

# Relative Permittivity Measurements of Gaseous, Liquid, and Supercritical Dimethyl Ether

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The relative permittivity ( $\epsilon_r$ ) of dimethyl ether (DME) was measured as a function of temperature and pressure in the gaseous, liquid, and supercritical states. The temperature and pressure ranges studied were (303 to 403) K and (0.04 to 33.2) MPa, respectively. The relative permittivity was fitted to the reduced density ( $\rho_r$ ) using the function  $(\epsilon_r - 1)/(2\epsilon_r + 1)$ , and the apparent dipole moment ( $\mu^*$ ) of the liquid phase was calculated using Kirkwood's theory of molecular polarizability.

## Introduction

There is increasing demand for the chemical industry to develop new, cleaner, more acceptable chemical processes. One area for process modification is the solvent. An increasing amount of research is focusing on supercritical fluids as alternatives to conventional organic solvents. Supercritical fluids are used in chromatographic, reaction, and extraction process applications. They are of interest because the fluid density is a highly tunable function of pressure. Density-dependent properties such as viscosity, diffusivity, and relative permittivity (often called the dielectric constant) can be altered by up to an order of magnitude at temperatures close to the critical temperature ( $T_c$ ) simply by altering the pressure. The relative permittivity ( $\epsilon_r$ ) is a macroscopic material property that is strongly related to molecular structure and can play an important role in solution properties.<sup>1,2</sup> Measurement of  $\epsilon_r$  has been shown to be a useful technique for characterizing molecular interactions and molecular ordering.<sup>3–5</sup>

Dimethyl ether (DME) has been used as an aerosol propellant,<sup>6</sup> a refrigerant,<sup>7,8</sup> and a mobile phase in chromatographic applications<sup>9</sup> and has also been investigated as an alternative fuel.<sup>10,11</sup> Several publications report using DME as an alternative solvent for reaction<sup>12,13</sup> and extraction processes.<sup>14,15</sup>

Several research groups have investigated thermodynamic and physical properties of DME including saturated densities,<sup>16</sup> compressed liquid densities,<sup>17,18</sup> liquid viscosities,<sup>19</sup> vapor pressures,<sup>20,21</sup> surface tensions,<sup>22,23</sup> and critical parameters ( $T_c = 400.4$  K;  $P_c = 5.36$  MPa;  $\rho_c = 272$  kg·m<sup>-3</sup>),<sup>16</sup> but few researchers have characterized the fundamental solvent properties of this fluid. Lunt and Rau<sup>24</sup> reported that the relative permittivity of DME at 298 K was unaffected by frequency in the range (1 to 1000) kHz. Marsden and Maass<sup>25</sup> measured the relative permittivity of gaseous and liquid DME along the saturation curve from (298 to 409) K. In a later study, Lawley and Sutton<sup>26</sup> investigated the molecular association of DME in gas mixtures by measuring the pressure dependence of the relative permittivity. Gee et al.<sup>27</sup> reported the variation in the relative permittivity of DME against temperature in the range of (155 to 258) K. This work aims to further characterize the solvent properties of DME by reporting compressed liquid and

supercritical relative permittivity data of the commercial grade solvent over a range of temperatures and pressures.

## Experimental Section

The relative permittivity was measured using a direct capacitance method with the apparatus shown in Figure 1. The capacitance cell (CC) was connected to a Hewlett-Packard 4284A precision LCR meter (20 Hz to 1 MHz) using coaxial RG-316/U electrical leads (maximum working temperature 473 K) fitted with BNC connectors. The high-pressure electrical connectors for CC were supplied by Sitec Sieber Engineering (Switzerland). These were connected to an alternating six-plate capacitor manufactured at Industrial Research Limited. The capacitor plate spacing was 1 mm, and each circular plate was 20 mm in diameter.

