Experiments
Учебен експеримент в природните науки

VAPOR PRESSURES OF 1-BUTANOL OVER WIDE RANGE OF THEMPERATURES

[1,2]Javid Safarov, [2]Bahruz Ahmadov, [2]Saleh Mirzayev,
[2]Astan Shahverdiyev, [1]Egon Hassel
[1]University of Rostock, Germany
[2]Azerbaijan Technical University, Azerbaijan

Abstract. Vapor pressure (VLE) of 1-butanol was studied at temperatures T=(274.15 K to 468.15) K using the two different static method installations. A glass cell was used below T = 323.15 K. Experimental uncertainties for the glass cell are ΔT = ±0.01 K and ΔP = ±(10 to 30) Pa (MKS Baratron pressure sensor). A metal cell was used in the range T = (323.15 to 468.15) K. Experimental uncertainty of temperature measurements for the metal cell is ΔT = ±0.01 K. Pressure was measured with two different 35 X HTC Omega-Keller pressure transmitters. Reproducibility of the vapor pressure measurements was ΔP = ±1.5 kPa for the pressures below P = 300 kPa and ΔP = ±5 kPa in the range P = (300 to 1000) kPa is. A fundamental literature analysis of 1-butanol has been done and experimental values were compared with the literature data. Observed deviation have been discussed. Measured values were fitted with the Antoine and Clausius-Clapeyron type equations. The best fit is that by Clausius-Clapeyron equation with four parameters.

Keywords: 1-butanol, vapor pressure, wide range of temperatures, Clausius-Clapeyron type equation

Introduction

The price of traditional fuel is increasing every day. Alternative and renewable energy sources such as solar, wind energy, bio-diesel and biogas are becoming very important in many countries. 1-butanol has been proposed as an alternative to conventional gasoline and diesel fuels. Use of 1-butanol as an alternative to conventional gasoline and diesel fuels dramatically increased last years. It can be successful used as a fuel in an internal combustion engine. Butanol has been demonstrated to work in vehicles with gasoline engines without modification. 1-butanol can be produced from biomass (Bernardes, 2011).

A challenge is caused by the use of 1-butanol as a fuel at very high pressures. Current fuel injection systems of compression-diesel engines reach pressures up to 200 MPa for transport systems. In a near future, injection systems can be designed for higher pressures up to 400 MPa. Number of injections at such high pressures per cycle can be expanding and the time of one injection process can be reduced. That is why it is so important to have reliable knowledge of thermophysical properties of the fuel under high pressures. Upon injection of the fuel in a cylinder, large depressurization of the fuel results in a significant change of the viscosity and other properties of the fluid (Duncan et al., 2010). Study of basic thermophysical properties (density, vapor pressure, viscosity, speed of sound, heat capacity etc.) of 1-butanol would allow modeling, understanding, and optimizing the processes in an internal combustion engine.

A new method for the analysis of thermophysical properties of substances at high pressures and over wide range of temperature was developed by our research group (Safarov et al., 2013). This work is an application of that method to 1-butanol. The entire research consists of the following parts: (i) (p,ρ,T) properties of 1-butanol at T = (253.15 to 468.15) K and at pressures up to p = 200 MPa; (ii) vapor pressure measurements P/Pa of 1-butanol at T = (274.15 to 468.15) K; (iii) heat capacity measurements $c_{p0}/(\mathrm{J \cdot kg^{-1} \cdot K^{-1}})$ of 1-butanol at T = (253.15 to 468.15) K and at ambient pressure.

1-butanol has the normal boiling temperature around T_s=390.65 K. Vapor pressure in a wide temperature range must be consistent with the heat capacities of the condensed and gas phases. Measurement of density at elevated pressures allow construction of an EOS and propagation of the knowledge of all thermophysical properties to high pressures.

Publications on vapor pressure of 1-butanol have been reviewed and the summary of these works are presented in the Table 1. The first investigation of the vapor pressure of 1-butanol was by Butler et al. (1935). He used a modification of the isotensiscope method for determination of vapor pressure of 1-butanol at T=(293.13 to 383.35) K. It was found possible to keep the temperature of the bulb constant to ΔT = ±10 mK, below T=373.15 K and ΔT = ±20 mK, above T=373.15 K in one experiment by manual handling. The precision of the vapor pressure results was better than ΔP =±6.67 Pa.

Shemilt et al. (1959) measured vapor pressure of 1-butanol at T=(273.15 to 560.15) K. The 1-butanol (c.p. grade) was distilled at high reflux in a glass-helices packed column. The calculated vapor pressure values in a wide range of temperature was also presented. The uncertainty of stabilised temperature was around ΔT = ±30 mK. The pressure was measured using a dead-weight test gauge with an uncertainty of ΔP = ±0.1 %.

Brown & Smith (1959) studied liquid-vapor equilibrium for the systems n-propanol+benzene and n-butanol+benzene at T=318.15 K. The data were used to calculate the excess free energy of mixing for these systems.

Ambrose & Townsend (1963) investigated vapor pressures of 1-butanol using a vertical glass tube apparatus, which was held in a metal fitting and communicated via a mercury-filled tube and another glass tube with an oil-operated, dead-weight piston-gauge. The pressure exerted by the vapor was the sum of the barometric pressure, that determined from the gauge, and the hydrostatic heads of oil, mercury, and alcohol. The standard instrument for the temperature measurements was a platinum resistance thermometer used with a Mueller bridge.

Biddiscombe et al. (1963) measured vapor pressure of 1-butanol at T=(362.36 to 398.84) K using the comparative ebulliometry. The compounds used in this work were dried by treatment with calcium hydride and were >99.9% pure. The precision of the vapor-pressure results was better than ΔP =±13.3 Pa.

