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# Spectroscopic Study of the Polystyrene//CO<sub>2</sub>/Ethanol System

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It is well-known that liquid ethanol at ambient conditions is a nonsolvent for polystyrene (PS). Surprisingly, the supercritical (SC) CO<sub>2</sub>/ethanol mixture is able to solvate PS, allowing the use of such media to perform fractionation of PS.<sup>1</sup> The first part of this work is devoted to the determination of the solubility of PS in the SC CO<sub>2</sub>/ethanol solution and to assess the selectivity of the mixture using UV spectroscopy. The second part concerns an infrared absorption and Raman scattering study aimed at the understanding of the microscopic interactions involved in this system. We have performed measurements on CO<sub>2</sub>/ethanol mixtures at various compositions (weight % of ethanol = 10, 30, and 42) in the temperature range 333–423 K and at pressures ranging from  $P = 15$  up to 35 MPa. Several species were found to coexist, namely, ethanol aggregates and monomers. In addition, evidence of a weak interaction between CO<sub>2</sub> and ethanol was found. Finally, monomeric ethanol is likely to be responsible for the PS solvation in the SC CO<sub>2</sub>/ethanol mixture.

## Introduction

Several authors have studied the polymer fractionation with a supercritical (SC) fluid processing during this past decade.<sup>1,2</sup> The fractionation of polymer chains with narrow molar mass distribution or the extraction of residual monomers is performed by adjustment of the fluid density which permits the modulation of the solute solubility. So, uniform and clean materials can be easily and quickly obtained in comparison with ionic polymerization or others separation techniques such as dialysis.

Carbon dioxide is generally used for these studies, but the polymer solubility is poor. To increase the polymer solubility in the medium, a solvent can be added to carbon dioxide. In this context, an experimental study has been performed on the ability of a CO<sub>2</sub>/ethanol SC mixture to fractionate a hydrophobic (nonpolar) polymer such as polystyrene (PS:  $-\text{[CH}_2\text{CH(C}_6\text{H}_5\text{)]}_n-$ ).<sup>1,3</sup>

The aim of the present work is first to determine the solubility of PS in the SC CO<sub>2</sub>/ethanol solution and the selectivity of this mixture using UV spectroscopy.

The second part will be devoted to a vibrational spectroscopic study aimed at the understanding of the microscopic interactions involved in this system.

## Experimental Details

CO<sub>2</sub> is provided by Air Liquide. Ethanol is a Prolabo product (99.9% purity), and other organic solvents originate from Aldrich (purity > 99%). Critical temperatures and pressures of CO<sub>2</sub>/ethanol mixtures have been determined by Kiran and co-workers.<sup>4</sup>

The PS sample comes from Polymer Expert. It is characterized by a broad molar mass distribution:  $1000 < M_i < 30\,000$  g/mol,  $\bar{M}_n = 5000$  g/mol,  $\bar{M}_w = 8800$  g/mol, and  $I = 1.7$  (where  $M_i$  is the  $i$ -mer mass,  $\bar{M}_n$  is the number-average molar mass,  $\bar{M}_w$  is the weight-average molar mass, and  $I$  is the molar mass distribution).

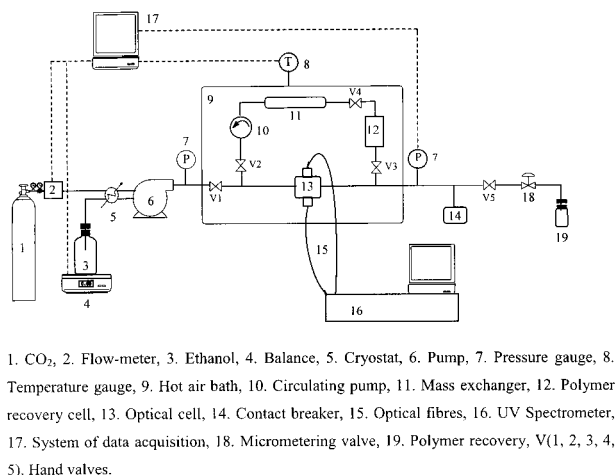
**1. UV Spectroscopy.**<sup>3,5</sup> The main component used to perform the on-line UV measurements experimental setup is a closed loop consisting of a circulating pump, a mass exchanger (which contains the polymer), a recovery cell, and a UV optical cell (path length = 10 mm) connected to a UV spectrometer (Cary 1C) by optical fibers (Figure 1). The optical cell is equipped with silica windows and with a focusing optical setup. A PS amount ( $m^p$ ) is put in the mass exchanger located in the hot air bath. The system is heated at the working temperature and filled with the solvent at the working pressure (the CO<sub>2</sub>/ethanol mixture with a given composition in weight percent) using the high-pressure pump. The loop is then isolated (by closing valve 1 and 5). Valve 2 is also closed to avoid the polymer dragging in the UV cell. Valve 2 is opened and the circulating pump activated. The mixture goes through the loop and dissolves a part of polymer. The concentration of the solution is measured in the optical cell by UV absorption. When the transmitted light shows no variation, the system is in equilibrium and the circulating pump is stopped ( $C_t$  determination). Valves 2 and 3 are closed and valves 1 and 5 opened. The CO<sub>2</sub>/ethanol binary mixture is pumped again until there is no polymer trace in the optical cell. Another reference spectrum of the fluid (without polymer) is performed to verify the optical setup stability. Then, valve 4 is closed and valve 2 opened. The system is depressurized except the recovery cell, which is isolated. The recovery cell contains the dissolved polymer, which is recovered and characterized by size-exclusion chromatography (SEC).