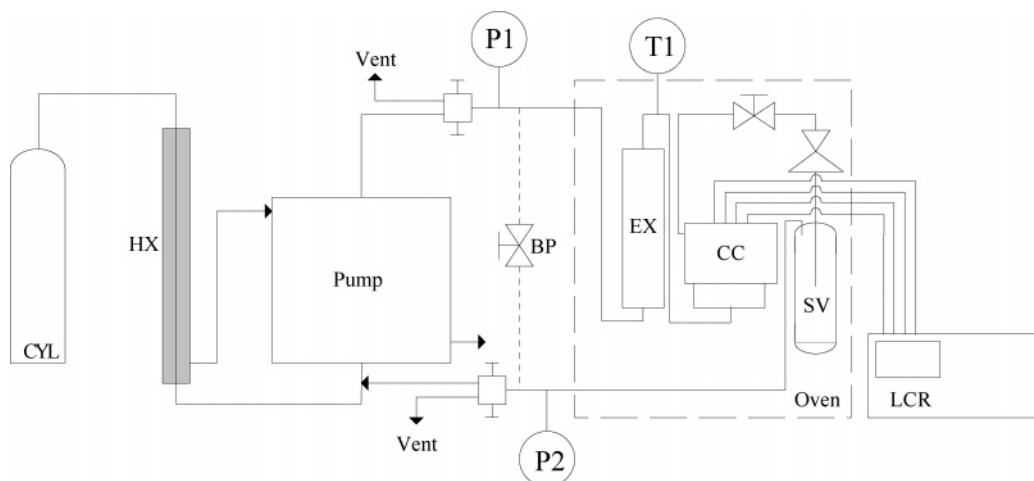
The apparatus was heated in an oven to the desired temperature, which was monitored using a Type K ServoTech thermocouple ( $\pm 0.5$  K), T1. The capacitance of CC was measured in air with an applied potential of 1.0 V at 60.0 kHz. The cell capacitance ( $C_o$ ) was measured to be 16.55 pF and was found to be independent of temperature. The pressure dependence of the cell constant was negligible over the pressure ranges studied. Prior to experiment CC was purged with DME to remove the air, and pressure was applied using piston pump MP1. Pressure was monitored using gauge P1. Pressure measurements made in the liquid and supercritical phases have an associated uncertainty of  $\pm 0.2$  MPa. For gaseous phase measurements the pressures have an uncertainty of  $\pm 0.02$  MPa. The capacitance ( $C$ ) of DME at given temperature and pressure conditions was measured, and  $\epsilon_r$  was given by

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

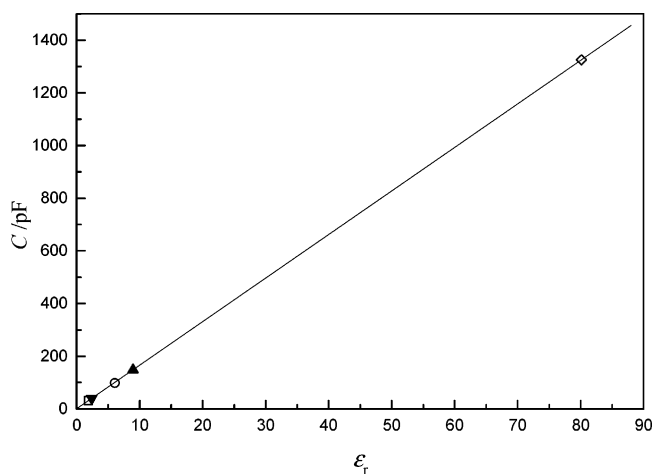
Each data point is the average of at least three replicate measurements (maximum standard deviation,  $\sigma$ , for a given condition over all temperatures and pressures studied = 0.01). Each replicate measurement was made by refilling CC with DME.

