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Coaxial probe and apparatus for measuring the dielectric spectra of high pressure liquids and supercritical fluid mixtures

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A probe and apparatus were developed for measuring the dielectric spectra (complex permittivity) of high pressure liquids and supercritical fluid mixtures. The probe consisted a 2.2 mm semirigid coaxial cable that was cut off flat and mounted into a high pressure tube. The apparatus for measuring complex permittivity consisted of the dielectric probe, cell, densimeter, piston for varying the system density at constant composition, and magnetic pump for agitation and recirculation, all of which were housed in a constant temperature air bath. The probe is simple, robust, inexpensive, and further, its design allows for quick connection to high pressure systems. Probe accuracy is estimated to be ± 0.5 in ϵ' and ± 0.5 in ϵ'' from 200 MHz to 18 GHz based on replicate measurements of calibration and 2σ deviations over the interval. Dielectric spectra were measured over the 200 MHz–20 GHz range for methanol+carbon dioxide mixture at 323.2 K and a pressures up to 18 MPa. © 2000 American Institute of Physics. [S0034-6748(00)02112-2]

I. INTRODUCTION

The relative permittivity, $\epsilon'(0)$ is important for understanding molecular orientation and reactivity in supercritical fluid mixtures.¹ A number of researchers have made dielectric measurements on supercritical fluids and their mixtures^{2–10} with the goal to relate their data to parameters that describe solution structure or solution behavior. However, data for supercritical fluid mixtures are scarce, most likely due to the lack of suitable cells or probes.

The frequency dependence of the relative permittivity is referred to here as dielectric spectra or complex permittivity $\epsilon^*(\omega)$. Measurement of $\epsilon^*(\omega)$ is expected to provide greater insight into the solution structure of supercritical fluid mixtures than the relative permittivity, since $\epsilon^*(\omega)$ provides an actual measure of the dynamics of polar aggregates in solution. The only measurements of $\epsilon^*(\omega)$ at supercritical regions in the literature are those of Okada *et al.*,^{11,12} who studied pure water¹¹ and deuterated water¹² with a highly specialized probe and cell arrangement. In their design, a sample is confined within the inner space of two quartz capillary tubes spaced 10 mm apart. The quartz tubes are surrounded by a tightly fitted platinum tube and a single fine platinum wire (<0.5 mm) runs through the center of the two capillary tubes. Each end is connected to a high pressure feedthrough and the entire assembly is placed in a large autoclave. Upon application of inert gas to a hydrostatic liquid leg in the assembly and local heating of the sample space, the complex permittivity could be measured in transmission mode up to 40 GHz.

The apparatus of Okada *et al.*¹¹ is applicable to study substances that can be loaded as liquids at room temperature and those authors have demonstrated the measurement of the

complex permittivity at supercritical conditions. Measurement of liquid mixtures, mixtures where one component is a gas at loading conditions, or gas mixtures with their apparatus would be difficult or impossible with their technique due to the requirements for loading the capillary tube and the method of applying hydrostatic pressure. Further, the coaxial capillary assembly is very delicate and since the sample must be confined within a void space, use of the probe as a sensor is not possible.

Considering these factors, our objective in this work was to develop a probe and apparatus that are simple and robust in design and that could be used for measuring the complex permittivity of high pressure liquids and fluid mixtures. Our design uses a reflectance technique and a standard 50 Ω 2.2 mm coaxial cable that was modified for use at high pressures. Probe performance is demonstrated by measurements of methanol in the presence of carbon dioxide solvent.

II. MATERIALS

Anhydrous methanol (99.8%) and water (HPLC grade) were obtained from Wako Pure Chemicals (Osaka) and were used without further purification. CO₂ (99.99%) was obtained Nihon Sanso (Sendai) and was dried by passing the gas through a column of silica gel and then filtered with a 0.5 μm sintered filter.