**2. Mid-Infrared Spectroscopy.**<sup>3,6</sup> The measurements were performed on a Biorad interferometer (type

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**Figure 1.** On-line UV measurements experimental setup.

FTS-60A) equipped with a globar source, a KBr beam splitter, and a DTGS detector. Single-beam spectra recorded in the spectral range 400–6000  $\text{cm}^{-1}$  with a 2  $\text{cm}^{-1}$  resolution were obtained by the Fourier transformation of 100 accumulated interferograms.

We have used a special inconel cell which has four cylindrical sapphire windows, two for the infrared absorption measurements with a path length of 12 mm (which can be varied from 3 to 25 mm) and the others for direct observation of the solution using a video camera to ensure that there is no demixing in the sample. The optical cell has been shown in detail in ref 3. To be sure that the solution is at the equilibrium, mixing is performed with a stirrer put in the cell and the acquisition of the spectra is performed 10 min. after a pressure change. The sealing is obtained using the unsupported area principle. All windows are positioned on the flat surface of the inconel plug with a 100  $\mu\text{m}$  gold foil placed between the window and the plug in order to compensate for imperfections at the two surfaces. Flat copper seals are used to ensure sealing between the plug and the cell body. The heating of the cell is performed by four cartridge heaters which are disposed in the body of the cell in which two thermocouples are placed: the first one is located close to one cartridge to achieve the temperature control, and the second is kept close to the sample area in order to ensure a good temperature regulation with an accuracy of about  $\Delta T \sim \pm 2^\circ\text{C}$ . The cell was connected via a long stainless steel capillary to a hydraulic pressurizing system which permits control of the pressure up to 1000 bar with an absolute uncertainty of  $\pm 1$  bar plus a relative error of  $\pm 0.3\%$ . The lower part of the cell was loaded with an excess of PS powder over that needed for saturation, and the cell was evacuated under vacuum. Then, it was filled with ethanol at the requested weight percent concentration. The cell was heated to 423 K, and  $\text{CO}_2$  was then added up to the desired pressure.

**3. Raman Spectroscopy.** The Raman spectra were collected on a DILOR Omars 89 double monochromator spectrograph equipped with a CCD (charged coupled device) detector. The source was a Spectra Physics argon ion laser operating at a wavelength of 514.5 nm with a power of 600 mW. The polarized  $I_{VV}(\bar{\nu})$  spectra were recorded in the spectral range 3400–3800  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  using the standard  $90^\circ$  scattering geometry. The Raman cell used here is the same as the infrared cell. However, in this case, the entrance and

exit windows are made of fused silica in order to perform proper spectroscopic polarization observation.

