Dielectrometry in Supercritical Fluids. A New Approach to the Measurement of Solubility and Study of Dipole Moment Behavior of Polar Compounds

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Radio frequency (rf) dielectrometry has been used to study the solubility and dipole moment behavior of polar compounds in supercritical fluid. The isothermic equilibrium solubility and dipole moments of acetonitrile, acetone, cyclopentadienyl manganese tricarbonyl (CpMn(CO)$_3$), and copper(II) hexafluoroacetyl-acetonate hydrate (Cu(hfac)$_2$·H$_2$O) in near- and supercritical CO$_2$ were measured at 313 K over the pressure range 5−15 MPa. It was found that dipole moment values for acetonitrile, acetone, and CpMn(CO)$_3$ in CO$_2$ are close to those in benzene and cyclohexane, in contrast to Cu(hfac)$_2$·H$_2$O, which has an enhanced dipole moment indicating strong interaction with carbon dioxide molecules.

Introduction

The study of equilibrium solubility of liquid and solid compounds in supercritical fluids (SCF) is of great importance both for fundamental science (to establish models and theories of solute−solvent interaction[1] and SCF phase equilibrium[2]) and for a wide variety of applications (SCF extraction,[3] impregnation,[4] chemical reactions,[5] thin films,[6,7] macroparticle formation,[8] etc.). Many experimental techniques (mainly IR, UV−vis, and NMR spectroscopy and supercritical fluid chromatography) have been developed[9,10] for measuring solubility, and a number of equilibrium solubility data for various compounds in SCF have been published[11] over the past decade. Nevertheless, dielectrometry appears to be a promising approach for polar compounds because it is reliable and, in contrast to spectroscopy and chromatography, is relatively inexpensive and easy to use. Dielectrometry has already proved to be a useful tool for determining the electronic structure of the molecules, their solvation, and intermolecular interactions in conventional organic solvents[12,13] and for measuring static dielectric constants of SCF solvent and cosolvent.[14−16] Moreover, dipole moments of the molecules are highly sensitive to complex formation.[17] Therefore, the study of dipole moment behavior of the molecules in SCF may provide information on their interaction with the SCF itself and/or with the cosolvent. In addition, dielectrometry can be used as an analytical tool to measure concentrations of polar solutes, and hence, this technique can be applied to determine the solubilities of various substances in SCF.[18] The technique has the additional advantage that it can be used in the case of turbid or opaque media where conventional optical spectroscopy is useless.

In this paper, we present the results of dielectrometric studies of the isothermic equilibrium solubility and dipole moment behavior of acetonitrile (MeCN), acetone, cyclopentadienyl manganese tricarbonyl (CpMn(CO)$_3$), and copper(II) hexafluoroacetylacetonate hydrate (Cu(hfac)$_2$·H$_2$O) in near- and supercritical CO$_2$ over the pressure range 5−15 MPa.
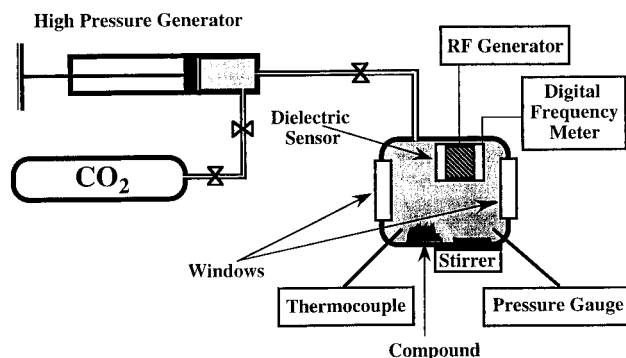

Figure 1. Schematic view of the apparatus for dielectric measurements in SCF.