III. THEORY

The complex permittivity of a fluid can be described by the following equation:

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega), \quad (1)$$

where $\epsilon^*(\omega)$, $\epsilon'(\omega)$, and $\epsilon''(\omega)$ are the sample complex permittivity, relative permittivity, and loss factor, respectively, and ω is the angular frequency equal to $2\pi f$. The phenomenological theory and empirical description of Eq.

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(1) has been discussed in detail in Ref. 13. For measurement of $\epsilon^*(\omega)$, the method adopted in this work is based on a reflecting electromagnetic wave from the interface between a waveguide cutoff and sample.

A coaxial cable that is terminated in a cutoff provides a useful sensor for measuring the complex permittivity of fluids.^{14,15} In principle, a microwave source generates an electromagnetic wave, which is guided through a conduit and reflected at the coaxial cable termination and sample interface. Collection and analysis of the incident and reflected wave allows determination of the reflection coefficient Γ^* that is related to the normalized probe admittance Y^* as

$$\Gamma^* = (1 - Y^*) / (1 + Y^*). \quad (2)$$

A number of theories have been proposed for relating Γ^* (or Y^*) to the complex permittivity ϵ^* of a sample at the coaxial waveguide termination and these have been critically reviewed by Clarke and co-workers.¹⁶ Essentially, there is the forward problem of calculating Γ^* from ϵ^* and the reverse problem of determining ϵ^* from measured Γ^* . The numerical techniques necessary for these calculations have been compared by Jenkins *et al.*¹⁷

As summarized in Ref. 16, there have been two basic approaches to the modeling of Γ^* : (i) methods based on lumped circuit equivalents and (ii) methods based on rigorous solutions of the electromagnetic field equations. In this work, we adopted the method of Blackham¹⁸⁻²⁰ in which the coaxial probe is modeled as an aperture opening on an infinite ground plane according to relations proposed by Misra²¹ for the normalized admittance

$$Y^* = ik^2 / \pi k_c \ln(b/a) \cdot \int_a^b \int_a^b \int_0^\pi \cos \phi \frac{e^{-ikR}}{R} d\phi dr dr', \quad (3)$$

where

$$R = \sqrt{r^2 + r'^2 - 2rr' \cos \phi} \quad (4)$$

and

$$k = \omega \sqrt{\epsilon^* \epsilon_0 \mu_0}, \quad (5)$$

$$k_c = \omega \sqrt{\epsilon_c \epsilon_0 \mu_0}. \quad (6)$$

In Eqs. (3) and (4), a and b refer to the radii of the inner and outer conductor, respectively, and the integration is over the cutoff. In Eqs. (5) and (6), the ϵ_0 and μ_0 represent the vacuum permittivity and vacuum permeability, respectively. For a teflon cable, the relative permittivity ϵ_c of the cable dielectric is equal to 2.3. The exponential in Eq. (3) can be expanded in terms of a Taylor series and the resulting simplifying terms can be approximated with polynomial expressions.¹⁸ This allows computations to be fast for both the forward problem ($\epsilon^* \rightarrow \Gamma$) and especially for the reverse problem ($\Gamma^* \rightarrow \epsilon^*$), which tends to be more time consuming.

Although in principle, it is possible to apply theoretical corrections or to use more precise representations of the coaxial cutoff, in practice it is more reliable to use calibration standards with well-known complex permittivity behavior to

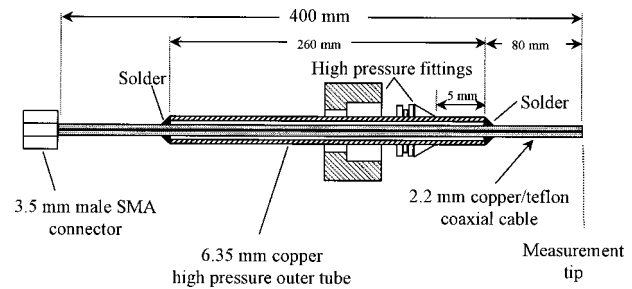


FIG. 1. High pressure coaxial probe design.

