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Density, viscosity, and saturated vapor pressure of ethyl trifluoroacetate

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ABSTRACT

The properties of ethyl trifluoroacetate ($CF_3COOCH_2CH_3$) were measured as a function of temperature: density (278.08 to 322.50) K, viscosity (293.45 to 334.32) K, saturated vapor pressure (293.35 to 335.65) K. The density data were fitted to a quadratic polynomial equation, and the viscosity data were regressed to the Andrade equation. The correlation coefficient (R^2) of equations for density and viscosity are 0.9997 and 0.9999, respectively. The correlation between saturated vapor pressures and temperatures was achieved with a maximum absolute relative deviation of 0.142%. In addition, the molar evaporation enthalpy in the range of T = (293.35 to 335.65) K was estimated by the Clausius–Clapeyron equation.

1. Introduction

The trifluoroacetyl group has been widely used as an amine protecting group in organic synthesis due to the ease of its removal under mild conditions [1]. Therefore, ethyl trifluoroacetate (ETFA) acting as a powerful reagent has been recognized as an important fine chemical intermediate and widely used for preparing a variety of pesticides, pharmaceuticals, dyes, and liquid crystal. ETFA can also be used as solvent in the manufacture of other fine chemicals. It can be synthesized through the esterification reactions of trifluoroacetic acid with ethanol using homogeneous catalysts. A batch process for the preparation of ETFA by using sulfuric acid as catalyst was proposed by Amiet [2]. Zhang et al. used *p*-toluenesulfonic acid as catalyst to synthesis ETFA with the yield 75.9% [3].

Despite the fact that ETFA has been used in the manufacture of industrial chemical for a long time, there is scarce information available regarding its thermochemical properties in the literature. As we all know, a reliable thermodynamic model including physical and transport properties is of importance for the simulation and design of chemical process [4,5]. Hence, the present work is mainly focused on investigating density and viscosity of ETFA within the ranges of T = (278.08 to 322.50) K and T = (293.45 to 334.32) K, respectively, measuring saturated vapor pressure of ETFA by a static method at the temperatures between (293.35 and 335.65) K. Moreover, based on the present measurements, the experimental data of viscosity are correlated to the Andrade equation, and the relationship between the saturated vapor pressures and temperatures is correlated with the Antoine equation. Eventually, the molar vaporization enthalpy is derived from the temperature dependence of vapor pressure data.

2. Experimental section

2.1. Chemicals

ETFA used for the measurement of physical and transport properties was supplied by Aladdin Chemical Company with mass fraction purity of 0.9965. ETFA purity was checked by a gas chromatograph equipped with a PEG-20M capillary column (30 m · 0.32 mm · 0.50 μm). The refractive index value at 293.15 ± 0.1 K was determined by an Abbe refractometer (NAR-3T, ATAGO Co., Ltd.) with an accuracy of ±0.0001. And the measured value is n_D^{20} = 1.3086 which is in accordance with the literature data (n_D^{20} = 1.3079 [6], n_D^{20} = 1.3077 [7]). Methanol used to evaluate the accuracy of experimental apparatus was supplied by Sinopharm Chemical Reagent Co., Ltd. with the mass purity of 0.9998.

2.2. Density measurements

Density measurement of ETFA was carried out by using a calibrated glass pycnometer with a bulb volume of 50 cm^3. The volume of the pycnometer was calibrated as a function of temperature using distilled, deionized, and degassed water at various temperatures [8]. The pycnometer was cleaned, dried, weighed carefully, and filled with sample, then kept in a thermostat water bath with temperature control precision of ±0.01 K. When the thermal

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equilibrium reached, the pycnometer was taken out of the water bath and weighed again after being wiped. The measurements of density were accomplished at different temperatures. Each experimental density value was repeated three times, and the results were averaged.

2.3. Viscosity measurements

The liquid kinematic viscosity of ETFA was obtained by utilizing a commercial capillary viscometer of Ubbelohde type with capillary diameter of 0.36 mm. The flow time was recorded by a digital stopwatch with the precision of 0.01 s. Under the desired temperature, experiments were also accomplished in the thermostat water bath (as mentioned inSection 2.2). Each measurement was repeated 3 times and averaged as the final result, which was taken for the calculation of viscosities. The kinematic viscosity can be expressed as the following equation:

$$\upsilon = k \cdot t, \tag{1}$$

where υ is the kinematic viscosity, t is the flow time of ETFA in the viscometer, and k is the calibration viscometer constant supplied by the manufacturer with value of 0.001295 $mm^2 \cdot s^{-2}$. The dynamic viscosity can be calculated by the following expression:

$$\eta = \upsilon \cdot \rho, \tag{2}$$

where η is the dynamic viscosity, ρ is the density. To verify the reliability of the apparatus, the dynamic viscosities of methanol were measured in a range of temperature (302.45 to 333.85) K. The results were presented intable 1. It can be observed that the present experimental values of dynamic viscosity were in good agreement with those reported in the literature [9].

