Relative Permittivity Measurements of Dimethyl Ether + Carbon Dioxide Mixtures

Wayne Eltringham,* Stephen J. Tallon, Owen J. Catchpole, and Kristina Fenton

Industrial Research Limited, P.O. Box 31-310, Lower Hutt, New Zealand

The relative permittivities (ϵ_r) of dimethyl ether (DME) + carbon dioxide (CO_2) mixtures [(0.25, 0.48, and 0.75) mass fraction of DME] were measured at (313 and 333) K in the pressure range (3.9 to 32.5) MPa. The Peng–Robinson equation of state was used to calculate the mixture compressed liquid densities (ρ_{calcd}), and the relative permittivity was fitted to ρ_{calcd}, the temperature (T), and the mass fraction of DME (φ_1) using a simple empirical equation.

Introduction

Supercritical fluids have received a great deal of attention as alternative solvents because of the marked changes in solvent properties that can occur following modest changes in temperature and/or pressure. The ability to vary the solvating power by simple manipulation of system conditions offers a means of control and selectivity for various chemical applications including chromatographic,[1,2] extraction,[3,4] and reaction processes.[5] Supercritical carbon dioxide (CO_2) in particular has received much attention because it has relatively low critical parameters (critical temperature (T_c) = 304.18 K; critical pressure (P_c) = 7.38 MPa),[6] is environmentally benign, and is available in high purity at low cost. Unfortunately, due to the low polarity of CO_2, its applications are limited to low-to-medium molecular weight, nonpolar solutes. The solvating power of CO_2 can be enhanced by the addition of organic cosolvents such as ethanol[7] or fluorinated hydrocarbons.[8] Polar fluids such as 1,1,1,2-tetrafluoroethane (HFE 134a),[9,10] difluoromethane (HFE 32),[11] and dimethyl ether (DME)[12] have also been shown to be useful alternative solvents for polar molecules, and the fundamental solvent properties of these pure fluids have been reported over a range of temperatures and pressures.[13–16] Mixtures of polar fluids with each other and with nonpolar fluids have also been investigated as potential solvent systems.[17–20]

In this work, we begin characterizing the solvent properties of DME + CO_2 mixtures by measuring the relative permittivity at elevated pressures. The relative permittivity (ϵ_r) is a macroscopic material property which is strongly related to molecular structure and can play an important role in solution properties.[21,22] Measurement of ϵ_r has been shown to be a useful technique in characterizing molecular interactions and molecular ordering.[23–25]

Experimental Section

The relative permittivity was measured using a direct capacitance method. The cell capacitance in air (C_o) and the capacitance of the pure fluid (C) were measured, and ϵ_r was given by

$$\epsilon_r = \frac{C}{C_o} \qquad (1)$$

Capacitances were measured with an applied potential of 1.0 V at 60.0 kHz using a Hewlett-Packard 4284A precision LCR meter (20 Hz to 1 MHz). The LCR meter was connected to an alternating six-plate capacitor using coaxial RG-316/U electrical leads (maximum working temperature 473 K) fitted with BNC connectors. The capacitor plate spacing was 1 mm, and each circular plate was 20 mm in diameter. The high-pressure electrical connectors were supplied by Sitec Sieber Engineering (Switzerland). The cell capacitance in air was measured to be 16.55 pF and was found to be independent of temperature. The pressure dependence of the cell constant was negligible over the pressure ranges studied ($<7 \cdot 10^{-5}$ % variation in C_o). Temperature was monitored using a type K ServoTech thermocouple (± 0.5 K). Pressure measurements have an associated uncertainty of ± 0.2 MPa. The experimental procedure and equipment validation has been described in detail elsewhere.[16]

Each data point is the average of at least three replicate measurements, with the maximum standard deviation (σ) for a given condition over all temperatures and pressures studied = 0.002. Each replicate measurement was made by refilling the capacitance cell with the fluid mixture.