Experimental Section

The experimental apparatus has been described elsewhere[18] and is illustrated schematically in Figure 1. It is based on a stainless steel high-pressure cell (HPC) with a total volume of 12.5 cm^3, a high-pressure generator, a gas-handling system, and pressure and temperature gauges. The cell has a built-in dielectric sensor, a pressure transducer with an accuracy ±0.015 MPa, a thermocouple, two silica windows (fitted in the threaded window holders) for optical monitoring of the solution sample, and inlet and outlet connectors. This cell can be used up to a pressure of 20 MPa. The high-pressure generator is a custom-built, manually operated piston screw pump with an active volume capacity per stroke of 200 cm^3 and a maximum pressure of about 50 MPa. The gas-handling system permits the use of different gases (for example, Xe, CO$_2$, or CF$_3$Cl) or mixtures of them as supercritical fluids. The cell and the piston pump are equipped with electronically controlled external heaters. The temperature inside the cell can be maintained with an accuracy of ±0.2 K.

The dielectric sensor (17 pF capacitor) is formed from two coaxial stainless steel cylinders 50 mm in length and mounted in a threaded insert with a high-pressure electrical feedthrough to the exterior of the cell. This capacitor is built into the oscillatory circuit of a frequency-stabilized generator operating at 1.0 MHz. Changes in the dielectric constant ($\Delta\epsilon$) of the fluid

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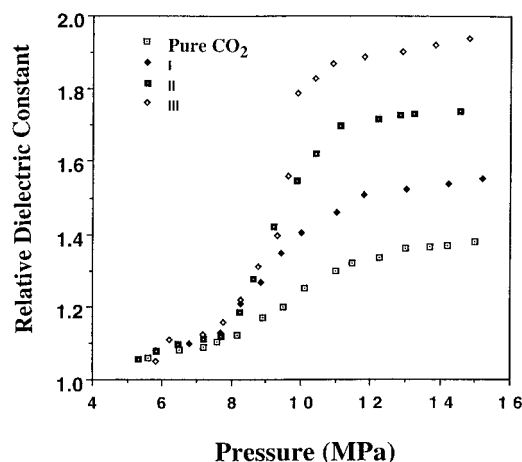⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

Figure 2. Pressure dependence of the dielectric constant of pure CO_2 and CO_2 in presence of 0.083 (I), 0.148 (II), and 0.261 g (III) of MeCN in the cell (volume = 12.5 cm³) at 313 K.

inside the cell cause a shift of generated frequency that is measured by a digital frequency meter. Any drift of the fundamental frequency of the generator was controlled using a timer-controlled short-circuiting of the sensor capacitor. In principle, this apparatus can achieve an accuracy of 0.0001 in the measurement of the dielectric constant. However, the actual precision in our experiments was about 0.005 (largely determined by temperature variations in the cell). The apparatus was calibrated using pure liquids (benzene, hexane, carbon tetrachloride) and pure gases (nitrogen and carbon dioxide) at pressures up to 15 MPa.

Acetonitrile was purified by distillation over P_2O_5 prior to use. HPLC grade acetone (99.5%) was used without further purification. Copper(II) hexafluoroacetylacetonate hydrate and cyclopentadienyl manganese tricarbonyl (Aldrich Chemical Co.) were used as recieved. CO_2 had a purity of 99.8% and was used without further purification.

The routine procedure of our experiment was the following. A weighed amount of the compound to be studied was loaded at the bottom of the HPC and then purged with CO_2 to remove any residual air. The cell was then sealed, its temperature raised to a predetermined value (313 K), and the internal volume was pressurized by CO_2 up to 5 MPa. After a few minutes of equilibration the measurement was started. To study the pressure dependence of the dielectric constant, the pressure (p) of the fluid was gradually rised by 0.5 MPa steps. After each step the magnitude of the dielectric constant was monitored continuously until a constant reading was attained. This procedure was repeated five times for each combination of materials (sample or calibration compounds), and the averaged results were plotted as curves of ϵ versus p.