DME was supplied by Damar Industries Limited (New Zealand) with a purity of 99.8 % by volume and was used immediately as received. Impurities as stated by certificate of analysis were as follows: water, 60.0  $\mu\text{L}\cdot\text{L}^{-1}$ ; methanol, 1.0

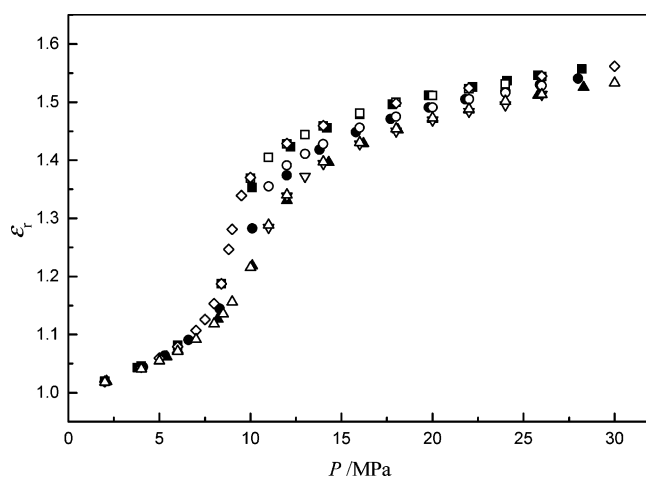
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**Figure 1.** Apparatus used to measure the relative permittivity ( $\epsilon_r$ ) of DME: CYL, solvent cylinder; HX, heat exchanger; P1/2, pressure gauge; T1, temperature monitor; BP, bypass valve; CC, capacitance cell; LCR, Hewlett-Packard 4284A high-precision LCR meter (20 Hz to 1 MHz).

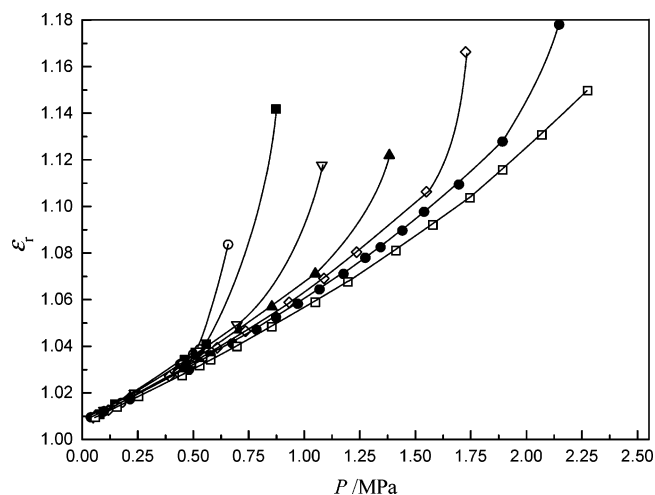


**Figure 2.** Measured capacitance ( $C$ ) values vs expected (literature) relative permittivities ( $\epsilon_r$ ) for several pure liquids (ambient temperature and pressure) to determine the stray capacitance of the capacitance cell, CC:  $\square$ , hexane;<sup>28</sup>  $\nabla$ , toluene;<sup>29</sup>  $\circ$ , ethyl acetate;<sup>30</sup>  $\blacktriangle$ , dichloromethane;<sup>31</sup>  $\diamond$ , water.<sup>32</sup>  $C = 16.5499 \epsilon_r + 0.0550$  (standard deviation,  $\sigma = 2.243$  pF).

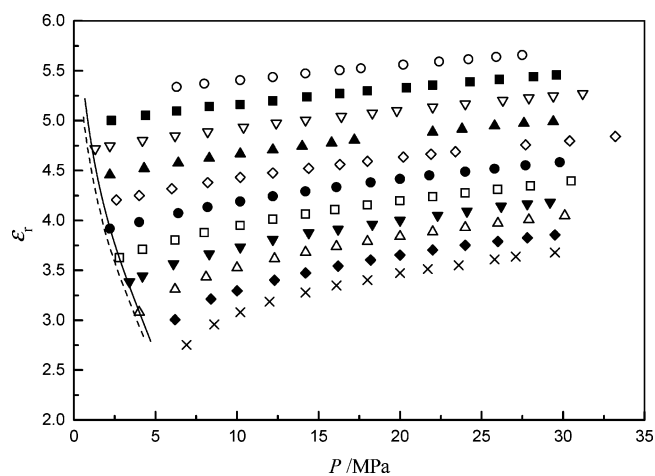


**Figure 3.** Validation of the equipment used in this work. Comparison of carbon dioxide relative permittivities ( $\epsilon_r$ ) with literature values:  $\square$ , ref 33, 313.7 K;  $\circ$ , ref 33, 318.3 K;  $\nabla$ , ref 33, 323.3 K;  $\diamond$ , ref 34, 313.2 K;  $\triangle$ , ref 34, 323.2 K;  $\blacksquare$ , this work, 312.8 K;  $\bullet$ , this work, 318.0 K;  $\blacktriangle$ , this work, 323.5 K.