### Quantitative Study of the Fractionation of PS in a $\text{CO}_2$ /Ethanol Mixture

The quantification of the fractionation process is usually inferred from the partition coefficient determination.<sup>7</sup> So, we have used this method to determine the polymer solubility in SC solvent mixtures and value their selectivity. These data are obtained directly from the expression of the partition coefficient  $K_i$ , which is defined as the ratio of the  $i$ -mer mass concentration in the solvent-rich phase  $C_i^s$  (g of  $i$ -mer/g of solvent) to the  $i$ -mer mass concentration in the polymer-rich phase  $C_i^p$  (g of  $i$ -mer/g of solvent-free polymer).

$$K_i = C_i^s / C_i^p$$

The partition coefficient is classically log-linear dependent on the  $i$ -mer degree of polymerization,  $i$ , and so on for its molar mass  $M_i$ .

$$\log(K_i) = \log(C_i^s / C_i^p) = -\Gamma i + \beta$$

The separation factor  $\Gamma$ , which gives an estimation of the mixture selectivity, is a function of the pressure, temperature, and polymer concentration and  $\beta$  is a constant.

To calculate  $C_i^s$  and  $C_i^p$ , which are respectively given by<sup>5</sup>

$$C_i^s = P_i^s C_t^s \quad \text{and} \\ C_i^p = (P_i^p m^0 - P_i^s C_t^s m_{\text{solvent}}) / (m^0 - C_t^s m_{\text{solvent}})$$

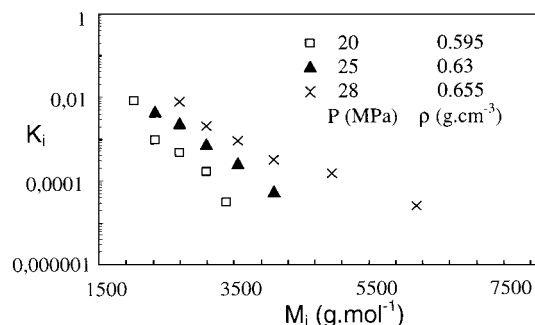
it is necessary to know several experimental parameters such as the  $i$ -mer mass fraction in the solvent-rich phase,  $P_i^s$ , the saturated mass concentration of the dissolved polymer in the solvent-rich phase (g of monomer/g of solvent),  $C_t^s$ , the solvent mass,  $m_{\text{solvent}}$ , the initial mass of polymer,  $m^0$ , and the initial mass fraction of the  $i$ -mer,  $P_i^p$ .

The experimental procedure which has been developed to determine polymer partition coefficients in SC media is based on on-line UV measurements of polymer concentration in the solvent-rich phase and on the knowledge of the molar mass distribution of the dissolved polymer. The UV spectroscopy has been chosen to determine  $C_t^s$ , the saturated concentration of polymer in the solvent-rich phase. Solvent mixtures do not absorb in the studied UV domain. So, it is easy to estimate the polymer concentration in the  $\text{CO}_2$ /ethanol medium using the Beer–Lambert law. For a given wavelength, we have

$$\log(I_0/I) = A = \epsilon l C$$

where  $I_0$  is the transmitted intensity by the solution without polymer,  $I$  is the transmitted intensity by the polymer solution,  $A$  is the absorbance,  $\epsilon$  is the absorption coefficient ( $\text{L/mol}\cdot\text{cm}$ ),  $l$  is the optical length (cm), and  $C$  is the solute concentration ( $\text{mol/L}$ ).

This relation allows one to determine the polymer saturated concentration in the solvent-rich phase. Nevertheless, it is necessary to know the PS absorption coefficients and the evolution of these values with respect to the temperature and pressure. Therefore, we



**Figure 2.** Evolution of the partition coefficient  $K_i$  (see text) as a function of the molar mass  $M_i$  of the  $i$ -mer for the PS/CO<sub>2</sub>/ethanol system.

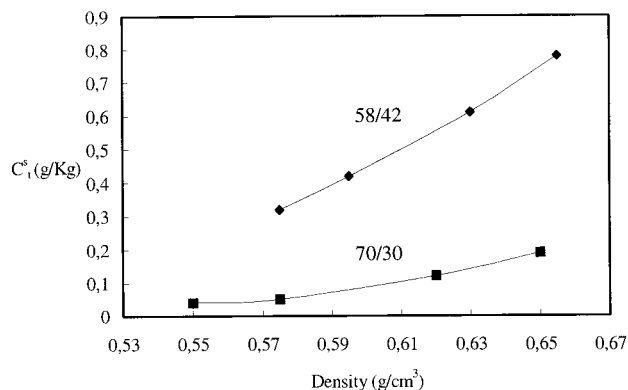
have performed a study to obtain calibration curves. Previous works have shown that the molar absorbance in UV-vis of the solutes dissolved in SC fluids depend on the density of the medium.<sup>8</sup> However, the density domain investigated here is low (in the range 0.55–0.65 g·cm<sup>-3</sup>) and, therefore, the pressure effect is negligible. Because it is impossible to validate the absorption coefficient value of PS in the CO<sub>2</sub>/ethanol mixture at ambient conditions, we have studied the effects of temperature on the PS/tetrahydrofuran (THF) system. Five calibrated solutions of PS in THF have been prepared. Experiments have been carried out at 298 K and 0.4 MPa and 423 K and 20 MPa (general conditions of our fractionation experiments). The absorption coefficients have been measured at 260, 265, and 270 nm. As expected, we observe a spectral broadening when the system is heated. Therefore, absorption coefficient  $\epsilon$  measured at ambient conditions is undervalued, so concentration correction and  $\epsilon$  calculation, at 423 K and 20 MPa, are necessary and are used to evaluate the PS concentration in CO<sub>2</sub>/ethanol mixtures, at 423 K and between 15 and 30 MPa.

