

# INVESTIGATION OF SOLUTE BEHAVIOUR IN SUPERCRITICAL FLUIDS BY DIELECTRIC SPECTROSCOPY

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## INTRODUCTION

Industrial application of supercritical fluids as solvent media both for separations and reactions was rapidly growing in the past decades. In this context, supercritical carbon dioxide becomes the elective choice as it cumulates favourable physico-chemical and technical properties (mild critical conditions, wide availability at low cost, inertness, good safety profile). However, a proper design of any process in sc fluids requires a preliminary knowledge of the phase behaviour of the system. A reliable and easy access to such information is thus of primary importance.

We have employed the impedance spectroscopy technique to investigate the phase behaviour of compounds dissolved in scCO<sub>2</sub>. Measurements of dielectric constant of pure CO<sub>2</sub> have been already described in the literature about seventy years ago [1, 2], and have been extended more recently to selected binary systems [3-5]. Anyway, to our knowledge, only two papers [6, 7] describes a possible application of such technique to the measurement of solubility of solutes in scCO<sub>2</sub>. In this case the solubility of naphtalene has been calculated from the static dielectric constant measured at fixed value of frequency of the alternating electric field (1 kHz), thus losing information about the dynamic behaviour of the system with the potential risk of underestimating loss effects which could become significant in the case of polar solutes.

The novelty of the present communication lays in two aspects: i) the overall impedance spectrum of the sc fluid, recorded in a large frequency interval, is analysed; ii) the solute behaviour of sc phases containing both low molecular weight or macromolecular solutes was investigated.

## MATERIALS AND METHODS

CO<sub>2</sub> from Sol (purity: 99.998%) was used as a solvent sc fluid, naphtalene (99.9%) and polydimethylsiloxane monomethacrylate (PDMS-mMA) (M<sub>n</sub>=10000 g/mol, n=130, M<sub>w</sub>/M<sub>n</sub>=1.1) [8] both from Aldrich, and chloro-perfluoropolyether ammonium carboxylate (PFPE-A) Tradename: Fluorolink 7004A (water content lower than 1.0 % w/w), kindly supplied from Solvay Solexis were used as model solutes without further treatments.

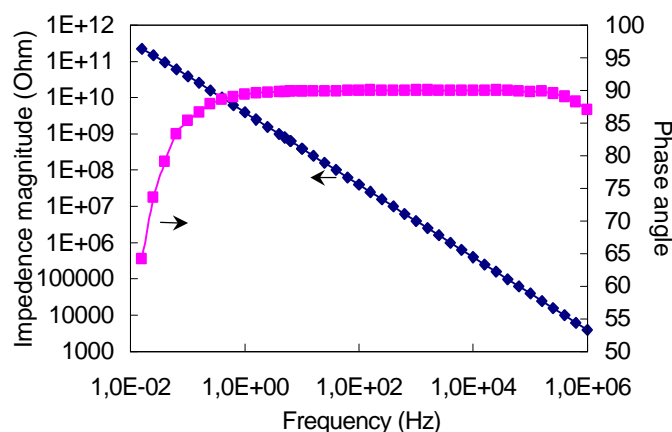
Impedance spectroscopy of the sc fluid solution was performed in the frequency range between 0.01 and 10<sup>6</sup> Hz using a Frequency Response Analyzer (FRA, Solartron mod. 1255) equipped with a 1296 Dielectric Interface, apt to measure very high impedances (up to 10<sup>14</sup> ohm). The measuring element consisted of a custom made parallel plate capacitor (gold plated stainless steel plates, diameter 5.2 cm) having a 0.7 mm thick spacer of MACOR<sup>®</sup> insulating

material sustained inside an AISI 316 high pressure vessel (free volume 205 cm<sup>3</sup>) by an insulating screw. The electrical connections to plates, a thermocouple probe and a tubing for the delivery of the supercritical solvent were inserted in the vessel through a Conax PL-18-A4-G pressure sealing assembly. Temperature control of the vessel was performed by a thermally insulated Haake thermostatic bath; pressure was measured by a Barksdale UPA 3 transducer. In order to avoid electrical noises, all measuring apparatus and the vessel were put in a Faraday cage.

After addition of selected amounts of the solute the vessel was closed and carefully washed with gaseous CO<sub>2</sub>, then the solvent was delivered as a liquid in such amount to reach the desired value of density. Depressurization of the measuring cell was carried out in supercritical conditions at 45°C, both the closure and the body of the vessel were cleaned in a good liquid solvent for the solute under test.