$\mu\text{L}\cdot\text{L}^{-1}$ ; oil,  $3.0 \mu\text{L}\cdot\text{L}^{-1}$ ; other gases (oxygen, carbon dioxide, nitrogen, propane, butane), volume fraction of 0.1 %.



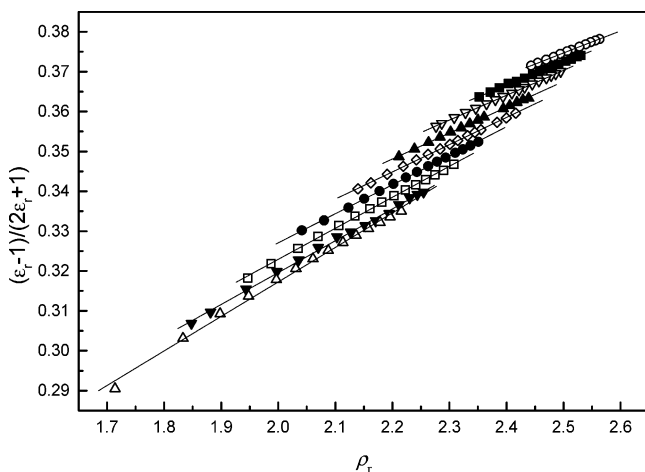
**Figure 4.** Pressure dependence of the relative permittivity ( $\epsilon_r$ ) of gaseous DME at various temperatures:  $\circ$ , 303.7 K;  $\blacksquare$ , 313.3 K;  $\nabla$ , 323.0 K;  $\blacktriangle$ , 333.4 K;  $\diamond$ , 343.2 K;  $\bullet$ , 353.1 K;  $\square$ , 363.4 K. Lines are drawn to aid the eye.



**Figure 5.** Pressure dependence of the relative permittivity ( $\epsilon_r$ ) of liquid and supercritical DME at various temperatures:  $\circ$ , 303.7 K;  $\blacksquare$ , 313.3 K;  $\nabla$ , 323.0 K;  $\blacktriangle$ , 333.4 K;  $\diamond$ , 343.2 K;  $\bullet$ , 353.1 K;  $\square$ , 363.4 K;  $\blacktriangledown$ , 372.9 K;  $\triangle$ , 382.9 K;  $\blacklozenge$ , 393.0 K;  $\times$ , 402.9 K; —, saturated liquid values from eq 2 in this work; - - -, saturated liquid values of ref 25.

The equipment was validated at both ambient and high-pressure conditions. The stray capacitance of CC was obtained from the intercept of Figure 2, which shows a plot of expected





**Figure 6.** Linear dependency of  $(\epsilon_r - 1)/(2\epsilon_r + 1)$  on the reduced density ( $\rho_r$ ) of liquid DME. The standard deviation ( $\sigma$ ) for each linear correlation is given in parentheses:  $\circ$ , 303.7 K ( $3.4 \times 10^{-5}$ );  $\blacksquare$ , 313.3 K ( $9.3 \times 10^{-5}$ );  $\nabla$ , 323.0 K ( $6.4 \times 10^{-5}$ );  $\blacktriangle$ , 333.4 K ( $9.6 \times 10^{-5}$ );  $\diamond$ , 343.2 K ( $1.0 \times 10^{-4}$ );  $\bullet$ , 353.1 K ( $1.2 \times 10^{-4}$ );  $\square$ , 363.4 K ( $2.6 \times 10^{-4}$ );  $\blacktriangledown$ , 372.9 K ( $5.1 \times 10^{-4}$ );  $\triangle$ , 382.9 K ( $8.5 \times 10^{-4}$ ).