We have studied the PS/CO<sub>2</sub>/ethanol system and the influence of pressure, temperature, and ethanol concentration on the fractionation process. We have performed solubility measurements and determined partition coefficients on 58/42 and 70/30 CO<sub>2</sub>/ethanol mixtures (in weight percent) at 423 K and in the pressure range 15–30 MPa. We have also investigated the CO<sub>2</sub>/ethanol (70/30) system, at 398 K in the same pressure range.

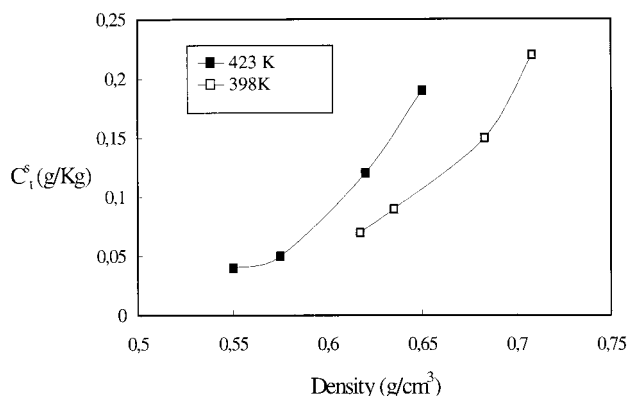
**Pressure Influence.** The values of  $K_i$  as a function of the molar mass  $M_i$  are reported on Figure 2 for the PS/CO<sub>2</sub>/ethanol system. The molar mass reported here corresponds to the higher molar masses dissolved in the solution at a given pressure and temperature.

We can see that the logarithm of  $K_i$  depends on the molar mass of the polymer dissolved in a linear fashion, when temperature and pressure are fixed. As usually observed, low molar masses are more dissolved than high molar masses. When the pressure increases, the density rises and leads to three effects: (i) for a given pseudocomponent, the partition coefficient increases; (ii) higher molar masses are dissolved and, finally, the curve slopes (absolute value) are lower; (iii) the mixture selectivity decreases. These results show the ability of these media to fractionate polymer compounds with respect to their molar masses with fluid density variations.

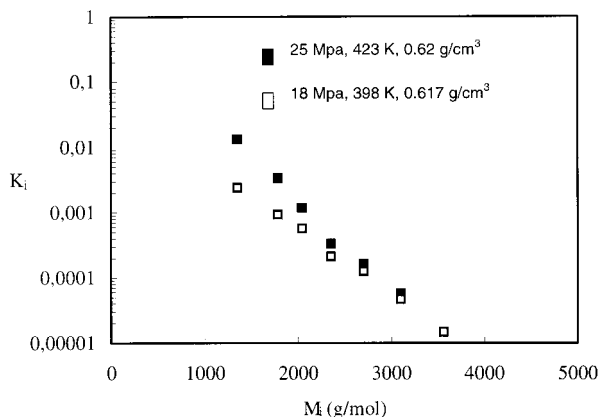
**Ethanol Amount Influence.** The evolution of the PS solubilities in the 58/42 and 70/30 CO<sub>2</sub>/ethanol mixtures is compared with respect to the density in



**Figure 3.** Solubility of PS in the 58/42 and 70/30 CO<sub>2</sub>/ethanol mixtures as a function of the density of the medium at  $T = 423$  K.



**Figure 4.** Solubility of PS in the 70/30 CO<sub>2</sub>/ethanol mixture as a function of the temperature and density of the medium.