## EXPERIMENTAL RESULTS

The reliability of our experimental set-up has been checked by performing measurements with pure CO<sub>2</sub>, both in subcritical and supercritical conditions. Fig.1 shows the frequency dispersion (Bode diagram) of the total measured impedance for pure sc-CO<sub>2</sub> at T=40 °C and P=128 bar. The impedance spectrum displays a constant phase angle, very close to 90°, from about 5 to more than 10<sup>5</sup> Hz, thus indicating an ideal capacitive behaviour of the system. Experimental data were fitted adequately using the Z-Plot software<sup>®</sup> by employing a simple electrical equivalent circuit, consisting of a series resistance (ascribed to the contact contribution plus various cell components) and a parallel between a resistance (R<sub>p</sub>) and a capacitance (C<sub>p</sub>). Analogous Bode plots were recorded in the presence of the investigated solutes and also in blank "empty cell" experiments: after subtracting the contribution coming from the empty cell, from the fitting line we derived reliable values of the sc fluid capacitance and hence of its dielectric constant. The values computed for pure CO<sub>2</sub> at different



**Figure 1.** Bode plot (impedance magnitude and phase angle) for scCO<sub>2</sub> at 40°C and 128 bar.

**Table 1** - Dielectric constant values derived for pure carbon dioxide.

T (°C)	P,bar	$\epsilon$ (fit)	$\epsilon$ (lit)	$\Delta\epsilon/\epsilon$ (%)
23	62	1.446	1.450	0.3
20	11	1.010	1.018	0.8
40	128	1.428	1.437	0.6
40	142	1.446	1.462	1.1
50	108	1.274	1.280	0.5
50	142	1.386	1.403	1.2

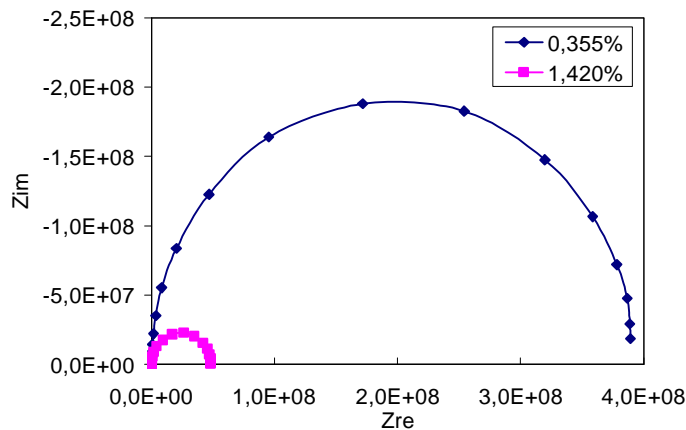
The value at 23°C refers to the liquid phase.  
The value at 20°C refers to the gas phase.

temperatures and pressures (Tab 1) are in excellent agreement with the reported in the literature [1].

Previous findings are based on the hypothesis of conductive medium; for dielectric materials the frequency dependence of the dielectric constant must be taken into account. In order to get an estimation of the static and dynamic components of the fluid permittivity, we have performed a check by interpolating data according to a model equivalent circuit which considers the frequency dependent complex dielectric constant of the dielectric medium [9],  $\epsilon^* = \epsilon' - j \epsilon''$ .

The results indicate that for pure CO<sub>2</sub>  $\epsilon'$  is always much higher (at least two orders of magnitude) than  $\epsilon''$ , thus confirming that values reported in Table 1 can be ascribed to the static dielectric constant of the fluid.

As for the fluid resistance, values of the order of  $10^{12}$  -  $10^{13} \Omega$  were obtained from from the fitting of experimental data pertaining to pure sc-CO<sub>2</sub>; however, we must say that



**Figure 2.** Nyquist plots for the PFPE-A/scCO<sub>2</sub> system at 65°C and 252 bar for different solute concentrations (% w/w).

seldom these values were fully reliable: in this case the extremely low conductance of the medium should have required an investigation at even lower frequencies.

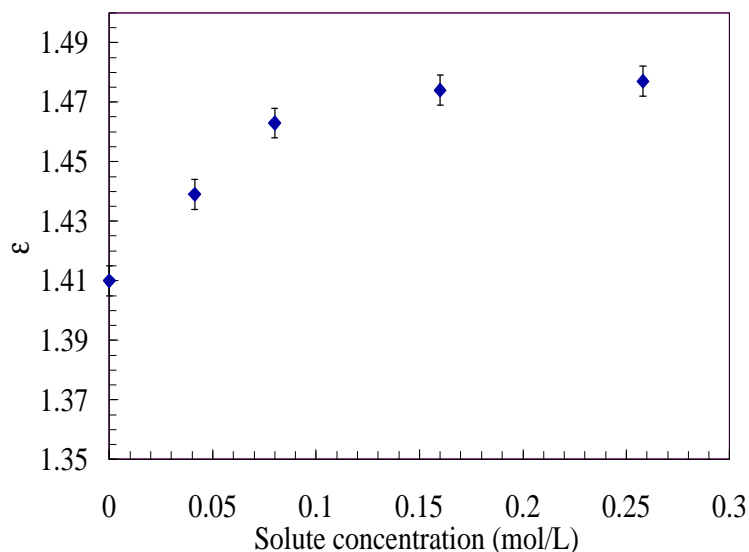
The situation changes totally when increasing amounts of a conducting salt are added to the sc phase: Fig.2 shows the Nyquist plots for two different concentrations of PFPE-A, consisting of two almost perfect semi-circles, according to the equivalent circuit previously employed. Similar measurements were performed by varying temperature and density of the sc phase. After correction for the empty cell impedance, the fitting of these impedance data has allowed to derive both the dielectric constant and the resistance of the sc fluid. The latter was greatly decreasing with increasing solute concentration, as evident in Fig.2, whilst the  $\epsilon$  values were increased with respect to pure CO<sub>2</sub> at corresponding densities.