Results and Discussion

Figure 2 shows the curves of ϵ versus p for the MeCN/CO_2 system obtained for various initial amounts of acetonitrile. At low pressure (<5 MPa), these curves virtually coincide with the curve for pure CO_2. Hence, the solubility of acetonitrile over this pressure range is negligible (as estimated below). Noticeable deviations are observed only at pressures above the critical value (p_{cr} = 7.28 MPa), when a steep rise of the solubility occurs. Above a particular pressure (depending on the initial weight of the sample g_S), the ϵ versus p curves are parallel to the curve for pure CO_2, thus indicating the complete dissolution of the substance. The complete dissolution is confirmed also by the linear dependence of $\Delta\epsilon$ versus g_S at the highest pressure (15 MPa), where $\Delta\epsilon$ is the difference between
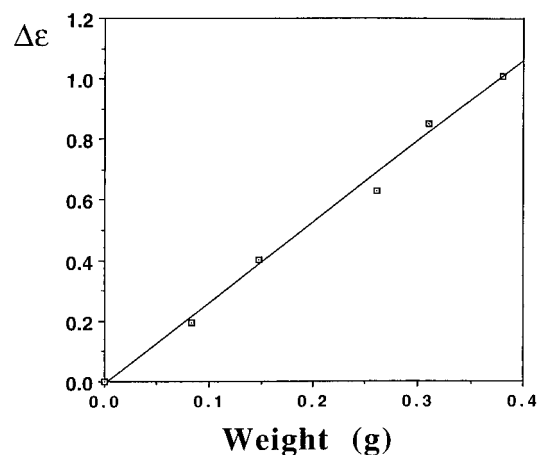

Figure 3. Dependence of the dielectric constant at 15 MPa for the MeCN/CO_2 system on the weight of acetonitrile in the cell at 313 K.

the dielectric constant of the MeCN/CO_2 system and ϵ of pure CO_2 at 15 MPa (Figure 3).

Dipole Moments of Solutes in SCF. To calculate the dipole moments of solutes, we assume that the Debye model for dielectric polarization[19] can be applied. In this case, if C_S and C_{SCF} are the concentrations of solute (S) and solvent (SCF) (in mol/cm³), the polarization of the unit volume of solution (expressed by Debye function $f_D = (\epsilon - 1)/(\epsilon + 2)$) is given as

$$f_D = P_S C_S + P_{SCF} C_{SCF} \tag{1}$$

where P_S and P_{SCF} are the molecular polarizations of the solute and SCF, respectively. For each batch of the solute, the difference $\Delta f_D = f_D - f_{D0}$ (here, f_D and f_{D0} correspond to the fluid with solute and pure SCF, respectively) at a particular pressure is given as

$$\Delta f_D = P_S C_S - P_{SCF}(C_{SCF0} - C_{SCF}) \tag{2}$$

The second term in eq 2 reflects the change in concentration of solvent caused by dissolution of the solute. Correct evaluation of this change is possible only if one knows the density of the solution. However, even without these data an estimation can be made. In our work, we have used the simplest model that assumed that a certain part of the volume initially occupied by the solvent is now occupied by the solute. That means

$$C_{SCF} = C_{SCF0} - C_S r \tag{3}$$

where r corresponds to the number of SCF molecules substituted by one molecule of S. We assume that r is equal to the ratio of molar volumes of S and SCF ($r = V_S/V_{SCF}$). Unfortunately, there is a problem estimating partial molar volumes of solid solutes. Therefore, we used the approximation $r = M_S/M_{SCF}$, where M_S and M_{SCF} are the molecular weights of the solute and SCF, respectively. Indeed, the ratios of molar volumes and molecular weights are quite close to each other. For example, V_{CO_2} = 59.0 L/mol at 313 K and 15 Mpa (from the data of ref 20). Using the values of molar volumes for MeCN and acetone (calculated from the densities of these liquids at room temperature) of 52.8 and 74.1 L/mol, one can see a good agreement of M_S/M_{SCF} (0.93 for MeCN and 1.32 for acetone) and V_S/V_{SCF} (0.89 for MeCN and 1.26 for acetone). Of course, in general, this approximation is crude. Nevertheless, as our calculations show, the second term in eq 2 is not large for rather polar solutes (μ > 3 D) of which the molecules are small. For example, for acetonitrile it is just about 4% of the first term. It means that the error we get with this approach is negligible.