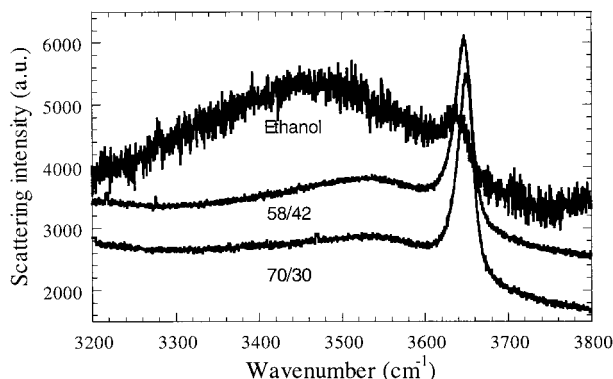


**Figure 5.** Partition coefficient  $K_i$  of PS in the 70/30 CO<sub>2</sub>/ethanol mixture as a function of the temperature and molar mass  $M_i$  of the  $i$ -mer.

Figure 3. Clearly, the 70/30 mixture is less efficient than the 58/42 one. Indeed, at constant density, the PS sample is less soluble and the dissolved molar masses are lower in the 70/30 mixture than in the 58/42 medium. Therefore, when we increase the ethanol proportion in the CO<sub>2</sub>/ethanol mixture, the PS solubility rises but the medium becomes less selective. So, a good balance between the solubility and selectivity can be achieved by varying the ethanol amount in the CO<sub>2</sub>/ethanol mixture.

**Temperature Influence.** The variation of the polymer concentration and partition coefficients at fixed temperatures (398 and 423 K) is reported as a function of density respectively in Figures 4 and 5. At a fixed temperature, the polymer solubility increases with





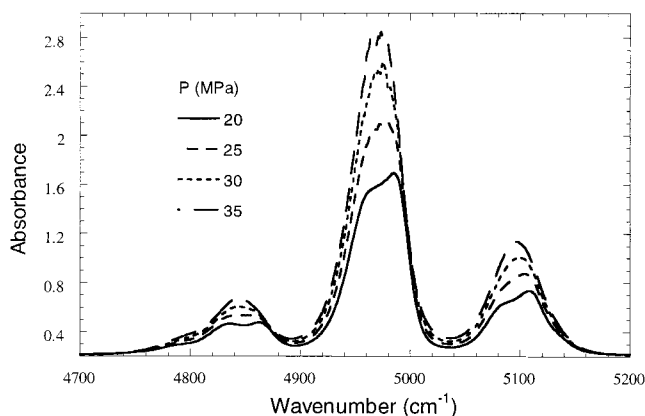
**Figure 6.** Comparison of the Raman spectra of ethanol in the 70/30 and 58/42 CO<sub>2</sub>/ethanol mixtures with pure ethanol at 423 K and 35 MPa. For clarity, the two upper curves have been shifted upward.

density, whereas at constant density, the solubility increases with temperature. We observe the same trend for partition coefficients. This increase is significant only when molar masses are less than 2000 g/mol. If we examine the curve slopes in Figure 5, we deduce that the mixture is more selective at 423 K. Indeed, we find respectively at 398 and 423 K slopes equal to  $-1.1 \times 10^{-3}$  and  $-1.4 \times 10^{-3}$  mol/g. So, we can conclude that temperature variation has no significant effect on the polymer fractionation efficiency, under our experimental conditions.

#### Infrared and Raman Scattering Study of PS in a CO<sub>2</sub>/Ethanol Mixture

The solubility of PS in a SC CO<sub>2</sub>/ethanol mixture is rather surprising because PS is soluble neither in CO<sub>2</sub> nor in ethanol at ambient  $T$  and  $P$ . Therefore, to understand the solvation process on a microscopic scale, we have investigated the PS/CO<sub>2</sub>/ethanol system using Raman and infrared spectroscopies.

