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PVT Measurements of Liquid Ethanol in the Temperature Range from 310 to 363 K at Pressures up to 200 MPa[1]

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Density measurements in the compressed liquid phase for ethanol were performed with a metal-bellows variable volumometer for temperatures between 310 and 363 K at pressures from the vapor pressure to 200 MPa. The results cover the high-density region from 727 to 882 kg · m^{-3}. The experimental uncertainties (total errors) of temperature, pressure, and density were estimated to be no greater than 3 mK, 0.1%, and 0.1%, respectively. Measurements of saturated liquid density at temperatures of 310, 340, and 360 K are also reported.

KEY WORDS: density; ethanol; *PVT* properties; saturated liquid density.

1. INTRODUCTION

Ethanol has been used as a natural refrigerant and a solvent. Recently it has attracted much attention for use as a cosolvent in supercritical fluid technology. We measured and reported the vapor pressures of this substance at temperatures from 310 to 400 K [1]. As a continuation of this investigation, we have been studying the thermophysical properties of ethanol in a wide range of temperatures and pressures. The present paper presents *PVT* measurements for liquid ethanol by the variable-volume method with a metal bellows in the temperature range between 310 and 363 K at pressures from the vapor pressure to 200 MPa. The measurements of saturated liquid density at 310, 340, and 360 K are also reported.

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2. EXPERIMENTS

The measurements were performed by a metal-bellows volumometer, by which densities of trifluoroethanol [2, 3], its aqueous mixtures [4–7], and ammonia [8] have been measured before. The apparatus and experimental procedures have been described in detail in our previous publications [2, 3, 5]. A sample of known mass was loaded into the bellows in a pressure vessel. Nitrogen gas was supplied to the outside of the bellows from the pressure-measurement system for compression or expansion of the bellows. The mass of the sample was measured with a precision chemical balance (Chyo Model C_2-3000) with an uncertainty of ± 2 mg. The inner volume of the bellows was calibrated from the known density of water with an uncertainty of $\pm 0.04\%$ as a function of temperature and the bellows displacement, because no pressure effect was found. The sample density was obtained from the mass of the sample and the inner volume of the bellows. We estimated the uncertainty (total error) in density measurements to be within $\pm 0.10\%$.

The pressure vessel was immersed in a thermostated bath filled with silicone oil, and its temperature was measured with the aid of a 25-Ω platinum resistance thermometer (Chino Model R 800-2) by a thermometer bridge (Tinsley Type 5840) on ITS-90. The thermometer was calibrated with a precision of ± 1 mK and its resistance at the triple-point temperature of water was measured periodically. We estimated the uncertainty (total error) in temperature measurements to be within ± 3 mK.

The pressure of the nitrogen gas was measured with three pressure gauges depending on the pressure range: an air-piston pressure gauge (Ruska Model 2465) for pressures below 7 MPa, and two oil-operated deadweight pressure gauges (Futaba Models T and TL2) for pressures above 7 and above 30 MPa, respectively. The sample pressure was obtained by subtracting the difference between internal and external pressures of the bellows from the pressure of the nitrogen gas. This pressure difference was calibrated as a function of temperature and the bellows displacement with an uncertainty of ± 0.4 kPa. We estimated the uncertainty (total error) in pressure measurements to be within ± 1.0 kPa for $p < 7$ MPa, $\pm 0.03\%$ for $p < 50$ MPa, $\pm 0.05\%$ for $p < 150$ MPa, and $\pm 0.10\%$ for $p > 150$ MPa.

A sample C_2H_5OH was supplied by Wako Pure Chemical Industries, Ltd. The reported purity was better than 99.5% on a volume fraction basis. The sample was purified by fractional distillation and dried by molecular sieve 4A for 36 h. Then it was degassed three or four times by the crystallization in vacuum before loading.

3. RESULTS

We carried out three experimental runs and obtained 113 measurements for *PVT* properties and 3 for saturated liquid density. The results given in Table I cover the density range from 727 to 882 kg · m $^{-3}$ for temperatures between 310 and 363 K at pressures from the vapor pressure to 200 MPa. Experimental series 1 was performd along four isotherms of 310.000, 313.140, 318.138, and 323.137 K and includes a single measurement of saturated liquid density at 310.000 K. The densities at 313.140, 318.138, and 323.137 K were measured under the same conditions of temperature and pressure as the literature values [9–12] for the purpose of comparison. Experimental series 2 was performed along four isotherms of 310.000, 323.137, 333.134, and 348.130 K. The measurements at 310.000 and 323.137 K were carried out for the purpose of examining the reproducibility of the present results. Those at 323.137, 333.134, and 348.130 K were carried out under the same conditions of temperature and pressure as the literature values [9–11] for the purpose of compatison. Experimental series 3 was performed along five isotherms of 310.000, 333.134, 340.000, 360.000, and 363.126 K including two measurements of saturated liquid density at 340.000 and 360.000 K. The measurements at 310.000 and 333.134 K were carried out for the purpose of examining the reproducibility of the present results. Those at 333.134 and 363.126 K were carried out under the same conditions of temperature and pressure as the literature values [9, 12] for the purpose of comparison.