determine corrections for systematic errors.²² Systematic errors that occur in network analyzers are directivity e_d , frequency response e_r , and source match, e_s .¹⁸ These corrections are estimated by the following equation:

$$\Gamma_m^* = e_d + \frac{e_r \Gamma_a^*}{1 - e_s \Gamma_a^*}, \quad (7)$$

where Γ_a^* represents the actual reflection coefficient calculated by the coaxial model and the known complex permittivity of a fluid or electrical condition and Γ_m^* is the reflection coefficient measured by the network analyzer. Since Eq. (7) contains three unknowns at a given frequency, estimation of the systematic errors can be made by measuring three standards with known dielectric behavior. Standards that are commonly chosen are an electrical short, an electrical open, and a calibrated load (50 Ω).

IV. PROBE DESIGN

Figure 1 shows the high-pressure open-ended coaxial probe developed for measuring complex permittivity. A 2.2 mm copper/Teflon semirigid coaxial cable (model EZ 86/M17, SUHNER, Switzerland) was used that had a 50 Ω characteristic impedance and a usable bandwidth of 60 GHz. The cable was joined to a gold/CuBe male Subminiature A (SMA) type connector (model 11 SMA-50-2-15, SUHNER, Switzerland) that had a usable bandwidth of 33 GHz. The cable assembly was supplied as a 1 m length with male connectors that had been contact soldered at both ends. The cable was cut in half with an electric diamond saw, milled flat, and polished with a fine grade of sandpaper. A length of high pressure copper tubing (6.35 mm o.d., 2.75 mm i.d., 260 mm long) jacket was soldered onto the coaxial cable by gently filling the gaps between the cable and tubing with Pb-Sn solder. Hydrostatic pressure tests up to 22 MPa at 323.2 K confirmed the reliability of the construction method.

V. EXPERIMENTAL APPARATUS

The design of the experimental apparatus is shown in Fig. 2. The primary system components were the dielectric probe and cell, a densimeter, a magnetic pump, and a piston. As shown in Fig. 2, the components were arranged in a closed loop so that solutions could be agitated and pressurized. The dielectric probe, as described above, was inserted into a 30 cm³ cell that was constructed from stainless steel (SUS 316). A high pressure syringe pump (model DX-100, ISCO, Inc., Lincoln, NE), was used to load carbon dioxide into the system. The syringe pump was maintained at 278.2

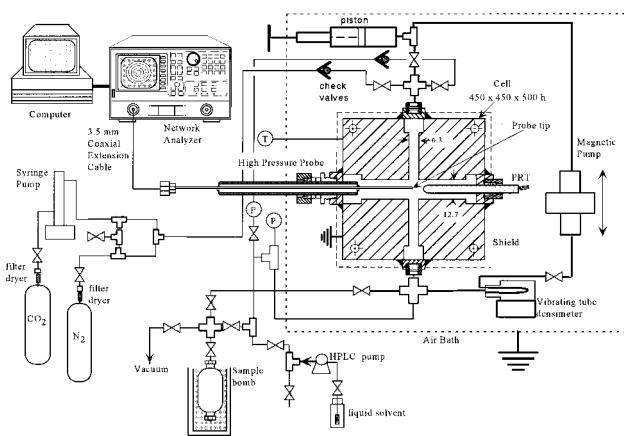


FIG. 2. Apparatus for measuring dielectric spectra and densities of liquids and supercritical fluid mixtures at elevated pressures.

K with a cooler (model EL-8, Taitec, Tokyo). A high pressure liquid chromatography (HPLC) pump (model 5GK90, GL Sciences, Tokyo) was used to load water and methanol. A magnetic pump was used to agitate solutions and to facilitate thermal and chemical equilibrium. A high pressure piston (model 65-6-10, H.I.P., Erie, PA) with 30 cm³ internal volume and Teflon packing was used to vary density at a given composition.