**Investigation of the SC CO<sub>2</sub>/Ethanol Mixture. (a) Raman Scattering.** We have studied the SC CO<sub>2</sub>/ethanol mixture at various ethanol concentrations (0, 30, and 42 wt %) at 423 K in the pressure range 15–35 MPa. Raman scattering measurements were performed in the spectral range between 2700 and 3800 cm<sup>-1</sup>, associated with the OH stretch of the ethanol molecule. Figure 6 displays the Raman spectra of CO<sub>2</sub>/ethanol mixtures at 35 MPa and 423 K at various ethanol concentrations (0, 30, and 42 wt %). The spectrum associated with the OH stretching mode of pure ethanol at 423 K and 35 MPa is composed of a narrow band centered at about 3640 cm<sup>-1</sup> assigned to monomeric ethanol, together with a broad band centered at lower wavenumber (about 3450 cm<sup>-1</sup>) corresponding to the ethanol molecules which are aggregated by hydrogen bonding.<sup>9</sup> This spectrum is not affected by a pressure variation between 10 and 35 MPa. Upon addition of CO<sub>2</sub> in the mixture, there is a strong modification of the shape of the spectra, as can be seen in Figure 6 for both 70/30 and 58/42 mixtures. The intensity of the broad profile associated with alcohol oligomers decreases at the expense of the narrow band associated with monomeric ethanol. Therefore, we can infer that the state of aggregation of the alcohol molecules is a function of the mixture composition and that the equilibrium between monomers and oligomers is displaced toward the formation of monomers as the CO<sub>2</sub> concentration increases in the medium. Moreover, we observe also that the



**Figure 7.** Evolution of the combination bands of pure CO<sub>2</sub> at 423 K as a function of the pressure.

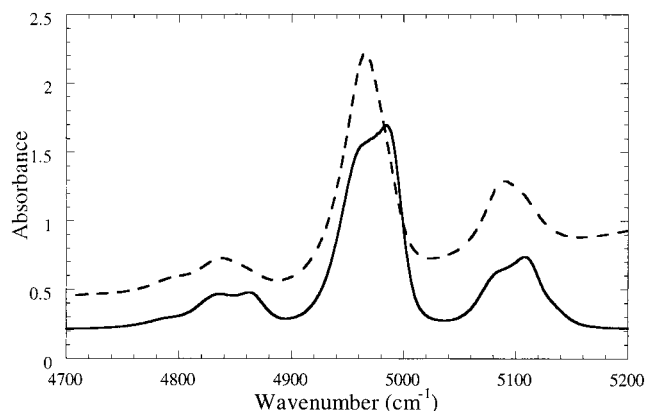
narrow band associated with the monomeric ethanol is red shifted at decreasing concentration of CO<sub>2</sub> in the mixture. Indeed, the peak maximum is respectively observed at 3637, 3647, and 3650 cm<sup>-1</sup> on going from the pure ethanol to the 58/42 and 70/30 CO<sub>2</sub>/ethanol mixtures. This band is the spectral signature of a solitary ethanol molecule surrounded by a cage composed of a mixture of CO<sub>2</sub> and ethanol molecules. Clearly, the red shift of the  $\nu_{OH}$  vibration of the central ethanol molecule shows that this vibrational mode probes mostly the attractive part of the intermolecular potential because of both the CO<sub>2</sub> and ethanol surrounding molecules. It is very likely that, in the electrostatic interaction, the dipolar field of the surrounding ethanol molecule (let us emphasize that there are no H bonds with the central molecule) leads to greater perturbation of the vibration than the quadrupolar field of the CO<sub>2</sub> molecule. For a given composition, the variation of pressure in the 20–35 MPa range has no noticeable effect on the absolute intensity of the band associated with the monomer and the aggregated species. This result is coherent with previously published studies as we look at small density variation.<sup>10,11</sup>

**(b) Infrared Absorption.** The strong absorption of the CO<sub>2</sub>/ethanol mixture precludes obtaining of information about internal modes of CO<sub>2</sub> and ethanol in the spectral range between 500 and 4000 cm<sup>-1</sup>. This drawback can be circumvented by looking at the combination modes of CO<sub>2</sub> and ethanol in the spectral range 4000–5000 cm<sup>-1</sup>, although the bands are weaker than the internal modes. To achieve this goal, we have used deuterated ethanol (CD<sub>3</sub>CD<sub>2</sub>OD), which will also allow one to observe in the PS/CO<sub>2</sub>/ethanol system the internal modes of the benzene ring of PS in the 3000–3100 cm<sup>-1</sup> spectral range. Moreover, we have also optimized the path length of the cell (12 mm) to detect with a good accuracy the combination modes of CO<sub>2</sub> in the range 4700–5200 cm<sup>-1</sup>.