Dimethyl ether was supplied by Damar Industries Limited (New Zealand) with a purity of 99.8 % by volume. Impurities for the DME as stated by certificate of analysis were: water, 60.0 $\mu L \cdot L^{-1}$; methanol, 1.0 $\mu L \cdot L^{-1}$; oil, 3.0 $\mu L \cdot L^{-1}$; other gases (oxygen, carbon dioxide, nitrogen, propane, butane), volume fraction of 0.1 %. Carbon dioxide was supplied by BOC Limited (New Zealand) with a purity of 99.8 % by volume. Impurities for the CO_2 as stated by the certificate of analysis were: water, 80 $\mu L \cdot L^{-1}$; oxygen, 100 $\mu L \cdot L^{-1}$; the balance being other nonspecified constituents of air, including rare gases. Both gases were used immediately as received and were premixed in a 1 L stainless steel pressure cylinder before being used for the ϵ_r measurements. The 1 L cylinder was flushed with DME, and a known mass of DME was added to the cylinder, followed by a known mass of CO_2 to give the desired overall composition. For all compositions studied, sufficient DME and CO_2 were added to the cylinder so that the liquid phase filled greater than 95 % of the cylinder volume. By keeping the gas phase volume in the cylinder small, the initial composition of the liquid phase will be close to the overall composition. The change in mixture composition during liquid withdrawal is discussed in more detail in the Results section.

---

* To whom correspondence should be addressed. Telephone: +64-4-9313318. Fax: +64-4-9313055. E-mail: w.eltringham@irl.cri.nz.

10.1021/je700748g CCC: $40.75

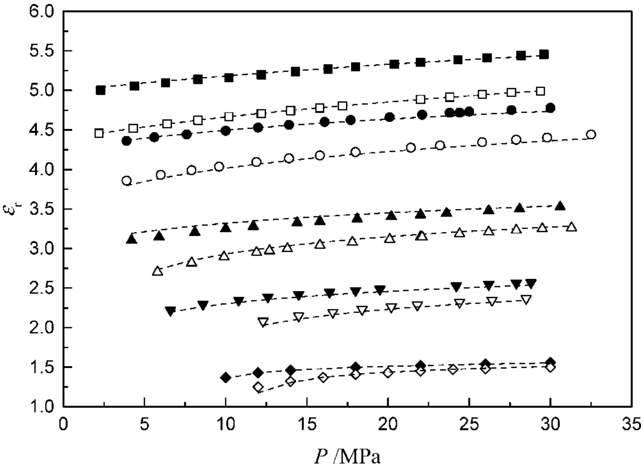

Figure 1. Pressure dependence of the relative permittivity (ϵ_r) of DME + CO_2 mixtures, where φ_1 is the mass fraction of DME in the mixture. Pure DME and pure CO_2 values are shown for comparison: ■, DME at 313.3 K;[16] □, DME at 333.4 K;[16] ●, $\varphi_1 = 0.75$ at 312.7 K; ○, $\varphi_1 = 0.75$ at 333.5 K; ▲, $\varphi_1 = 0.48$ at 312.7 K; Δ, $\varphi_1 = 0.48$ at 333.5 K; ▼, $\varphi_1 = 0.25$ at 312.7 K; ▽, $\varphi_1 = 0.25$ at 333.5 K; ♦, CO_2 at 313.2 K;[26] ◇, CO_2 at 333.2 K;[26] ---, correlation using eq 2.

Table 1. Relative Permittivity (ϵ_r) Values for DME + CO_2 Mixtures at (312.7 and 333.5) K, Where φ_1 is the Mass Fraction of DME in the Mixture[a]