2.4. Saturated vapor pressure measurements

The saturated vapor pressure of ethyl trifluoroacetate was measured by a static method. Experimental procedure followed the process described by Elena and Oprea [10]. The schematic diagram of the apparatus is shown in figure 1.

Almost all of the apparatus were immersed in a thermostat water bath. A sample of ETFA (30 ml) was introduced into the equilibrium cell, degassed by the freeze–thaw method under vacuum for 20 min at the beginning of experiment. This step was carried out when coupling valve was open. After degassing, coupling valve was closed and the equilibrium cell connected with the U-shaped tube was immersed in the water bath, where the desired temperature was set. Once heated, vapors were emitted that caused different levels in the U-shaped tube. While two levels of the mercury remained constant for 30 min, air was introduced slowly into the system via an inlet valve until the mercury in two branches of the tube had the same level. At this time, the vapor pressure and temperature were noted, respectively. Each datum was measured for three times. In order to verify the reliability of the apparatus, the saturated vapor pressure of methanol was measured in the temperature range of (293.35 to 335.95) K and compared with the data reported by Lu [9] (as shown in table 2).

TABLE 1
Experimental and literature values for the viscosity of methanol at 101.3 kPa.[a]

T/K	η/mPa · s		RD^b/%
	Lit.	Exp.	
302.45	0.510	0.513	0.66
313.50	0.438	0.443	1.03
323.55	0.384	0.386	0.41
333.85	0.340	0.345	1.53

[a] Standard uncertainty u is $u(p) = 0.1$ kPa.
[b] $RD = (\eta_{Exp} - \eta_{Lit})/\eta_{Exp} \cdot 100\%$.

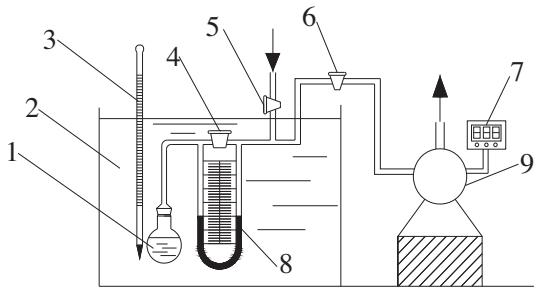

FIGURE 1. Apparatus for the measurement of vapor pressure 1, equilibrium cell; 2, thermostat water bath; 3, precision thermometer; 4, coupling valve; 5, inlet valve; 6, exhaust valve; 7, digital pressure indicator; 8, U-type tube with mercury; 9, vacuum.

TABLE 2
Experimental and literature values for the saturated vapor pressure of methanol.

p/kPa	T/K		RD^a/%
	Lit. [9]	Exp.	
13.54	293.94	293.35	−0.20
22.05	303.34	303.35	0.00
31.07	310.36	310.85	0.16
49.45	320.49	320.97	0.15
77.05	330.87	331.45	0.18
95.83	336.25	335.95	−0.09

[a] $RD = (T_{Exp} - T_{Lit})/T_{Exp} \cdot 100\%$.

3. Results and discussion

3.1. Density

Densities of ethyl trifluoroacetate were measured in the range of T = (278.08 to 322.50) K. The experimental data are shown in table 3 and the relationship between density and temperature for ETFA is presented in figure 2. From figure 2, it can be found that the present experimental pressure and temperature dependence for ETFA is an almost linear function. Because there is no theoretical guidance concerning the temperature dependence of density at atmospheric pressure, its evaluation is based on experimental data [11]. Therefore, the present measured densities for ETFA at 101.3 kPa were still fitted to the simple quadratic polynomial equation.

TABLE 3
Experimental densities of ETFA at 101.3 kPa as a function of temperature.[a]

T/K	ρ/kg · m^{-3}		RD^b/%
	Exp.	Cal.	
278.08	1218.9	1219.2	−0.029
285.15	1205.9	1205.5	0.030
289.23	1197.6	1197.6	0.001
293.68	1188.3	1188.9	−0.049
298.84	1179.0	1178.8	0.021
303.86	1168.0	1168.9	−0.073
307.89	1160.9	1160.9	0.002
312.65	1151.4	1151.4	−0.002
317.43	1142.2	1141.9	0.028
322.50	1131.3	1131.7	−0.038

[a] Standard uncertainty u are $u(T) = 0.01$ K, $u(p) = 0.1$ kPa and the relative standard uncertainty u_r is $u_r(\rho) = 0.0003$.
[b] $RD = (\rho_{Cal} - \rho_{Exp})/\rho_{Exp} \cdot 100\%$.