$\pm 1.5$  %. Values of DME liquid densities from (303 to 383) K were calculated from the equations of Ihmels and Lemmon,<sup>17</sup> with an uncertainty of  $\pm 0.1$  %.

## Results

Figures 4 and 5 show the relative permittivity of DME as a function of temperature and pressure compiled from the data in Table 1. The relative permittivity increases with increasing pressure and decreasing temperature. Hence, the isothermal density dependence,  $(\delta\epsilon_r/\delta\rho)_T$ , of  $\epsilon_r$  is always positive, and  $\epsilon_r$  has a linear dependency on density. The observed temperature dependent behavior is due to the presence of a dipole in the DME molecule. As temperature is increased the molecular thermal motion increases, and the ability of the molecules to orient and align their dipoles with the applied electric field is reduced. This reduced alignment of dipoles leads to a reduction in  $\epsilon_r$  at higher temperatures.

As carried out previously for hydrofluorocarbon solvents,<sup>35</sup> the relative permittivity data was fitted to

$$\frac{\epsilon_r - 1}{2\epsilon_r + 1} = A + B\rho_r \quad (2)$$

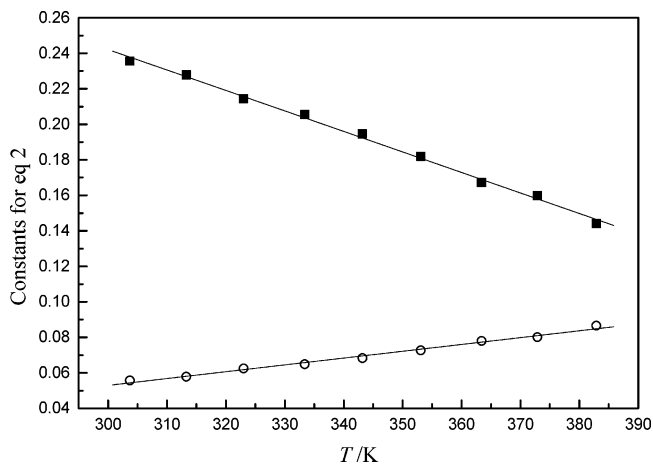
where  $\rho_r$  is the reduced density ( $\rho_r = \rho/\rho_c$ , where  $\rho$  is the density at given temperature and pressure conditions and  $\rho_c$  is the critical density), and  $A$  and  $B$  are constants given by

$$A = 0.4892297 - 0.000879626T \quad (3)$$

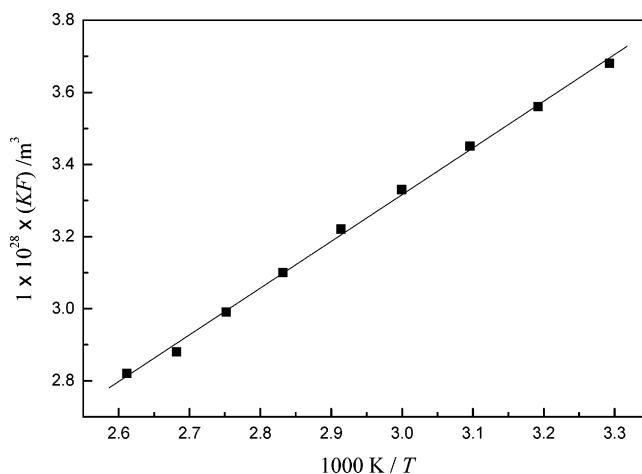
$$B = 0.0002663T - 0.019856933 \quad (4)$$

where  $T$  is the temperature in K. Fitting was carried out using literature<sup>17</sup> liquid densities from (303 to 383) K, and the correlation has a maximum deviation in density, [(calculated - literature)/calculated]  $\times 100$ , of  $\pm 1.9$  %. The function  $(\epsilon_r - 1)/(2\epsilon_r + 1)$  varies linearly with the isothermal reduced density (Figure 6), and the constants of proportionality vary linearly with  $T$  (Figure 7). Liquid densities ( $\rho_{\text{cal}}$ ) for DME at (303 to 383) K and (1.3 to 33.2) MPa calculated using eq 2 are reported in Table 1.