T/K = 312.7			T/K = 333.5		
P/MPa	ϵ_r	ρ_{calcd}/kg·m^{-3}	P/MPa	ϵ_r	ρ_{calcd}/kg·m^{-3}
		$\varphi_1 = 0.25$			
6.6	2.22	681.4	12.3	2.08	635.2
8.6	2.29	717.2	14.5	2.15	672.8
10.8	2.35	746.9	16.6	2.19	701.1
12.6	2.39	766.8	18.4	2.23	721.5
14.5	2.42	784.9	20.2	2.26	739.4
16.4	2.45	800.8	21.8	2.28	753.7
18.0	2.47	812.9	24.4	2.32	774.3
19.5	2.48	823.4	26.4	2.34	788.5
24.2	2.53	851.8	28.5	2.37	802.1
26.2	2.54	862.3			
27.9	2.56	870.7			
28.8	2.57	874.9			
		$\varphi_1 = 0.48$			
4.2	3.10	693.0	5.8	2.70	589.8
5.9	3.15	709.3	7.9	2.82	625.8
8.1	3.21	727.1	9.9	2.89	651.1
10.0	3.25	740.3	11.9	2.95	671.5
11.7	3.28	750.9	12.7	2.97	678.7
14.4	3.33	766.0	13.8	3.00	688.0
15.8	3.34	773.0	15.8	3.04	703.1
18.1	3.37	783.7	17.8	3.08	716.5
20.2	3.40	792.7	20.1	3.12	730.3
22.0	3.43	799.8	22.0	3.15	740.6
23.6	3.45	805.9	22.1	3.15	741.1
26.2	3.48	815.0	24.4	3.19	752.5
28.1	3.50	821.2	26.2	3.21	760.7
30.6	3.52	829.0	27.9	3.23	768.0
			29.5	3.25	774.5
			31.3	3.26	781.4
		$\varphi_1 = 0.75$			
3.9	4.36	682.5	3.9	3.86	611.2
5.6	4.41	691.1	6.0	3.93	628.8
7.6	4.44	700.2	7.9	3.99	642.1
10.0	4.49	710.0	9.6	4.04	652.6
12.0	4.53	717.5	11.9	4.09	665.2
13.9	4.56	724.0	13.9	4.14	674.9
16.1	4.60	731.1	15.8	4.18	683.3
17.7	4.63	735.9	18.0	4.22	692.3
20.1	4.66	742.7	21.4	4.28	704.6
22.1	4.69	748.0	23.2	4.30	710.6
23.8	4.72	752.3	25.8	4.34	718.7
24.4	4.72	753.7	27.9	4.38	724.7
25.0	4.73	755.2	29.8	4.40	729.9
27.6	4.75	761.2	32.5	4.44	736.8
30.0	4.78	766.4			

[a] Liquid densities (ρ_{calcd}) calculated using the Peng–Robinson equation of state are also given.

Results

Figure 1 shows the ϵ_r values of DME + CO_2 mixtures as a function of temperature and pressure compiled from the data in Table 1. The ϵ_r increases with increasing pressure and decreasing temperature. Hence, the isothermal density dependence, $(\delta\epsilon_r/\delta\rho)_T$, of ϵ_r is always positive and the isobaric temperature dependence, $(\delta\epsilon_r/\delta T)_P$, is always negative. Pure DME[16] and pure CO_2[26] values are also shown in Figure 1 for comparison. The progression from pure CO_2 to pure DME shows an almost linearly proportional change in the magnitude of the ϵ_r values as the mixture composition changes.

The ϵ_r measurements have an associated standard uncertainty of 4.1 % (95 % confidence level). The uncertainty calculation takes into account the maximum absolute variation in the DME + CO_2 mixture liquid phase composition as liquid is withdrawn from the high-pressure cylinder. The liquid phase composition will be slightly more enriched in DME compared to the overall composition because of the higher CO_2 vapor pressure, which gives rise to the preferential migration of CO_2 to the upper gas phase. The difference between the liquid phase composition and the initial overall mixture composition increases as the liquid phase is withdrawn from the bottle and the gas phase volume increases. To calculate the change in liquid phase composition during cylinder draw-down, the Peng–Robinson (PR) equation of state (EOS)[27] using van der Waals mixing rules, as described by Smith et al.,[28] was fitted to experimental measurements of the DME + CO_2 vapor–liquid equilibria by Jónasson et al.[29] Literature values for the critical properties of CO_2[6] and DME ($T_c = 400.4$ K; $P_c = 5.36$ MPa)[30] were used in the PR EOS. The PR EOS was then used to calculate densities and equilibrium compositions for the gas and liquid phases. The liquid phase densities calculated using the PR EOS are given in Table 1. Considering pure DME and CO_2, the PR EOS-calculated liquid phase densities of the pure fluids deviate from literature densities[31,32] by up to 3.8 %, which was assumed to be the maximum uncertainty in density for the DME + CO_2 mixtures. The uncertainty associated with the calculated density values was considered when calculating the uncertainty associated with the ϵ_r values.

