ON-LINE MEASURING REFRACTIVE INDEX OF SUPERCRITICAL MEDIUM

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A reliable and fast absolute refractive index sensor has been developed for in situ SCF process monitoring. This sensor works on the principle of the attenuated total reflection of the right angle prism placed in the SCF medium, the amount of laser beam reflected by prism is measured by a photodiode, which produces an integrated signal proportional to absolute refractive index of the SCF medium, which is capable of in situ measurements with accuracy higher than 10^{-2}. Refractive index of CO_2 - ethanol mixtures were measured at pressures between 70 and 200 bar and temperatures between 308 and 363K. These data were obtained for continuous flow of premixed solvents and, in addition, for equilibrium gas phase below the mixture critical pressure. It is shown that the refractive index of mixture is a linear function of ethanol mol fraction and can adequately describe mixing and phase behaviour in the vessel. For pure CO_2, refractive index was determined to be in a good agreement with the published data.

1. INTRODUCTION

Solvent refractive index, *n¢*, is very important for characterization and monitoring of SCF processes because it is related to such fundamental thermodynamic properties as solvent density, phase composition, solute concentration and interfacial tension [1]. This parameter can be directly and accurately measured using *in situ* optical techniques. In addition, detection of n_s is an attractive option for HPLC separation due to the universal nature of such detection [2]. However, for high-pressure compressible solvents such as CO_2, there are significant experimental problems associated with the intricate cell design, reproducibility and complexity of such measurements. For example, pass-length interferometers [3-8] are capable of measuring the absolute refractive index with precision *ca.* 10^{-5}. Although this technique is highly accurate, it is complex to operate and also unsuitable for dynamic processes such as mixing or separation in which n_s can fluctuate. Minimum-angle-of-deviation method [9,10] makes use of an auto collimating refractometer with overall possible error *ca.* 10^{-4}. This method requires relatively long measurement time (minutes per data point) and very elaborate optical cell design with an internal mirror. A beam displacement technique [11] gives an advantage of simple experimental design, which may, however, lacks accuracy, as a typical error is about 10^{-2}. To date, the refractive index of pure CO_2 has been measured using these techniques at temperatures between 298 - 373K and at pressures up to 2400 bar [7]; between temperatures 323 – 373K and pressures up to 230 bar [8] and between temperatures 310–394K and pressures up to 102 bar [10]. In addition, *n¢* of CO_2-n-butane system was measured at 310K and pressures up to 80 bar [9]. There is very little data available on the *n¢* of organic solvent–CO_2 mixtures. This is a considerable knowledge gap because CO_2 is miscible (or partly miscible below the critical mixture point) with most organic solvents, forming homogeneous 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. In particular for precipitation processes, solvent to CO_2 mol fraction and its fluctuation about average value, is one of the most important parameters that define supersaturation during mixing [12-14]. Refractive index can provide dynamic data and control parameters for such processes.

The main aim of this work is to develop an on-line measuring absolute refractive index sensor for in situ SCF process monitoring, which has proved to be a fast and reliable technique.

2. MATERIALS AND METHODS

The SCF system is shown in Fig. 1. The high-pressure stainless steel optical cell (about 30 cm^3 volume) was manufactured by Thar Designs Co. (Pittsburgh, US). It had two parallel silica windows. The cell aluminum jacket included four electrical cartridges and platinum resister thermometer connected to a digital controller (2132 PID, RS, UK). This allowed the cell temperature to be measured and controlled within ±0.1K. Pressure in the optical cell was controlled by computerized backpressure regulator (26-1761 with ER3000 controller, Tescom, US) and maintained within ±0.2 bar. The pressure transducer was calibrated against a certified pressure transducer within ±0.25%. Ethanol flow rate was provided by a metering pump (Jasco PU-986, Japan) and varied between 0.1 and 10 cm^3/min. The CO_2 flow, supplied from a surge tank by a water-cooled pump (Milton Roy B, UK), was typically kept constant at 18 ml/min (assuming 1 g/cm^3 liquid CO_2 density) using a metering valve. This flow corresponded to expanded gas flow about 9.5 Nl/min, which was monitored using a gas flow meter (SHO-Meter, Brooks Instruments B.V., Holland). Both the ethanol and CO_2 flows were preheated before entering the optical cell. Food grade CO_2 (Air Products, UK) was selected as a standard reference for calibration of RI sensor.