Temperatures on the inside and outside surfaces of the high pressure cell were measured with a three-wire platinum resistance thermometer (PRT) (model TF-A31, Keyence, Osaka) and a 4-wire PRT (model RMB-100SY02, Yamari, Osaka), respectively. Temperature control of the system was achieved to ± 0.1 K with a convection oven (model FV-450, Advantec, Tokyo). Pressure of the system was measured with a digital sensor (model SPX-G, Sokken, Tokyo) to an accuracy of 0.05 MPa. Time, temperature, and pressure were recorded by a scanner (model 34970A, Hewlett-Packard, Palo Alto) via RS-232 interface and computer (Aptiva, IBM Corp., Armonk) and software (Datalogger 1.0, Hewlett-Packard, Palo Alto).

Dielectric spectra were measured with a network analyzer (model HP 8720C). HP 85070B dielectric software (Hewlett-Packard Co., Palo Alto) was used for the data reduction. The network analyzer had a frequency range of 50 MHz–20 GHz and was controlled by computer on an IEEE-488 bus. A 1 m long semirigid 50 Ω characteristic impedance 3.5 mm extension cable (model 8120-6192, Hewlett-Packard, Palo Alto) was used to connect the probe to the network analyzer. Calibration of the dielectric probe was made according to procedures discussed below. After the calibration, CO₂ and methanol were introduced into the system by HPLC and syringe pump, and mixtures were agitated for 4–6 h by a magnetic pump until temperature, pressure, density, and the system stabilized.

Composition of the system was determined by weighing the loaded substances after the measurements were complete. Details of the procedure are as follows. First, a 125 cm³ stainless steel bomb was connected to the system and evacuated with a vacuum pump that was connected through a liquid nitrogen trap. Then, the valve between the sample bomb and trap/pump was closed and the valve leading to the sys-

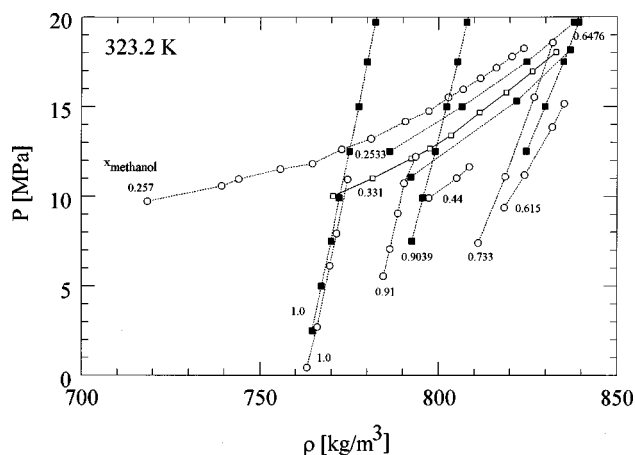


FIG. 3. Experimental densities determined for methanol at 323.2 K: (circles) this work; (filled squares) see Ref. 25.

tem was slowly opened. The sample bomb was held at liquid nitrogen temperatures for 3–4 h during which the pressure fell to subatmospheric pressure. Then, the sample bomb was changed to a glass trap that was cooled with liquid nitrogen and connected to a vacuum pump through a liquid nitrogen trap. The stainless steel bomb was slowly discharged into a beaker containing water to serve as a trap. Methanol mole fraction in the system was calculated from the material balance. The error in composition determination is estimated to be 0.005 in mole fraction.