The changing composition of the liquid phase in the pressure cylinder at 293 K was calculated starting with a completely full cylinder with a fixed composition, iteratively removing liquid volume from the cylinder, and then recalculating the composition of the remaining mass of fluid using the calculated densities and compositions of the gas and liquid phases. During the ϵ_r measurements, the liquid phase volume was never less than 50 % of the cylinder volume, so the maximum variation in the liquid phase composition was calculated between a completely full and 50 % full (with liquid phase) cylinder. The calculations assume that the draw-down of the liquid phase is slow enough so that the phases are at constant equilibrium and that the temperature of the mixture remains at ambient room temperature (293 K). The PR EOS analysis approach is comparable to that employed by Via et al.[33] for changes in the liquid phase composition of premixed CO_2 + methanol mixtures, which they found compared well with the experimentally measured changes. Via et al. were interested in initial compositions containing low levels of methanol, for which the change in liquid phase composition is more significant than for the DME + CO_2

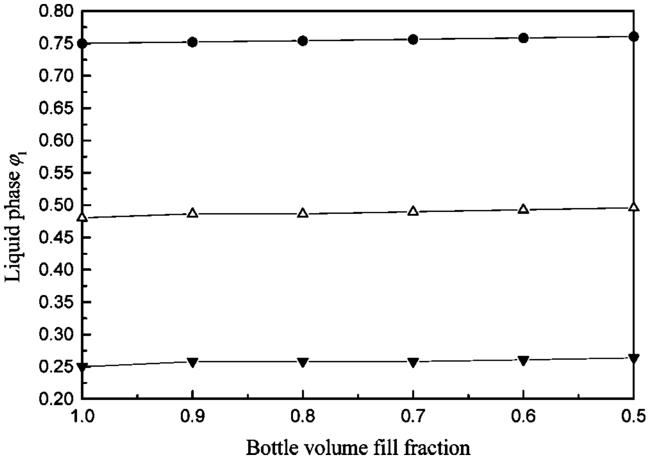

Figure 2. Change in liquid phase composition of the DME + CO_2 mixtures as liquid is withdrawn from the cylinder, where φ_1 is the mass fraction of DME: -▼-, initial $\varphi_1 = 0.25$; -△-, initial $\varphi_1 = 0.48$; -●-, initial $\varphi_1 = 0.75$.

Table 2. Constants for Equations 3 to 5

eq 3		eq 4		eq 5	
a_0	1498	b_0	0.5198	c_0	−1.935
a_1	−17.44	b_1	4.532	c_1	−31.98
		b_2	−6.567	c_2	46.33
		b_3	6.966	c_3	−47.40

mixtures described here. The change in composition for the DME + CO_2 mixture liquid phase is shown in Figure 2 for initial DME mass fractions (φ_1) of 0.25, 0.48, and 0.75. The calculations show a maximum absolute variation of 0.010 for the $\varphi_1 = 0.75$ mixture, increasing to 0.014 for the $\varphi_1 = 0.25$ mixture.

The relative permittivities were correlated to mixture composition, fluid density, and temperature using the simple empirical equation

$$\epsilon_r = \frac{A}{T} + B \ln \rho_{\text{calcd}} + C \tag{2}$$

where T is the temperature in K; ρ_{calcd} is the PR EOS-calculated fluid density in $\text{kg}\cdot\text{m}^{-3}$; and A, B, and C are constants given by

$$A = \varphi_1(a_0 - a_1) + a_1 \tag{3}$$

$$B = b_0 + b_1\varphi_1 + b_2\varphi_1^2 + b_3\varphi_1^3 \tag{4}$$

$$C = c_0 + c_1\varphi_1 + c_2\varphi_1^2 + c_3\varphi_1^3 \tag{5}$$

The constants for eqs 3 to 5 are given in Table 2. The correlation is applicable to pure CO_2, DME + CO_2 mixtures, and pure DME in the temperature range (313 to 333) K at pressures above the saturation curve. The experimental ϵ_r values are compared to the values calculated using eq 2 in Figure 1. The correlations have a maximum deviation, [(experimental − calculated)/experimental]$\cdot$100, of ± 2.8 % over all compositions.