Values of the dielectric constant derived for the PFPE-A/sc-CO<sub>2</sub> system at different temperatures and solute concentrations (weight %), for a fixed density of the sc phase, are reported in Table 2, where also the fluid resistance is displayed. An increase of temperature leads to a decrease of  $\epsilon$  and to an enhancement in the fluid resistance.

**Table 2** - Dielectric constant and fluid resistance measured for the PFPE-A/sc-CO<sub>2</sub> system.

T (°C)	r,g/mL	X <sub>w</sub>	e (fit)	R <sub>f</sub> (10 <sup>7</sup> W)
35	0.69	1.420	1.739	2.2
65	0.69	1.420	1.479	5.3
35	0.69	0.355	1.652	33.5
65	0.69	0.355	1.552	95.0

As for the dependence of the fluid dielectric constant upon solute concentration, different findings were observed, depending on the molecular structure of the solute. First we investigated the behaviour in the presence of a low molecular compound, like naphthalene, whose solubility in sc-CO<sub>2</sub> has been already studied by other researchers [6, 7]. Increasing amounts of the aromatic compound were added to the supercritical fluid at constant density (0.67 g/mL) and temperature (45 °C); as reported in Fig.3, the dielectric constant of the system, measured after attainment of equilibrium conditions, increases with increasing the solute concentration even if in limited extent, owing to the low polar nature of the solute (relative enhancement of  $\epsilon$  is 4% at saturation condition). A value of 1.477 has been computed at 0.258 M solute concentration in good agreement with the value of 1.463 obtained by Hourri et al. in the same experimental conditions. Analogous result was obtained at T=50°C, but with slightly larger increments of  $\epsilon$ , owing to the higher solubility of naphthalene at higher temperatures. This finding confirms the possibility of using dielectric spectroscopy for monitoring the solute behaviour in sc fluids.



**Fig. 3** - Dielectric constant of the naphthalene/sc-CO<sub>2</sub> system as a function of solute molar concentration at 45°C and 128 bar.

For PDMS-mMA/CO<sub>2</sub> binary system, the results of the dielectric spectroscopy were more complex and rather intriguing. Plotting the measured dielectric constant vs. the surfactant concentration a non monotonic trend has been obtained [10], thus suggesting that system polarizability undergoes a decrease by increasing polysiloxane concentration from 2.8 to 3.2 % w/w, similarly to what observed with amphiphiles soluble in aqueous systems. In the case of surface active agents soluble in aqueous system the onset of micellisation has been detected by plotting static dielectric constant of the medium as a function of amphiphile concentration and observing a singular point in the curve at the value of the critical micelle concentration (CMC) [11]. In the case of polydimethylsiloxane in sc-CO<sub>2</sub> such micellisation has been conjectured on the base of small angle neutron scattering spectra [12] at concentration values higher than 0.01 g/cm<sup>3</sup> at 65°C and 34 MPa, although in this case the interpretation of the results is complicated by the possible nucleation of a surfactant-rich phase [13]. However, partial confirmation of this possible explanation derives from our preliminary results on the PFPE-A/CO<sub>2</sub> system, for which also a non-monotonic dependence of the dielectric constant on the amount of solute added, at constant temperature and density, was observed. Previous considerations suggest that dielectric spectroscopy could be used also as a simple in-situ analytical tool for estimating the critical micelle concentration in sc fluids.

## CONCLUSIONS

The frequency dispersion of the impedance for a sc fluid phase revealed a simple behaviour, that could be interpolated by a R(CR) equivalent electrical circuit, both for pure CO<sub>2</sub> and solute/CO<sub>2</sub> systems. From the fitting of the experimental data, the sc phase resistance and capacitance were derived. The latter was related to the static dielectric constant of the sc fluid, which varies with temperature, density and concentration of solute. The

experimental findings reported here propose dielectric spectroscopy as a promising technique to investigate the phase and self-assembly behaviour of amphiphilic compounds dissolved in sc fluids.

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