**(i) CO<sub>2</sub>/Ethanol Mixture.** We have reported in Figure 7 the spectra of the three combination bands of pure CO<sub>2</sub> at 423 K and pressure ranging between 20 and 35 MPa. These bands observed at about 4840, 4960, and 5100 cm<sup>-1</sup> are respectively assigned to the combination  $4\nu_2 + \nu_3$ ,  $\nu_1 + 2\nu_2 + \nu_3$ , and  $2\nu_1 + \nu_3$ .<sup>12</sup> Clearly, it appears that the band shapes are modified and that their intensity increases when the pressure is raised. In contrast, there is no noticeable variation of the band center. The variation of the band shape can be qualitatively explained as follows. At low pressure, each band has the shape of the P-Q-R vibrational-rotational

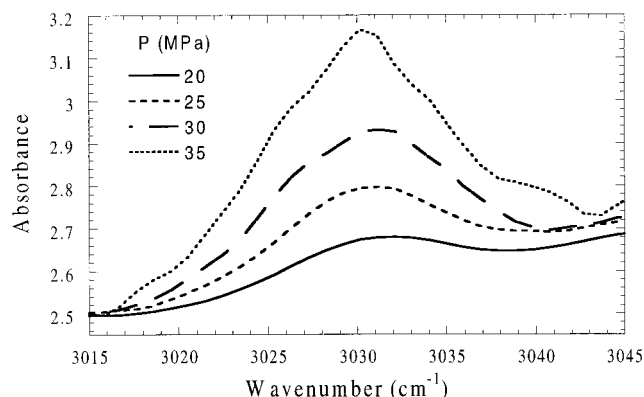
**Table 1. Concentration of PS in the 58/42 CO<sub>2</sub>/Ethanol Mixture at 423 K**

|   | <i>P</i> (MPa)       |                      |                               |                      |
|---|----------------------|----------------------|-------------------------------|----------------------|
|   | 20                   | 25                   | 30                            | 35                   |
| <i>C</i> <sub>t</sub> (g of monomer/g) IR | $3.5 \times 10^{-4}$ | $7.1 \times 10^{-4}$ | $1.1 \times 10^{-3}$          | $1.9 \times 10^{-3}$ |
| <i>C</i> <sub>t</sub> (g of monomer/g) UV | $4.2 \times 10^{-4}$ | $6.1 \times 10^{-4}$ | $8 \times 10^{-4}$ (28.8 MPa) |                      |

**Figure 8.** Comparison of the combination bands of CO<sub>2</sub> in the 58/42 CO<sub>2</sub>/ethanol mixture (—) with that of pure CO<sub>2</sub> (---) at 423 K and 20 MPa.

transition envelope characteristic of a parallel transition of a linear molecule.<sup>12</sup> As the pressure is increased, the doublet structure collapses, leading to a single profile centered at the mean frequency of the doublets. Indeed, with increasing pressure, molecular collisions are more frequent and therefore the rotation of CO<sub>2</sub> molecules is more perturbed.<sup>13</sup> The enhancement of the intensity is related to the increase of the medium density. Finally, to estimate the influence of ethanol on CO<sub>2</sub>, we have compared the spectrum of CO<sub>2</sub> to those of the 58/42 CO<sub>2</sub>/ethanol mixture under the same experimental conditions (Figure 8). Clearly, the three bands observed for the mixture are always shifted to lower frequencies compared to that of pure CO<sub>2</sub>. This shift varies approximately from 5 cm<sup>-1</sup> for the 70/30 CO<sub>2</sub>/ethanol mixture up to 9 cm<sup>-1</sup> for the 58/42 solution. Moreover, if we compare the shape of these two spectra, we remark that the doublet structure observed for pure CO<sub>2</sub> on the three bands vanishes when ethanol is added in solution. All of these observations allow one to infer that an interaction exists between ethanol and CO<sub>2</sub> and lead to a hindrance of the CO<sub>2</sub> molecule rotation. These results corroborate previous experimental investigations on CO<sub>2</sub>/methanol<sup>14–16</sup> and CO<sub>2</sub>/ethanol.<sup>17</sup> The nature of the interaction might be of the Lewis acid–base type in which the CO<sub>2</sub> carbon atom and the oxygen atom of the ethanol play respectively the role of the electron acceptor and donor. This conclusion is supported by *ab initio* theoretical work on the H<sub>2</sub>O/CO<sub>2</sub> system<sup>18,19</sup> and from experimental studies on polymer impregnation with CO<sub>2</sub>.<sup>20</sup>