Density was measured with a high pressure stainless steel oscillating tube densimeter connected to an electronic counter and digital readout instrument (model DMA 512P and DMA 60, Anton Paar, Graz, Austria). Density was recorded by a separate computer (model LC, Apple Computer Co., Cupertino, CA) via RS-232 interface and a custom BASIC language (QBASIC version 4.1, Microsoft Corp., Seattle, WA) program. The densimeter was calibrated using water and vacuum as reference fluids. For water, the equation of Pr \ddot{u} ss and Wagner²³ was used to provide properties up to 20 MPa. The calibration equation determined for use at 323.2 K was

$$\rho = A \cdot (\text{Per})^2 - B \cdot P - C, \quad (8)$$

where Per is the period of the fundamental frequency, P is the pressure in MPa, and A , B , and C , are constants determined by fitting to have values of $-657.052 \text{ kg s}^{-2} \text{ m}^{-3}$, $0.112 \text{ kg m}^{-3} \text{ MPa}^{-1}$, and $-9900.9 \text{ kg m}^{-3}$, respectively. Equation (8) was compared with the data of Goodwin²⁴ for methanol and it was found that the data were reliable to within 0.5 kg m^{-3} . Figure 3 shows density measurements for the methanol+carbon dioxide system at 323.2 K. The data compared well with the data of Galicia-Luna.²⁵ Good agreement can be seen for pure methanol and the same general trends can be seen for mixture densities.

VI. PROBE CALIBRATION

Measurement of the dielectric spectra was performed in the frequency domain. In the frequency domain method, calibration of the probe and cable system was carried out to determine error corrections as discussed in Sec. III. A com-

TABLE I. Cole–Cole parameters for calibration materials ($\alpha=0$) from Ref. 27: $\epsilon^*(\omega) = \epsilon'(\infty) + [\epsilon'(0) - \epsilon'(\infty)]/[1 + (i\omega\tau)^{1-\alpha}]$.

T/(K)	Fluids	$\epsilon'(0)$	$\epsilon'(\infty)$	τ/ps
293.2	air	1.0	1.0	0.0
	methanol	33.34	5.7	53.0
	water	80.4	5.2	9.44
323.2	air	1.0	1.0	0.0
	methanol	28.03	5.0	28.65
	water	70.7	5.8	4.83

mon method for calibration is through the physical termination of the probe with an electrical short, open, and load. Since this method is not feasible for systems at high pressure, we choose three calibration fluids as proposed by Kraszewski *et al.*²⁶ for systems at atmospheric pressure. The reference fluids chosen were air, methanol, and water, since their dielectric behavior is well-known over a wide range of frequencies and conditions and at the temperature of our measurements. Cole–Cole parameters were taken from Ref. 27 as given in Table I. For these reference fluids, the α parameter was zero, which reduced the Cole–Cole equation to the Debye equation for all cases.

VII. PROBE VERIFICATION

To verify probe performance at low pressure, we compared probe measurements to those of the equations in Table I. Figures 4 and 5 show the results for pure methanol, where deviations can be seen to be within ± 0.5 in both $\epsilon'(\omega)$ and $\epsilon''(\omega)$ except at frequencies lower than about 200 MHz and at the highest frequencies near 18 GHz. From these data, we concluded that the probe had sufficient stability and bandwidth in the 200 MHz–18 GHz region.

To verify the probe performance at high pressures, we made measurements of the dielectric constants obtained by making $\epsilon'(\omega)$ versus $\omega\epsilon''(\omega)$ plots and extrapolating the data to zero frequency. We compared the $\epsilon'(0)$ data to the literature values of Franck and Deul,²⁸ Roskar *et al.*,⁸ Drake and Smith,⁴ and Goldfarb *et al.*¹⁰ as shown in Fig. 6. The $\epsilon'(0)$ data were lower than the data of Roskar *et al.*,⁸ which may be explained to some extent by the differences in con-