Table I. Experimental Results for the Density of Ethanol

Temperature (K)	Pressure (MPa)	Density (kg · m $^{-3}$)
	Series 1	
310.000	200.00	881.77
	150.00	863.16
	100.00	841.28
	50.000	813.78
	0.9998	776.00
	0.0152[a]	775.00[b]
313.140	200.00	880.35
	100.00	839.36
	20.000	790.22
	0.0999	772.43
318.138	22.063	787.95
	2.7578	770.83

Table I. *(Continued)*

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
323.137	200.00	875.43
	189.70	871.64
	176.60	866.75
	100.00	833.29
	78.60	822.03
	40.000	797.97
	34.800	794.16
	29.500	790.12
	0.1001	763.59
	Series 2	
310.000	200.00	881.44
	150.00	862.79
	100.00	840.85
	50.000	813.36
	1.0004	775.69
323.137	200.00	874.65
	103.90	834.55
	29.500	789.58
	0.1000	763.13
333.134	200.00	869.35
	100.00	826.66
	40.001	790.06
	0.1001	754.03
348.130	196.20	860.27
	98.20	816.42
	29.500	770.15
	0.1003	739.93
	Series 3	
310.000	200.00	881.50
	150.00	862.76
	100.00	840.75
	50.000	813.26
	1.0002	775.79
333.134	200.00	869.42
	100.00	826.44
	39.999	790.09
	0.1001	754.01

Table I. *(Continued)*

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
340.000	200.00	865.98
	190.00	862.14
	180.00	858.29
	170.00	854.39
	160.00	850.42
	150.00	846.03
	140.00	841.58
	130.00	837.18
	120.00	832.46
	110.00	827.44
	100.00	822.44
	90.00	817.01
	80.00	811.24
	70.00	805.46
	60.00	798.95
	50.000	792.32
	39.999	784.87
	35.001	781.02
	30.000	777.12
	24.999	772.77
	20.000	768.24
	15.000	763.62
	10.000	758.55
	8.000	756.39
	5.9999	754.25
	5.0001	753.19
	4.0001	752.11
	3.0000	751.02
	1.9996	749.92
	1.4999	749.34
	1.0000	748.77
	0.5001	748.16
	0.1001	747.66
	0.0634[a]	747.62[b]
360.000	200.01	855.46
	190.00	851.75
	180.00	847.66
	170.00	843.43
	160.00	839.24
	150.00	834.97
	140.00	830.20
	130.00	825.36
	120.00	820.54
	110.00	815.21

Table I. (*Continued*)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)
	100.00	809.77
	90.00	804.24
	80.00	798.12
	70.00	791.93
	60.00	784.93
	50.000	777.75
	39.999	769.63
	34.999	765.45
	30.000	761.05
	25.000	756.24
	20.000	751.42
	15.000	746.07
	9.999	740.45
	8.000	738.21
	6.0001	735.77
	5.0000	734.48
	4.0000	733.08
	2.9998	731.76
	2.0000	730.42
	1.4998	729.75
	1.0000	729.08
	0.5000	728.38
	0.1407[a]	727.93[b]
363.126	22.063	750.75
	2.7578	728.23

[a] Vapor pressure.
[b] Saturated liquid density.

4. DISCUSSION

We measured densities for five pressures at 310.000 K by three series, for three pressures at 323.137 K by series 1 and series 2, and for four pressures at 333.134 K by series 2 and series 3. Percentage deviations in density measurements of series 1 and series 3 from the density measurements of series 2 are shown in Fig. 1. The density values of series 1 exceed those of series 2 by 0.04–0.05% at 310.000 K and by 0.06–0.09% at 323.137 K, respectively. The density values of series 3 agreed with those of series 2 within $\pm 0.02\%$ at 310.000 K and within $\pm 0.03\%$ at 333.134 K, respectively. The density values of series 1 exceed those of series 3 by 0.04–0.06% at 310.000 K.

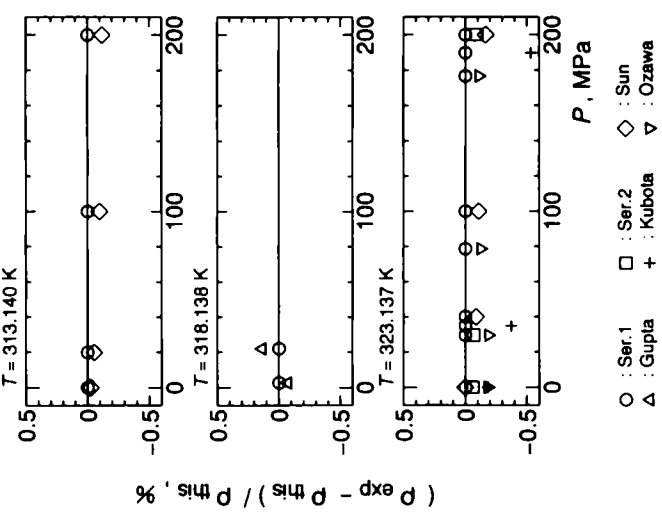

Fig. 2. Percentage deviations in density measurements of the literature values [9–12] from the present results at temperatures of 313.140, 318.138, and 323.137 K.

