation varied with the SCF density. According to Fig.2, for the pressures above mcp, the ethanol mole fraction at the maximum is smaller than mcp composition for the same temperature, therefore, co-solvent changes the entire character of fluctuation. These results are different from the case of dilute non-volatile solutes [5] where the density enhancement, directly calculated from the ξ and $\langle(\Delta N)^2\rangle/\langle N\rangle$ functions, coincided with the preexisting density enhancement in pure CO_2.
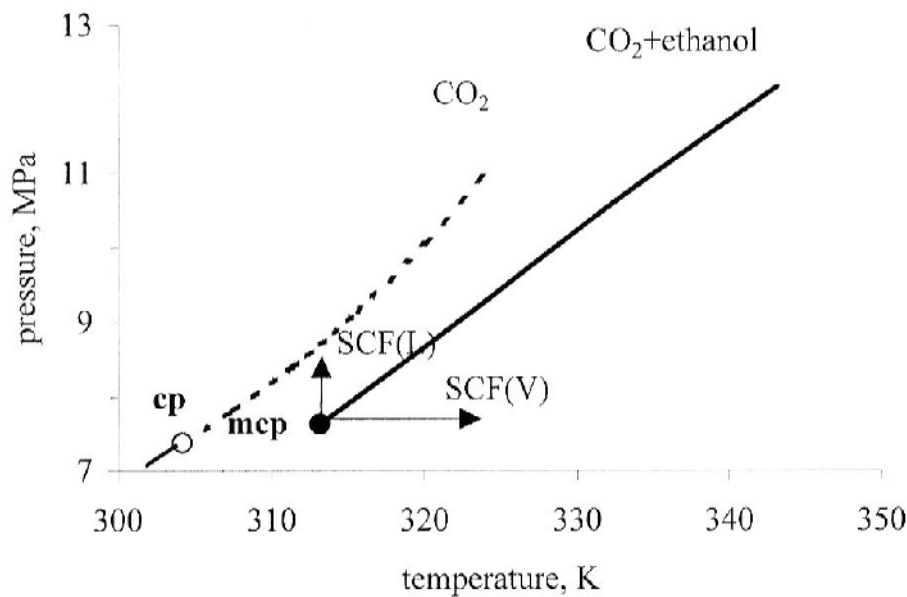

Fig. 3. Mixture critical curve for ethanol-CO_2 mixture in relation to the extension of the gas-liquid coexistence curve for pure CO_2.

3.2 Mixing Process

Micro-mixing in a turbulent SCF flow can be identified with the Batchelor microscale: $\eta_B = \eta \times Sc^{-1/2}$ where η is the Kolmogorov scale of turbulence and $Sc \cong 2\text{-}10$ is the Schmidt number. The typical value of η_B is in the order of 10^{-7} m [2]. On this scale, the large-scale concentration variance in the nozzle transformed into the fine-scale concentration fluctuations

which then disappear on molecular scale. Because most of the scattering occur from the structures below 100 Å, it is expected that SAXS measurements will be sensitive to mixing phenomena in the vicinity of the mixture critical curve. Table 1 shows that increase in the relative nozzle velocity at $P=11$ MPa, $T=333.15$K significantly increases the mean value of ξ.

Table 1. Correlation length, ξ, Å, as a function of relative flow velocity, u/u_0, at a constant ethanol mole fraction 0.04 and different temperatures.

u/u_0	11 MPa; 313.15K	11 MPa; $T=333.15$K	11 MPa; 353.15K
1	8.0	4.1	4.5
4	4.3	11.3	6.7

This increase can be related to the increase of the volume fraction of fluid mixed on molecular scale. In a gas-like CO_2 at a higher temperature 353.15K, increase of mixing also resulted in increase of ξ which can be explained from Fig. 3 by a shift of the mean volume flow composition toward the mixture critical curve. However, in a compressed, liquid-like CO_2 ($T=353.15$K), the correlation length decreased as the well-mixed part of the flow became even more dense, with less pronounced density fluctuation.

3.3 Nucleation

Measurements of particle scattering by SAXS is based on the Guinier approximation:

$$\ln I(s) \sim -4\pi^2 s^2 R_g^2 / 3 \qquad (4)$$

where R_g is the radius of gyration of the particle. This quantity corresponds to the mean volume particle diameter in the flow. An example in Fig. 4 gives the particle size of paracetamol versus ethanol mole fraction in the flow. This is a non-progressive dependence with a maximum size about 190 Å.
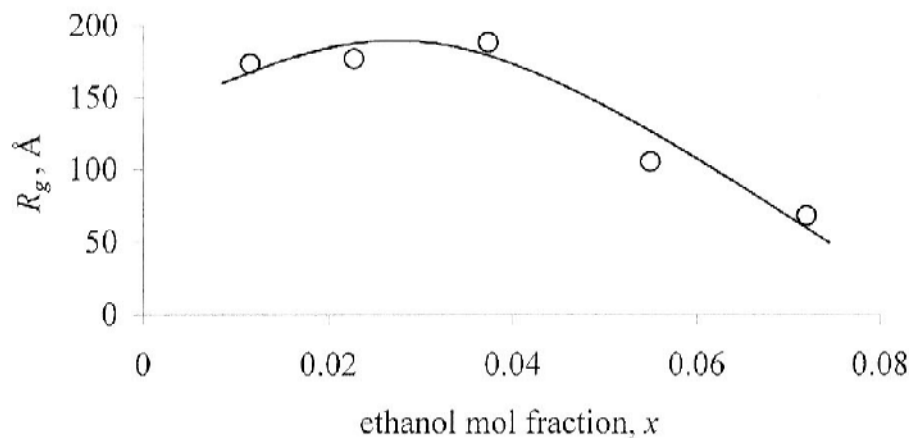

Fig. 4. The mean radius of gyration, R_g, of paracetamol particles as a function of ethanol mole fraction in the flow at $T = 333.15$K, $P = 15$ MPa.

Because SAXS technique is capable of measuring the size range $10 < R_g < 1000$ Å, this phenomenon concerns the nucleation process in the nozzle mixing zone. The maximum in Fig. 4 can be explained by the fact that supersaturation decreases as the ethanol mol fraction increases. However, as the ethanol mol fraction increases, the residence time in the nozzle became too short for the nuclei to develop and therefore, the nuclei size decreases in agreement with the model described by Shekunov et al [2]. In these experiments, the mean size of the nuclei could be determined above the solute volume fraction 10^{-4}.

It was found that the mean nuclei size decreases with the solute concentration and also reach a minimum along the mixture critical curve. Supercritical conditions above or below the mixture critical curve lead to different crystallization and aggregation mechanisms on macro-scale, in miscible and partly-miscible fluids [1] but also related to the nucleation and growth processes taking place on the molecular level. The most interesting phenomena occur in the vicinity of the mixture critical curve. Density fluctuations produce inhomogeneities of supersaturation and may result in an increase of the nuclei density. In addition, as it was discussed by Lockemann and Schlünder [8], the correlation length, ξ, is a measure of the interfacial mixing zone near the *mcp* where the fluctuations lead to a significant resistance to the mass-transfer. As a result, transport of solute molecules to nuclei is reduced leading to production of non-agglomerated and small particles under these critical conditions.

4. CONCLUSIONS

SAXS technique can provide a valuable insight into the phase behaviour, turbulent mixing and crystallization in supercritical solutions using such measurable thermodynamic quantities as density fluctuation and correlation length.

5. REFERENCES

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