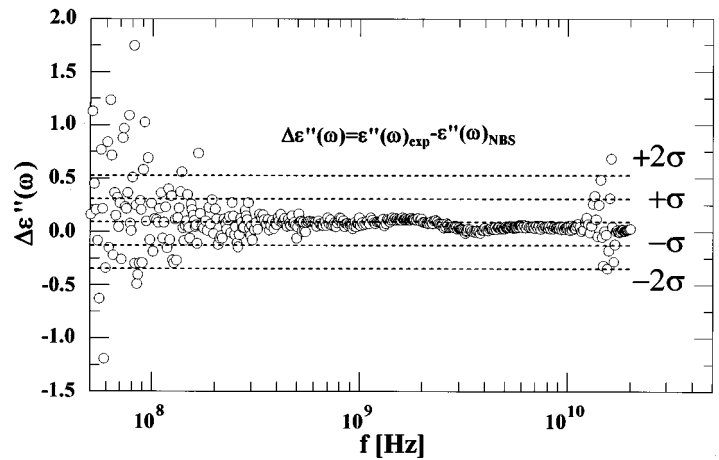


FIG. 5. Coaxial probe residuals for the imaginary portion of the relative permittivity vs frequency for methanol at 323.2 K and 0.1 MPa. See Table I for NBS equations.

ditions and to some extent by the extrapolations required in the data reduction. The trend of our data agreed well with measurements of Goldfarb *et al.*,¹⁰ Drake and Smith,⁴ and Deul and Franck.³ We concluded that the data were in sufficient agreement with the literature to verify our probe and apparatus.

VIII. MEASUREMENT OF COMPLEX PERMITTIVITY

With the probe and system, we made complex permittivity and density measurements of methanol in the presence of carbon dioxide at 323.2 K. Typical complex permittivity data obtained for the methanol+carbon dioxide system are shown in Fig. 7, where it can be seen that the addition of carbon dioxide to methanol had a significant effect on both the relative permittivity $\epsilon'(\omega)$ and the loss factor $\epsilon''(\omega)$.

The anomalous dispersion of the relative permittivity that occurs for polar fluids has been well documented.¹³ Debye attributed the dispersion to molecular reorientations that occur in the presence of an alternating electric field. The inverse of the relaxation time constant $1/\tau$ can be viewed as

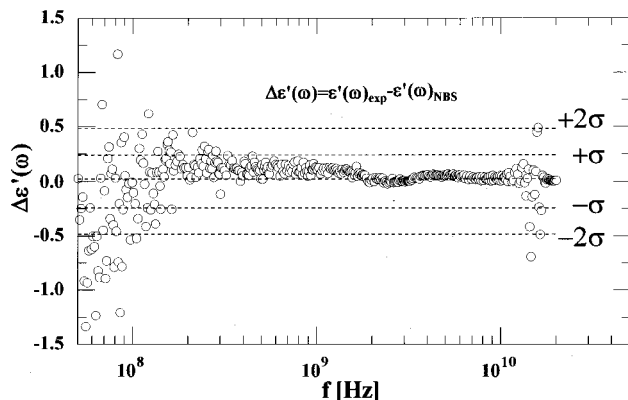


FIG. 4. Coaxial probe residuals for the real portion of the relative permittivity vs frequency for methanol at 323.2 K and 0.1 MPa. See Table I for NBS equations.

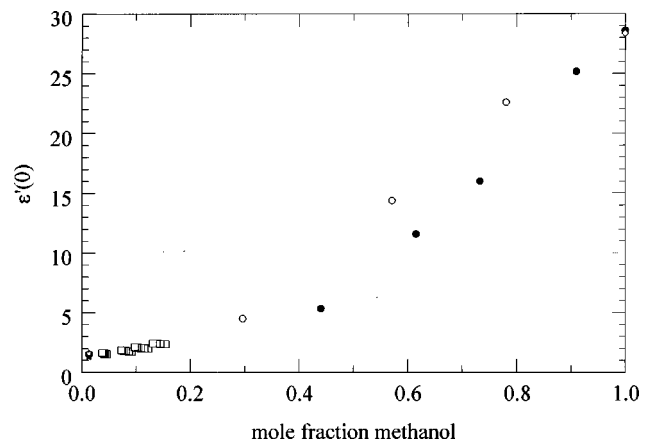


FIG. 6. Experimental relative permittivities for methanol+carbon dioxide mixtures at 323.2 K and approximately 11 MPa compared with literature data: (filled circles) this work; (squares) Ref. 10; (stars) Ref. 4; (diamonds) Ref. 28.