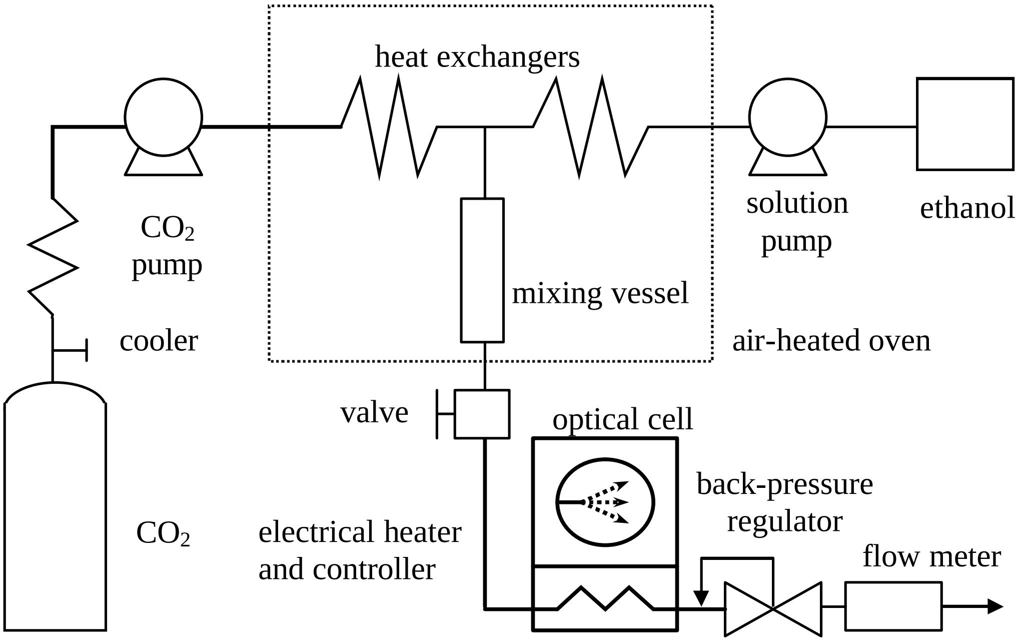

Figure 1 The Supercritical fluid system

The absolute refractive index sensor to measurement of the SCF RI is based on the attenuated total reflection (ATR). A schematic diagram of the sensor is shown in Fig. 2.

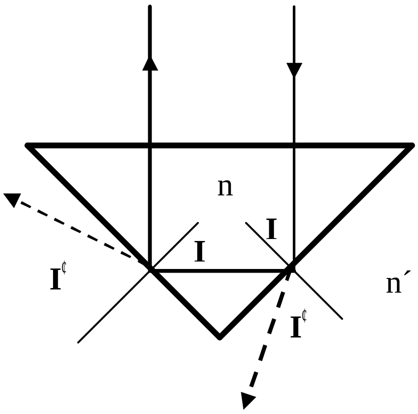

Figure 2 The attenuated total reflection using a right angle prism

The beam from a polarized, 5 mW, 632.8 nm He-Ne laser (Coherent Co, UK) will be reflected back by a right-angle prism placed in the SCF medium. The light is collected on a photodiode (PDA155, Thorlabs Inc, US), which produces an integrated signal proportional to the amount of light reflected by prism. In this geometry reflected light decreases when the RI of the medium increases. The Fresnel's equations give the components of the reflected and reflected disturbances

$$A_{2l} = A_{1l}\frac{\tan(I - I')}{\tan(I + I')} \qquad (1)$$

$$A_{2r} = A_{1r}\frac{\sin(I - I')}{\sin(I + I')} \qquad (2)$$

Where A_{2l}, A_{2r}, A_{1l}, A_{1r} are the amplitude components of reflection and incidence parallel to and perpendicular to the plane of incidence. I and I denote the angles of incidence and refraction¢, respectively. Using Snell's law,

$$n \sin I = n' \sin I' \qquad (3)$$

For a right angle prism, $I = 45^{\circ}$ and n is known, the refraction angle I' only depends on n', the refractive index of the SCF medium. Therefore, the reflected intensity collected by the PDA155 photodiode could measure the refractive index of the SCF medium.

3. RESULTS AND DISCUSSIONS

3.1 Extension of measuring range

The RI of SCF medium, n´, could be measured in a limited range, both the minimum $n'_{\min}$ and the maximum $n'_{\max}$ depend on the refractive index of the prism, n, for right angle prism,

$$n'_{\min} = 0.707\, n \qquad (4)$$

$$n'_{max} \approx 1.2\, n'_{min} \qquad (5)$$

Different measuring ranges of n´ can be reached by using right angle prisms with different materials, shown as the following

Table 1 Measuring ranges with right angle prisms made by different materials

Materials	n (20°c, 632.8nm)	n'_{min}	n'_{max}	Suitability
Fused silica	1.457	1.0303	1.2363	SCF
Bk7 glass	1.515	1.0713	1.2856	SCF
Sapphire	1.766	1.2488	1.4985	PEG+ CO_2
Heavy flint	1.89	1.3364	1.6037	
Diamond	2.42	1.7112	2.0535	

3.2 Modification temperature effect

The refractive index of the prism, n, is a function of temperature and laser wavelength, data modification is necessary for different temperatures although the temperature coefficient very small.

3.3 High reflection coating (HRC)

The prism with HRC enhances the signal, covering a wide range of RI (n´=1.04-1.20) with a better resolution and stability. Experimental data agrees with its calculated values.