**(ii) PS in a CO<sub>2</sub>/Deuterated Ethanol Mixture.** In view of the low solubility of the PS in the solution, the spectrum is very weak and obscured by the absorption of the CO<sub>2</sub>/ethanol mixture. The only accessible spectral range is limited to the CH stretching of the PS benzene ring<sup>21</sup> (3000–3100 cm<sup>-1</sup>) and only if deuterated ethanol is used. Knowing the solubility of PS in the mixture as measured by UV spectroscopy, we have optimized the path length of the cell (12 mm) to detect with a good accuracy the internal mode of the benzene ring of PS at about 3030 cm<sup>-1</sup>. We have recorded the spectra of PS in the spectral domain 3000 and 3100 cm<sup>-1</sup> at 423

**Figure 9.** Evolution of the infrared spectra of the CH stretch vibration mode of the benzene ring of PS in the 58/42 CO<sub>2</sub>/ethanol mixture as a function of the pressure at 423 K.

K for the 58/42 and 70/30 mixtures at various pressures ranging between 15 and 35 MPa (Figure 9). From this set of data, it was possible to calculate the PS concentration in the 58/42 CO<sub>2</sub>/ethanol mixture using the value of the molar extinction coefficient which has been previously evaluated from measurements of PS dissolved in liquid solvents.<sup>3,6</sup> The molar absorption coefficient of the band centered at 3030 cm<sup>-1</sup> is equal to 580 L·mol<sup>-1</sup>·cm<sup>-2</sup> and is found to be independent of the nature of the solvent within the experimental uncertainties. However, it is known that the molar absorbance in IR of the solutes dissolved in SC fluids depends on the density and the temperature. However, this effect is significant only upon strong variation of densities and upon the nature of the specific mode under investigation.<sup>10,22</sup> In our study, the density variations are low and in the range 0.55–0.65 g·cm<sup>-3</sup>. If we look carefully to the data on the molar absorbance reported in previous works as a function of the density range, we can see that under the current density variations the evolution of the molar absorbance is about 5%. Therefore, the effect of pressure variation in this study is negligible within the experimental uncertainties. In addition, the integrated area of the CH stretch of PS was almost independent of an increase of the temperature. The values of the PS concentration in the 58/42 CO<sub>2</sub>/ethanol mixture are reported in Table 1 and compared with those evaluated above using UV spectroscopy (see Figure 3). An overall good agreement is reached between the two data sets (within 15% of errors), which ensures the validity of the results and shows also that under the current experimental conditions solubility equilibrium was achieved.

## Conclusion

The main findings of this investigation of the PS/CO<sub>2</sub>/ethanol system are as follows. In the CO<sub>2</sub>/ethanol mixtures, there is equilibrium between the monomer and H-bonded ethanol molecule whose relative concentration depends only on the CO<sub>2</sub> concentration. Moreover, there is evidence for weak interaction between the CO<sub>2</sub> and ethanol molecules. These results cor-

robaborate previous experimental investigations on CO<sub>2</sub>/methanol<sup>14–16</sup> and CO<sub>2</sub>/ethanol.<sup>17</sup> The nature of the interaction might be of the Lewis acid–base type in which the CO<sub>2</sub> carbon atom and the oxygen atom of the ethanol play respectively the role of the electron acceptor and donor. This conclusion is supported by ab initio theoretical work on the H<sub>2</sub>O/CO<sub>2</sub> system<sup>18,19</sup> and from experimental studies on polymer impregnation with CO<sub>2</sub>.<sup>20</sup> Thus, the PS/CO<sub>2</sub>/ethanol system is made of several species, namely, PS chains, monomeric ethanol molecules interacting with CO<sub>2</sub>, aggregated ethanol molecules, and finally CO<sub>2</sub> molecules. The ethanol is in large excess compared to the polymer. Estimations indicate that there is respectively about 1000 and 4000 ethanol molecules per styrene unit in the SC 70/30 and 58/42 mixtures. Therefore, even if ethanol molecules are partly aggregated, there is still a large amount of ethanol monomers which are likely responsible of the PS solvation in the SC CO<sub>2</sub>/ethanol mixture.

### Acknowledgment

This work was performed under the auspices of the “programme pluri-formation no. 971022” entitled “Etude spectroscopique de fluides dans le domaine supercritique” from the University of Bordeaux I.

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Received for review February 3, 2000

Revised manuscript received June 14, 2000

Accepted June 15, 2000

IE000154N