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PvT and thermal-pressure coefficient measurements of diethyl ether (DEE) in the critical and supercritical regions

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ABSTRACT

The pressures (P) and its temperature derivatives or thermal-pressure coefficient, $\gamma_V = (\partial P/\partial T)_V$, of DEE have been measured in the near- and supercritical regions as a function of temperature along the various liquid and vapour isochores. Measurements were made in the immediate vicinity of the liquid–gas phase transition and the critical points (single- and two-phase regions) using a high-temperature, high-pressure, nearly constant-volume adiabatic piezo-calorimeter. The constant-volume adiabatic calorimeter previously used for C_V measurements was additionally supplied with high accurate strain gauge (calibrated piezoelectric transducer) to measure simultaneously the PvT, $C_V vT$, and thermal-pressure coefficient γ_V. Measurements were made along 17 liquid and vapour isochores in the range from (212.6 to 534.6) $\text{kg} \cdot \text{m}^{-3}$ and at temperatures from (347 to 575) K and at pressures up to 18 MPa. The quasi-static thermo- (reading of PRT, T–τ plot) and barograms (readings of the high accurate strain gauge, P–τ plot) techniques were used to accurate measure of the phase transition parameters (P_S, ρ_S, T_S) and γ_V at saturation curve. Temperatures at the liquid-gas phase transition curve, $T_S(\rho)$, for each measured density (isochore) and the critical parameters (T_C and ρ_C) for DEE were obtained using the quasi-static thermograms technique. The expanded uncertainty of the pressure and its temperature derivative, $(\partial P/\partial T)_V$, measurements at the 95% confidence level with a coverage factor of $k = 2$ is estimated to be 0.05% and (0.12 to 1.5)% (depending on temperature and pressure), respectively. The measured pressures and temperature derivatives, $(\partial P/\partial T)_V$, have been used to calculate the internal pressure (or energy–volume coefficient) as $\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$. The effect of pressure and temperature on the internal pressure near the critical point was studied. The measured values of thermal-pressure coefficient, $(\partial P/\partial T)_V$, were used to determine accurately the behaviour of second temperature derivative $(\partial^2 P/\partial T^2)_V$ near the critical point and compared with our previous isochoric heat capacity measured results, $\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho = -\frac{\rho^2}{T}\left(\frac{\partial C_V}{\partial \rho}\right)_T$. The measured and derived thermodynamic properties of DEE near the critical point were interpreted in terms of theory of critical phenomena.

1. Introduction

In this work, we simultaneously directly measured PvT relationship and thermal-pressure coefficient, $\gamma_V = (\partial P/\partial T)_V$ of DEE in the critical and supercritical regions as a function of temperature along the various liquid and vapour isochores. The measured pressures (P) and its temperature derivatives, $(\partial P/\partial T)_V$, have been used to calculate the internal pressure (temperature derivatives of the internal energy) as

$$P_{\text{int}} = \left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{1}$$

In our previous publications [1,2], we have also measured the temperature derivatives of the internal energy $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ (isochoric heat capacity) of DEE in the critical and supercritical regions, including coexistence curve. The internal pressure and isochoric heat capacity describe the sensitivity of internal energy U to a change in specific volume v and temperature T. The internal energy-volume coefficient $(\partial U/\partial v)_T$ is very sensitive to changes in the structure of the liquid and nature of the interaction between molecules. Therefore, studies of the internal pressure of liquids and liquid mixtures can be used to examine solvent-solute (structural) interactions *i.e.*, provide useful information on the nature of the interaction between the molecules. It is obvious that for the ideal gas the internal

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pressure is zero, while for real gases and liquids it deviates significantly from zero and is much greater than the thermal pressure.

Previously the present technique of thermal-pressure coefficient measurement was successfully used to measure accurately the thermal-pressure coefficient (internal pressure) for pure DEE at saturation [1], quaternary mixture (water + n-octane + SDS + 1-pentanol) [3], and (water + ammonia) mixtures [4]. In most cases, the derivative $(\partial P/\partial T)_V$ (thermal-pressure coefficient) is calculated from the equation of state such as the Tait type, cubic EOS, or multi-parametric EOS using *PvT* properties. Direct measurements of the derivative $(\partial P/\partial T)_V$ are very rare. In the present work, we measured directly the values of $(\partial P/\partial T)_V$ and pressure P for DEE, and internal pressure. The indirect method of determination of the internal pressure is based on calculation of K_T and α_P (see below Eq. (2)). Usually, the values of K_T and α_P derived from speed of sound measurements. Dack [5] determined the internal pressure of several solutions at $T = 298.15$ K with a constant volume apparatus. The uncertainty in internal pressure determination via this method is about 2%. Dack [5] and Barton [6,7] also performed direct measurements of derivative $(\partial P/\partial T)_V$. This is the most frequently used method. Shukla *et al.* [8] studied internal pressure and its correlation with solubility parameter and pseudo-Gruneisen parameter for binary and multi-component liquid mixtures over a wide range of concentration at $T = 298$ K using the measured values of viscosity, density, and ultrasonic velocity. Grant-Taylor and Macdonald [9] directly measured thermal pressure coefficient of (acetonitrile + water) system at temperatures between (298 and 328) K. The measured values of $(\partial P/\partial T)_V$ were used to derive energy-volume $(\partial U/\partial v)_T$ coefficient and other thermodynamic quantities. Some authors [10,11] derived the values of internal pressure from direct measurements of the isothermal compressibility K_T and isobaric coefficient of thermal expansion α_P as