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TABLE 1: Dielectric Parameters of Solutes in sc-CO$_2$ at 313 K and 15 MPa in Gas and Liquid Solvents

| solute | M_S/M_{SCF} | P_S, cm^3 | R_S, cm^3 | dipole moment, D | | |
				sc-CO$_2$	gas[21]	solvent[21]
MeCN	0.93	280 ± 20	11	3.7 ± 0.2	3.9–4.0	3.4–3.6
Me$_2$CO	1.32	170 ± 10	16	2.8 ± 0.2	2.8–2.9	2.7–2.9
CpMn(CO)$_3$	4.32	340 ± 50	48	3.9 ± 0.5		3.3
Cu(hfa)$_2$·H$_2$O	11.3	350 ± 30	57	3.9 ± 0.3		1.5,[a] 1.8[b]

[a] Dipole moment of anhydrous compound in benzene.[22] [b] Dipole moment of hydrate in benzene (this work).

Thus,

$$\Delta f_D = C_S(P_S + P_{SCF}(M_S/M_{SCF})) \qquad (4)$$

and we can determine the value of P_S for each solution in SCF from the expression

$$P_S = \Delta f_D/C_S - P_{SCF}(M_S/M_{SCF}) \qquad (5)$$

and calculate the dipole moment μ_S as

$$\mu_S = 0.01283 \sqrt{(P_S - R_S)T} \qquad (6)$$

where R_S is the molar refraction of the solute and T is the temperature.

Table 1 summarizes the data on the dielectric parameters of the solutes studied in this work. The values of P_S and μ_S were calculated from ϵ of supercritical carbon dioxide (sc-CO$_2$) solutions at 15 MPa and 313 K, when the complete dissolution of compounds occurred. The data were averaged over three runs with various weights of the samples in the cell for acetone, CpMn(CO)$_3$, and Cu(hfac)$_2$·H$_2$0 and over five runs for acetonitrile. The same table also presents the literature data for these compounds in the gas phase and in common solvents (benzene, etc.).

As one can see, the values of the dipole moment of acetonitrile and acetone in sc-CO$_2$ are close to the literature values in the gas phase, which are only slightly higher than those in the conventional solvents.[21] This fact indicates that under these conditions carbon dioxide behaves like an ordinary liquid and does not form strong charge-transfer complexes with these compounds. Within the error of our experiment the dipole moment of CpMn(CO)$_3$ in sc-CO$_2$ corresponds to that in benzene or cyclohexane solution.

The value of μ (3.9 D) for Cu(hfac)$_2$·H$_2$O in sc-CO$_2$ differs significantly from that of the anhydrous compound in benzene.[22] To find out whether this discrepancy is caused by the presence of water in the hydrate, we determined μ of the hydrated compound in benzene at 298 K using eqs 5 and 6, i.e., the same approximation. The dipole moment of Cu(hfac)$_2$·H$_2$O ($\mu = 1.8$ D) proved to be close to that of the anhydrous compound (1.5 D). Therefore, the high polarity of the copper chelate hydrate is most probably caused by interaction with CO$_2$ molecules. One explanation is that a charge-transfer complex is formed, but clearly, this should be studied in more detail.