The saturated liquid densities of DME were calculated according to Wu et al.,<sup>16</sup> and eq 2 was used to calculate the saturated liquid  $\epsilon_r$  values at (303 to 393) K. The results are



**Figure 7.** Linear dependency on temperature for the constants of proportionality for eq 2. The standard deviation ( $\sigma$ ) for each linear correlation is given in parentheses:  $\blacksquare$ ,  $A$  (0.002);  $\circ$ ,  $B$  (0.001).



**Figure 8.** Determination of the apparent dipole moment ( $\mu^*$ ) of DME in the liquid phase by the Kirkwood representation ( $\sigma = 1.44 \times 10^{-30}$  m<sup>3</sup>).

compared to the values of Marsden and Maass<sup>25</sup> in Figure 5. The values in this work are slightly greater than those reported by Marsden and Maass with a maximum deviation of  $\pm 5.6$  %. The DME used by Marsden and Maass was distilled before use, and the observed deviation could be due to the impurities present in the commercial grade solvent used in the current work.

It has been shown previously<sup>36</sup> that Kirkwood's theory of molecular polarizability<sup>37</sup> can be used to estimate the dipole moment of liquid solvents. The apparent dipole moment ( $\mu^*$ ) of a polar liquid can be related to  $\epsilon_r$  through

$$KF = \frac{(\epsilon_r - 1)(2\epsilon_r + 1)}{9\epsilon_r} \left( \frac{3M}{N_A \rho} \right) = \left( \alpha + \frac{\mu^{*2}}{3\epsilon_0 k_B T} \right) \quad (5)$$

where  $M$  is the molar mass,  $N_A$  is the Avogadro constant,  $\alpha$  is the molecular polarizability,  $\epsilon_0$  is the vacuum permittivity, and  $k_B$  is the Boltzmann constant.

By performing a linear regression as a function of  $1/T$ , the value of  $\mu^*$  can be determined. The Kirkwood function (KF) was approximately independent of density at each temperature. The mean KF is plotted as a function of  $1/T$  from (303 to 383) K in Figure 8, giving a  $\mu^*$  value for DME of  $\{(6.89 \pm 0.1) \times 10^{-30}\}$  C·m. The uncertainty is based on the uncertainties associated with the density values ( $\pm 0.1$  %),<sup>17</sup> temperature measurements ( $\pm 0.5$  K), and relative permittivity values ( $\pm 1.5$  %). The gas-phase dipole moment ( $\mu$ ) for DME is reported to be  $4.37 \times 10^{-30}$  C·m.<sup>38</sup> The apparent liquid-phase dipole

moment is greater than that of the gas phase because of the dipole inducing effect of neighboring molecules in the liquid state. The apparent liquid-phase and gas-phase dipole moments are related through  $\mu = g^{1/2}\mu^*$ , where  $g$  is the Kirkwood correlation parameter, which is a measure of the restriction to rotation imposed by a cage of molecules around a given molecule.<sup>36</sup>

## Conclusion

The relative permittivity of gaseous, liquid, and supercritical DME has been measured at temperatures ranging from (303 to 403) K and at pressures from (0.04 to 33.2) MPa. Under these conditions, the isothermal pressure dependence of the relative permittivity,  $(\partial\epsilon_r/\partial P)_T$ , is always positive and the isobaric temperature dependence,  $(\partial\epsilon_r/\partial T)_P$ , is always negative. The relative permittivity has been fitted to the reduced density at (303 to 383) K using the function  $(\epsilon_r - 1)/(2\epsilon_r + 1)$ . At pressures above the saturation curve and in the temperature range of (303 to 383) K, this function can be used to calculate the liquid densities of DME to within  $\pm 1.9\%$  of experimental values. The apparent dipole moment of DME in the liquid phase is also reported.

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