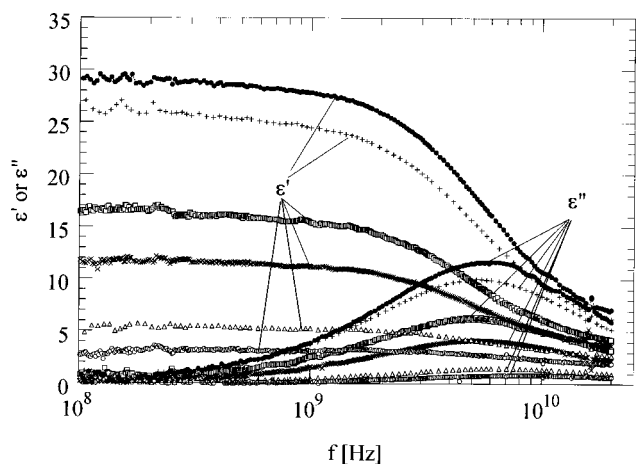


FIG. 7. Dielectric spectra (complex permittivity) for carbon dioxide (1)+methanol (2) mixtures at 323.2 K and 11 MPa: (filled circles) pure methanol; (plus signs) $x_2=0.91$; (white squares) $x_2=0.733$; (multis) $x_2=0.615$; (triangles) $x_2=0.44$; (white circles) $x_2=0.247$.

a constant of proportionality of the orientation polarization. The relaxation time is calculated from $1/2\pi f$, where f is the frequency at which the loss factor $\epsilon''(\omega)$ attains its maximum value. At this frequency, the absorption of electromagnetic energy becomes a maximum. The dielectric relaxation process has also been considered as a rate process.¹³ The data in Fig. 7 were smoothed with the Cole–Cole equation to obtain relaxation time constants. The relaxation times obtained were plotted against composition as shown in Fig. 8. Relaxation time τ increased from 28 to 31 ps as carbon dioxide mole fraction increased from 0.0 (pure methanol) to 0.277 as shown in Fig. 8. The increase in relaxation time as the carbon dioxide mole fraction increased clearly demonstrates strong CO_2 –methanol attraction over in the methanol rich composition region. The structure of methanol has been

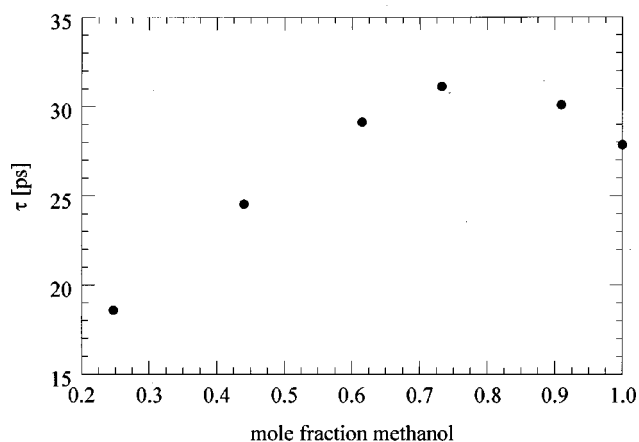


FIG. 8. Relaxation times for methanol vs methanol mole fraction for the CO_2 +methanol system at 323.2 K and approximately 11 MPa.

shown to consist of mainly hexamers over a wide range of conditions.^{29–31} The CO_2 –methanol attraction as given by the composition dependence of τ in Fig. 8 is an interesting feature that may have significance in chromatography applications. Future work on supercritical fluid systems will consist of detailed studies regarding temperature dependence of the complex permittivity and evaluation of probe models that will reduce the calibration effort.

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