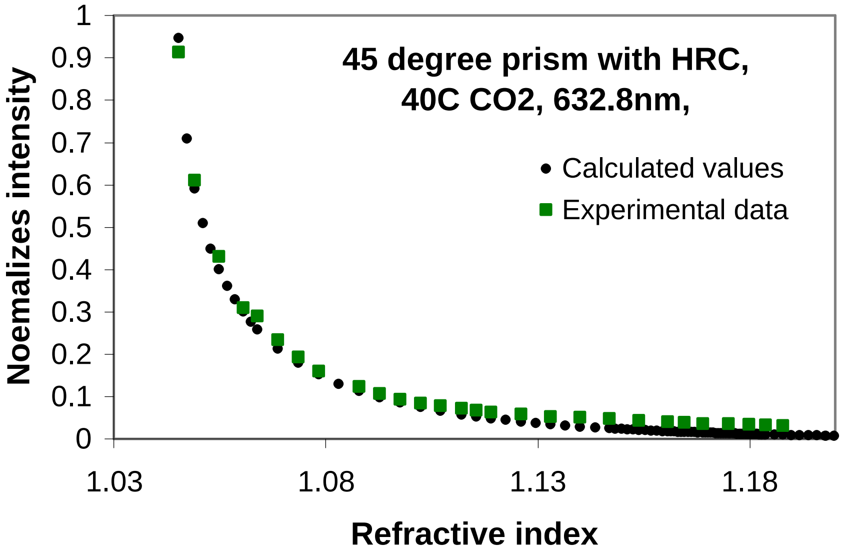

Figure 3 Result of high reflection coating sensor

3.4 Small angle incidence (SAI)

Calculation indicates that SAI far from critical incidence angle of total reflection can improve the linearity and stability of output signal and the minimum n'_{min} as desired one. Experiment with sapphire window verified SAI very simple and effective.

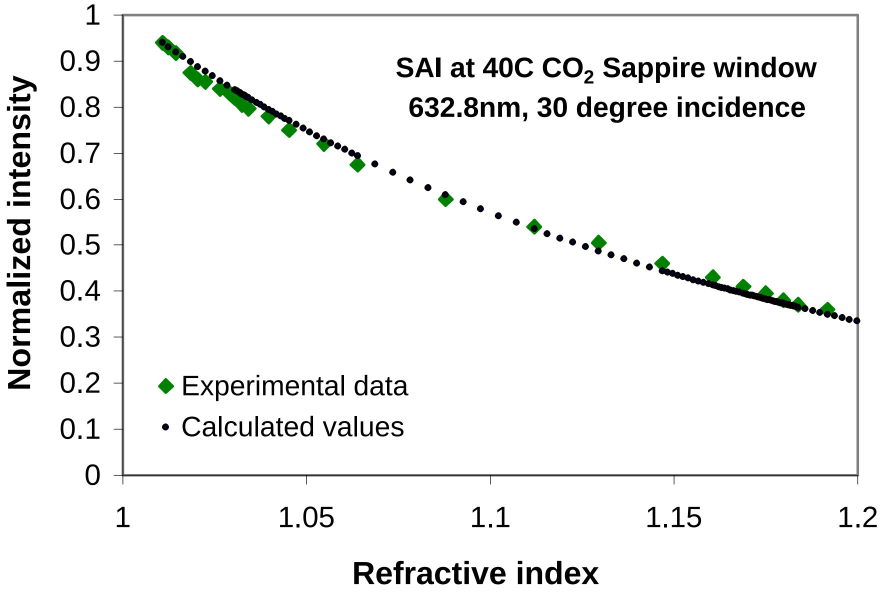

Figure 4 Result of small angle incidence sensor

3.5 RI of ethanol-CO_2 mixtures

The refractive indices of ethanol-CO_2 mixtures at selected pressures and temperatures are measured; the following linear relations can approximate the dependencies:

$$n' = 0.423x + 1.049 \quad (6)$$

$$n' = 0.651x + 1.039 \quad (7)$$

$$n' = 0.160x + 1.151 \quad (8)$$

Where (6), (7) and (8) correspond to 313K/75 bar, 363K/90 bar and 323K/200 bar, x is the molar refractivity of ethanol. In both cases of completely miscible and partly miscible solvents, empirical linear equations can be obtained for each pressure and temperature. This simple approach allows the ethanol mol fraction to be determined on the basis of refractive index measurements.

4. CONCLUSIONS

A new sensor for measurements of refractive index of SCF medium was developed which is based on principle of the attenuated total reflection of the right angle prism placed in the SCF medium. The sensor proved to be sufficiently fast and accurate to on-line measure SCF refractive index in dynamic flow configurations as well as in stationary phase. Refractive index of pure CO_2 and ethanol-CO_2 mixtures was determined at selected pressures and temperatures. For pure CO_2, the data obtained are in a good agreement with the published data and with the theoretical predictions. For CO_2-ethanol mixtures, empirical linear dependences of n´ on ethanol mol fraction are shown, the slope of these dependences being a function of pressure and temperature.

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