Evaluation of Solubilities by Dielectrometry. Dielectrometry can be successfully used to evaluate the equilibrium solubilities of polar substances in SCF from ϵ versus p curves within the range of incomplete dissolution of the samples in the cell (coexistence of two phases). In this case, the equilibrium concentration of solute $C_S(p)$ in the fluid phase is expressed by

$$C_S(p) = \Delta f_D(p)/\alpha_f = \Delta \epsilon(p)/\alpha_\epsilon \qquad (7)$$

where α_f and α_ϵ are molar increments of the functions f_D and

TABLE 2: Solubilities of Substances in sc-CO$_2$ at 313 K

| p, MPa | C, mol/L | | | |
	MeCN	Me$_2$CO	CpMn(CO)$_3$	Cu(hfac)$_2$·H$_2$O
5.0	<0.01	<0.01		
6.0		0.04 ± 0.02		
7.0	0.03 ± 0.01	0.08 ± 0.02	<0.01	<0.01
8.0	0.06 ± 0.01	0.15 ± 0.04		
9.0	0.17 ± 0.02		0.05 ± 0.02	0.03 ± 0.01
10.0	0.49 ± 0.04	>0.64	0.11 ± 0.02	0.11 ± 0.01
11.0	>0.73		0.19 ± 0.02	>0.13
12.0			>0.21	

ϵ, respectively, and are equal to the tangents of dependencies Δf_D versus C_S and $\Delta \epsilon$ versus C_S at complete dissolution of the solute.

To be sure that some part of the sample is indeed not dissolved, one does not need to observe it visually. For a given weight of the sample g_S, the condition for incomplete dissolution in volume V_c is given by

$$\Delta f_D(p)/\alpha_f = \Delta \epsilon(p)/\alpha_\epsilon < g_S/(M_S V_S) \qquad (8)$$

Table 2 summarizes our data for the solubilities of the studied compounds in sc-CO$_2$ at 313 K and over the pressure range 5–12 MPa. The values are obtained by interpolation of the experimental ϵ versus p curves up to particular pressures. The error corresponds to the scattering of points on these curves.

Our data indicate that all the substances are quite soluble in nonpolar sc-CO$_2$, although their dipole moments are comparatively large. Evidently, their high solubility is a reflection of the strong dipole–quadrupole interaction with asymmetric charges in the CO$_2$ molecule. This fact is confirmed, for example, by the data of Cornish et al.[23] who established that acetonitrile is much more soluble in tetrachloroethylene than in n-hexane (critical temperatures for these solutions were 286 and 354 K, respectively).

Cu(hfac)$_2$·H$_2$O is a special case. M'Hamdi et al.[24] pointed out that this chelate has high solubility (mole fraction > 0.1 at 443 K and 12 MPa) and increased thermal stability in sc-CO$_2$. Our experimental data are in a good agreement with this conclusion. The high dipole moment of Cu(hfac)$_2$·H$_2$O in the supercritical solvent indicates that its interaction with carbon dioxide is strong. The origin of such an interaction is not clear yet, but we can conclude that it involves either the formation of charge-transfer complexes between chelate and CO$_2$ molecules or a significant distortion of the chelate molecular structure.

Conclusions

We have demonstrated that dielectrometry is a useful tool for studying the solubilities of polar compounds in SCF. The dipole moments and isothermic equilibrium solubility of acetonitrile, acetone, cyclopentadienyl manganese tricarbonyl (CpMn(CO)$_3$), and copper(II) hexafluoroacetylacetonate (hydrate) in near- and supercritical CO$_2$ have been measured over the 5–15 MPa pressure range. The dielectrometry was applied to probe the SCF solution with a high concentration of polar

compounds and can be successfully used for this purpose even in the case of turbid and opaque media where the spectral measurements are somewhat complicated because of the effect of an optically thick layer or strong light scattering. The apparatus for dielectric measurements is easily compatible with spectroscopic and chromatographic equipment and rather inexpensive and simpler to use. In addition, dielectrometry provides important information on the electronic state of solutes in solutions and can be effectively used to study intermolecular interactions in "solute−SCF cosolvent" systems.

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