Conclusion

The relative permittivities of DME + CO_2 mixtures [(0.25, 0.48, and 0.75) mass fraction of DME] at (313 and 333) K have been measured in the pressure range (3.9 to 32.5) MPa. Under these conditions, the isothermal pressure dependence of the relative permittivity, $(\delta\epsilon_r/\delta P)_T$, is always positive, and the isobaric temperature dependence, $(\delta\epsilon_r/\delta T)_P$, is always negative. The change in liquid phase composition during cylinder drawdown was calculated using the Peng–Robinson equation of state, and the maximum absolute variation in composition was considered in the relative permittivity uncertainty calculations. The relative permittivity was fitted to the temperature, mixture density, and mass fraction of DME using a simple empirical equation. At pressures above the saturation curve, this empirical equation can be used to estimate the relative permittivity of CO_2, DME + CO_2 mixtures, and pure DME in the temperature range (313 to 333) K to within ± 2.8 % of experimental values.

Acknowledgment

We thank Murray Early, Keith Jones, Laurie Christian, and Peter Saunders of the Measurement Standards Laboratory, Industrial Research Limited, for very useful discussions.

Literature Cited

(1) Combs, M. T.; Ashraf-Khorassani, M.; Taylor, L. T. Packed column supercritical fluid chromatography mass spectroscopy: A review. *J. Chromatogr. A* **1997**, *785*, 85–100.

(2) Smith, R. M. Supercritical fluids in separation science - the dreams, the reality and the future. *J. Chromatogr. A* **1999**, *856*, 83–115.

(3) McHugh, M.; Krukonis, V. J. *Supercritical Fluid Extraction*; 2nd edition; Butterworth-Heinemann: Boston, 1994.

(4) Taylor, L. T. *Supercritical Fluid Extraction*; J. Wiley & Sons: New York, 1996.

(5) *Chemical Synthesis using Supercritical Fluids*; Jessop, P. G., Leitner, W., Eds.; Wiley-VCH: Weinheim, 1999.

(6) Suehiro, Y.; Nakajima, M.; Yamada, K.; Uematsu, M. Critical parameters of $\{xCO_2 + (1\text{-}x)CHF_3\}$ for $x = 1.0000, 0.7496, 0.5013$, and 0.2522). *J. Chem. Thermodyn.* **1996**, *28*, 1153–1164.

(7) Catchpole, O. J.; Grey, J. B.; Noermark, K. A. Solubility of fish oil components in supercritical CO_2 and CO_2 + ethanol mixtures. *J. Chem. Eng. Data,* **1998**, *43*, 1091–1095.

(8) Berthod, M.; Mignani, G.; Lemaire, M. New perfluoroalkylated BINAP usable as a ligand in homogeneous and supercritical carbon dioxide asymmetric hydrogenation. *Tetrahedron: Asymmetry* **2004**, *15*, 1121–1126.

(9) Abbott, A. P.; Eltringham, W.; Hope, E. G.; Nicola, M. Solubility of unsaturated carboxylic acids in supercritical 1,1,1,2,-tetrafluoroethane (HFE 134a) and a methodology for the separation of ternary mixtures. *Green Chem.* **2005**, *7*, 210–216.

(10) Abbott, A. P.; Eltringham, W.; Hope, E. G.; Nicola, M. Hydrogenation in supercritical 1,1,1,2-tetrafluoroethane (HFC 134a). *Green Chem.* **2005**, *7*, 721–725.

(11) Abbott, A. P.; Corr, S.; Durling, N. E.; Hope, E. G. Solubility of substituted aromatic hydrocarbons in supercritical difluoromethane. *J. Chem. Eng. Data* **2002**, *47*, 900–905.

(12) Catchpole, O. J.; Tallon, S. J.; Grey, J. B.; Fenton, K.; Fletcher, K.; Fletcher, A. J. Extraction of lipids from aqueous protein-rich streams using near-critical dimethylether. *Chem. Eng. Technol.* **2007**, *30*, 501–510.

(13) Abbott, A. P.; Corr, S.; Durling, N. E.; Hope, E. G. Hydrogen bond interactions in liquid and supercritical hydrofluorocarbons. *J. Phys. Chem. B* **2003**, *107*, 10628–10633.

(14) Abbott, A. P.; Eardley, C. A. Solvent properties of liquid and supercritical hydrofluorocarbons. *J. Phys. Chem. B* **1999**, *103*, 2504–2509.