$$P_{\text{int}} = T\alpha_P K_T^{-1} - P. \tag{2}$$

Frequently some authors used the values of K_T and α_P derived from speed of sound and *PvT* measurements. Zorębski [10] studied the effect of pressure on the internal pressure. Marczak and Kielek [12] also used the strict thermodynamic relation (2) to calculate the internal pressure of eight binary aqueous mixtures. To calculate of K_T they used isobaric heat capacity C_P, isentropic compressibility K_S, and speed of sound data. Goharshadi and Nazari [13] studied temperature and pressure effect on the internal pressure of liquids using statistical mechanical equation of state. Kumar *et al.* [14] used measured ultrasonic velocity and density data to study internal pressure of binary mixtures (acetone-CCl_4 and acetone-benzene). The data were used to study the molecular interactions in binary liquid mixtures. Vadamalar *et al.* [15] also used acoustic and viscometric parameters to calculate the internal pressure for binary mixtures of tert-butanol and isobutanol with methyl methacrylate. Verdier and Anderson [16] used indirect method to estimate internal pressure of mixtures, using thermal expansivity (determined by microcalorimeter) and isothermal compressibility (determined by density measurements). Korolev [17] studied the internal pressure of alcohols using the values of volumetric coefficients (thermal expansion and isothermal compressibility coefficients). Suryanarayan [18] derived the following expression for the internal pressure on the basis of dimensional analysis using free volume concept

$$P_{\text{int}} = bRT\left(\frac{K\eta}{C}\right)^{1/2}, \tag{3}$$

where b is the packing factor, $K = 4.28 \cdot 10^9$ (in cgs units) is a constant (independent on temperature); η is the viscosity and M is the molar mass, and C is the speed of sound. Westwater *et al.* [19] and Smith and Hildebrand [20] measured $(\partial P/\partial T)_V$ directly using the constant-volume thermometer apparatus. The liquid is confined to a glass bulb with a capillary neck in which its level may be maintained at a fixed point by an electrical contact to a mercury interface. The coefficient $(\partial P/\partial T)_V$ is found directly as a slope of the graph of pressure against temperature for the liquid in such an apparatus. The isochoric P–T curves are nearly a straight line, except at the critical point, where the temperature dependence of the pressure $P(\rho_C, T)$ along the critical isochore is $\propto (T - T_C)^{2-\alpha}$. Therefore, their slopes are easy to determine in the range far from the critical point (in the liquid phase). The thermal-pressure coefficient changes smoothly $\gamma_V = (\partial P/\partial T)_V \propto (T - T_C)^{1-\alpha}$ with temperature without any anomaly, even at the critical point, although its first temperature derivative discontinuity (weakly diverges) at the critical point as $(\partial \gamma_V/\partial T)_V = (\partial^2 P/\partial T^2)_V \propto (T - T_C)^{-\alpha}$, where $\alpha = 0.11$ universal critical exponent of the isochoric heat capacity. The acoustic method was used by Dzida [21] to calculate the internal pressure of cyclopentanol at pressures up to 100 MPa and at temperatures from (293 to 318) K

$$P_{\text{int}} = \left[T\alpha_P\left(\frac{1}{\rho u^2} + \frac{\alpha_P^2 T}{\rho C_P}\right)^{-1}\right] - P. \tag{4}$$

Macdonald and Hyne [22] reported thermal pressure and energy-volume coefficient measurements for dimethyl sulfoxide–water mixtures at temperatures between (13 and 55) °C and at atmospheric pressure. McLure and Arruaga-Colina [23] reported thermal-pressure coefficient measurements for ethanenitrile, propanenitrile, and butanenitrile from $T = (297$ to $398)$ K. Measurements were made with an apparatus consisting of a constant-volume thermometer in which the pressure is controlled and measured for a series of temperatures at a series of different constant densities. McLure *et al.* [24] also measured the thermal-pressure coefficient for five dimethylsilioxane oligomers over the temperature range from (298 to 413) K. Thermal–pressure coefficients were measured in Pyrex cells (dilatometers). The sample was confined by mercury, and changes in its volume were monitored by weighing the amount of mercury expelled from or drawn into the dilatometer. Measured isochore slopes, $(\partial P/\partial T)_V$, were corrected using the effect of the thermal expansion and compression of both quartz and mercury. The uncertainty in thermal-pressure coefficient measurements is about 1.0%. Adams and Laidler [25] measured the compressibility of acetone at temperatures from (298 to 328) K and at pressures up to 0.1 GPa. These data were used to calculate the internal pressure which was used for interpretation structural properties of liquids. Kartsev *et al.* [26,27] studied the internal pressure and its relation with structure of liquids and liquid mixture. They studied the pressure dependence of the internal pressure and its temperature derivative using dilatometric apparatus.

2. Experimental

The *PvT* and thermal-pressure coefficient (γ_V) measurements of DEE were performed using the same apparatus as was employed for the isochoric heat capacity, $C_V vT$, measurements in our previous publications [28–39]. This is a high-temperature and high-pressure nearly constant-volume adiabatic piezo-calorimeter. The experimental details (the physical basis and the theory of the method, the apparatus, procedures of the measurements, and the uncertainty assessment) of the simultaneous measurements of isochoric heat-capacity $(C_V vT)$, thermal-pressure coefficient, $(\partial P/\partial T)_V$, and the *PvT* relationship have been described in our earlier publications [1–4,39]. Only a brief review will be given here. The pressure (P) and the thermal-pressure coefficient, γ_V, were measured with a highly accurate strain gauge (barograms technique). The measurements of pressure in the piezo-calorimeter were performed at constant temperature before the isochoric heat-capacity measurements. Then, after turning on the heater, both temperature changes