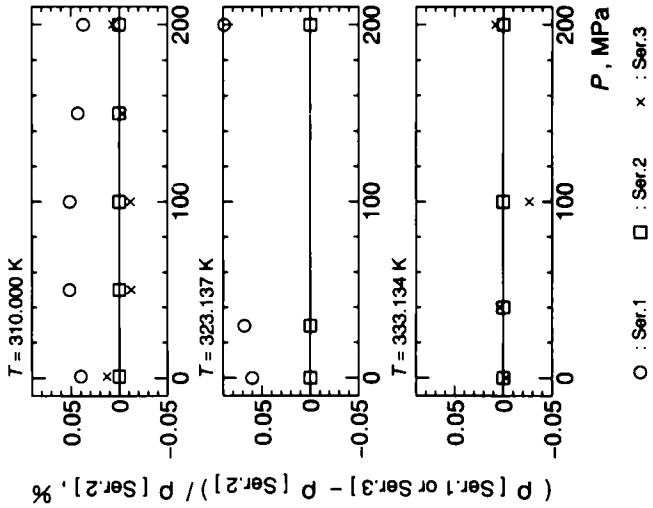

Fig. 1. Percentage deviations in density measurements of series 1 and series 3 from the density measurements of series 2.

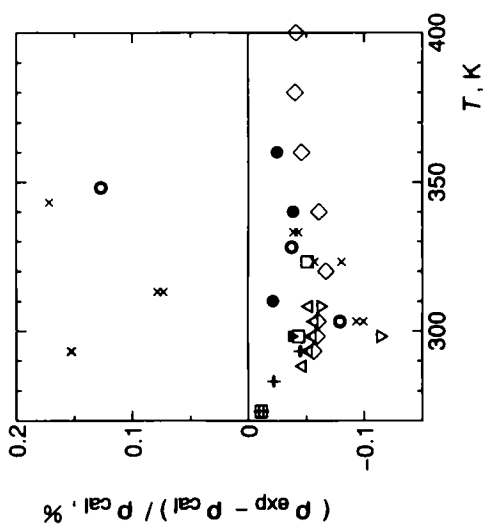

Fig. 4. Percentage deviations of the present results and the literature values [13–20] for the saturated liquid density from a correlation by Stephan and Hildwein [21].

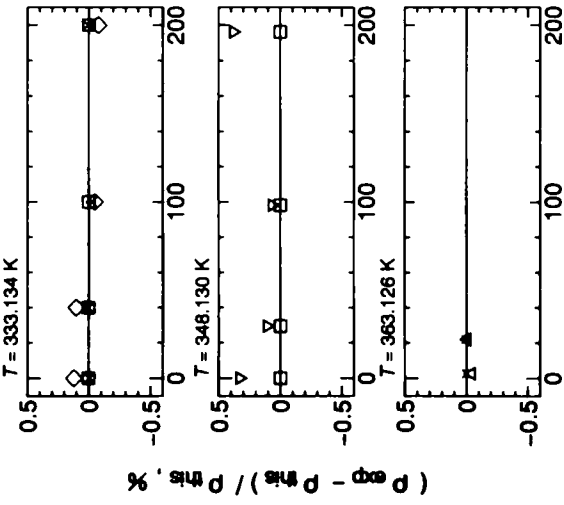

Fig. 3. Percentage deviations in density measurements of the literature values [9, 11, 12] from the present results at temperatures of 333.134, 348.130, and 363.126 K.

Figures 2 and 3 show percentage deviations in density values of the literature [9–12] from the present results. The data of Sun et al. [9] at 313.140 K exceed the present results by 0.03–0.12%. At 318.138 K, the data of Gupta and Hanks [12] exceed the present results by 0.14% at 22.063 MPa, and fall below them by 0.07% at 2.758 MPa. At 323.137 K the data of Sun et al. [9] agree with the present results of series 2 within ±0.1%. At 323.137 K the data of Ozawa et al. [11] and those of Kubota et al. [10] are lower than the present results by 0.11–0.19 and by 0.12–0.53%, respectively. At 333.134 K the data of Sun et al. [9] agree with the present results within ±0.12%. The data of Ozawa et al. [11] at 348.130 K are 0.07–0.38% above the present results. The data of Gupta et al. [12] at 363.126 K are 0.01–0.04% below the present results.

Figure 4 shows percentage deviations of the present results and of the literature values [13–20] for the saturated liquid density from a correlation by Stephan and Hildwein [21]. The present results agreed with the literature values except the data of Price [13] and those of Ling and Winkle [15] within a density deviation being smaller than the uncertainty of the present results.

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