(15) Abbott, A. P.; Eardley, C. A.; Tooth, R. Relative permittivity measurements of 1,1,1,2-tetrafluoroethane (HFC 134a), pentafluoroethane (HFC 125), and difluoromethane (HFC 32). *J. Chem. Eng. Data* **1999**, *44*, 112–115.

(16) Eltringham, W.; Catchpole, O. J. Relative permittivity measurements of gaseous, liquid and supercritical dimethyl ether. *J. Chem. Eng. Data* **2007**, *52*, 363–367.

(17) Abbott, A. P.; Eardley, C. A.; Scheirer, J. E. CO_2/HFC 134a mixtures: alternatives for supercritical fluid extraction. *Green Chem.* **2000**, *2*, 63–65.

(18) Wesch, A.; Dahmen, N.; Ebert, K. H. Measuring the static dielectric constants of pure carbon dioxide and carbon dioxide mixed with ethanol and toluene at elevated pressures. *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 1368–1371.

(19) Deul, R.; Franck, E. U. The static dielectric constant of the water-benzene mixture system to 400 °C and 2800 bar. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 847–853.

(20) Goldfarb, D. L.; Fernández, D. P.; Corti, H. R. Dielectric and volumetric properties of supercritical carbon dioxide(1) + methanol(2) mixtures at 323.15 K. *Fluid Phase Equilib.* **1999**, *158–160*, 1011–1019.

(21) Dannhauser, W.; Flueckinger, A. F. Dielectric constant and intermolecular association of some liquid nitriles. *J. Phys. Chem.* **1964**, *68*, 1814–1819.

(22) Janini, G. M.; Katrib, A. H. Determination of the dipole moment of polar compounds in nonpolar solvents. *J. Chem. Educ.* **1983**, *60*, 1087–1088.

(23) Ghanadzadeh, A.; Beevers, M. S. Effect of surface and molecular structure on the dielectric behaviour in thick layers of cyanobiphenyl liquid crystals. *J. Mol. Liq.* **2002**, *100*, 47–57.

(24) Ghanadzadeh, A.; Beevers, M. S. Dielectric investigations and molecular association in non-mesogenic and mesogenic solutions. *J. Mol. Liq.* **2003**, *102*, 365–377.

(25) Ghanadzadeh, A.; Mamaghani, M.; Anbir, J. Dipole moments and intermolecular association of some carbonyl compounds in nonpolar solvents. *J. Solution Chem.* **2003**, *32*, 625–636.

(26) Moriyoshi, T.; Kita, T.; Uosaki, Y. Static relative permittivity of carbon dioxide and nitrous oxide up to 30 MPa. *Ber. Bunsen. Phys. Chem.* **1993**, *97*, 589–596.

(27) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

(28) Smith, J. M.; Van Ness, C. H.; Abbott, M. M. *Chemical Engineering Thermodynamics*, 6th ed.; McGraw-Hill: New York, 2001; pp 98–100 and pp 538–553.

(29) Jónasson, A.; Persson, O.; Fredenslund, A. High pressure solubility of carbon dioxide and carbon monoxide in dimethyl ether. *J. Chem. Eng. Data* **1995**, *40*, 296–300.

(30) Wu, J.; Liu, Z.; Wang, B.; Pan, J. Measurement of the critical parameters and the saturation densities of dimethyl ether. *J. Chem. Eng. Data* **2004**, *49*, 704–708.

(31) Bobbo, S.; Scattolini, M.; Fedele, L.; Camporese, R. Compressed liquid densities and saturated liquid densities of dimethyl ether (RE170). *J. Chem. Eng. Data* **2005**, *50*, 1667–1671.

(32) *NIST Chemistry WebBook, NIST Standard Reference Database*; Linstrom, P. J., Mallard, W. G., Eds.;Number 69, 2005: http://webbook.nist.gov/chemistry/.

(33) Via, J.; Taylor, L. T.; Schweighardt, F. K. Experimental determination of changes in methanol modifier concentration in premixed carbon dioxide cylinders. *Anal. Chem.* **1994**, *66*, 1459–1461.

Received for review December 19, 2007. Accepted January 16, 2008. This work was supported by the Foundation for Research Science and Technology, New Zealand; CO8X0305.

JE700748G