Efremov (1966) studied vapor pressure of 1-butanol at T=(353.15 to 553.15) K using the capillary ampoule method. The temperature were measured with the uncertainties in ΔT = ±100 mK.

Kemme & Kreps (1969) used a differential thermal analysis method for the experimentally determination of vapor pressure of 1-butanol over a wide range of temperature at T=(295.75 to 390.95) K. The Chromel-Alumel thermocouples used during the measurements of temperature. The temperature values are averages of several replications at the stated pressures; at most they varied ΔT = ±100 mK between replications. The experimental data obtained for each compound were fitted by the Antoine equation.

Ambrose & Sprake (1970) investigated vapor pressures of 1-butanol using the vertical glass tube apparatus, which was held in a metal fitting and communicated via a mercury-filled tube and another glass tube with an oil-operated, dead-weight piston-gauge. The pressure exerted by the vapor was the sum of the barometric pressure, that determined from the gauge, and the hydrostatic heads of oil, mercury, and alcohol. The standard instrument for the temperature measurements was a platinum resistance thermometer used with a Mueller bridge.

Koba & Polishchuk (1971) and Polishchuk & Koba (1972) used the Clausius-Clapeyron type equations for fitting of literature vapor pressure values of 1-butanol. The first equation was developed for the describing of vapor pressure results up to P=101.325 kPa. The second equation is able to describe the vapor pressure values of 1-butanol from P=(101.325 to 5066.250) kPa. The authors suggested the uncertainty of developed equations ΔP = ±(1 to 3)%.

Munday et al. (1980) measured vapor pressure of 1-butanol over the T=(273.15 to 323.31) K temperature range with the static method. The maximum estimated error in the pressure reading is the less than 20 Pa. Temperatures (IPTS 68) are measured by using a platinum resistance thermometer calibrated by the National Bureau of Standards.

Krestov et al. (1983) studied vapor pressure of 1-butanol at T=(298.15 to 368.15) K using the static method. The Antoine equation was used for fitting of the experimental results.

Gregorowicz et al. (1987) measured vapor pressure of 1-butanol in T=(360.766 to 390.542) K temperature interval using a modified Swietoslawski ebulliometer. The equilibrium temperature was measured within 0.001 K. Temperature fluctuation during runs lasting several hours was within $\Delta T = \pm 10$ mK. Pressure was determined using a Texas Instrument 144-01 precision pressure gauge with a quartz Bourdon tube. The estimated pressure measurement error was not greater than $\Delta P = \pm 6.67$ Pa. The Antoine equation was used for fitting of the experimental results.

Tsymarniy & Palaguta (1990) studied vapor pressure of 1-butanol at T=(283.10 to 323.2) K using a constant volume piezometer. The vapor pressures of 1-butanol were measured using VTI type manometers with uncertainties 0.5%. The temperature of measurements was controlled within 0.1 K. The Mayer-Bogolyubov equation was used for fitting of the obtained results.

Shahverdiyev et al. (1992) measured (p,ρ,T) values of 1-butanol up to T=548.15 K. The constant volume piezometer method was used during the measurements the. The vapor pressure of 1-butanol was defined for the each density measured temperature. The uncertainties of experimental data measurements were as follows: for pressure ±0.05%, for temperature ±30 mK.

Gracia et al. (1992) measured vapor pressure of 1-butanol at temperatures T=(283.10 to 323.12) K using the static method. 1-butanol (better than 99.5 moles per cent) was Fluka products. The mass fraction purities checked by g.c. was w=0.9933. The cell containing 1-butanol was immersed in a water bath whose temperature was maintained constant to better than $\Delta T = \pm 0.01$ K using a Haake F3 thermostat. Manometer readings were made with a Wild KM-305 cathetometer to ±0.01 mm. Reproducibility of the pressure measurements is estimated to be better than $\Delta P = \pm 15$ Pa. Vapor pressure of 1-butanol were fitted by Antoine equation.

Deák et al. (1995) studied vapor pressure (bubble point pressures) of 1-butanol at temperatures T=(412.76 to 502.25) K in a high-pressure capillary glass tube apparatus, using the Cailletet apparatus synthetic method. During the experiments the temperature was maintained constant within $\Delta T = \pm 0.03$ K and was measured with a Ptl00 resistance thermometer, which was calibrated against a standard thermometer, with an accuracy of $\Delta T = \pm 0.01$ K. The pressure was measured with a dead-weight gauge (Budenberg) with an accuracy within $\Delta P = \pm 1$ kPa.

Gimeno et al. (2011) investigated vapor pressures of 1-butanol at temperatures T=(278.15 to 323.15) K by a static method. Manometric levels were read with a cathetometer to within ±0.01 mm, and pressure reproducibility was $\Delta P = \pm 10$ Pa. Experimental vapor pressure data of 1-butanol were fitted by the Antoine equation. The temperature of the liquid was measured by means of a digital thermometer ΑΣΛ with a Pt sensor with an uncertainty of $\Delta T = \pm 0.01$ K.

After the analysis of the available literature values we concluded that despite many measurements have been done and high accuracy was claimed, their results differ in the whole range (Figs. 4-5) in absolute and per cent deviations, so additional reliable measurements are necessary for arbitration.

Experimental

Materials

Ultra-pure 1-Butanol EMPLURA® (w=99.995%) was purchased from Merck Schuchardt OHG, Germany (CAS No. 71-36-3, Art. Nr. 8.22262.2500). 1-Butanol was thoroughly degassed in glass flasks with special vacuum leak-proof valves before measurements.

Experimental procedure

Vapor pressure of 1-butanol measured using the two high-accuracy static experimental installations (Figs. 1 and 2). Glass cells (3, 4, 27) are applied for vapor pressures lower than ambient pressure and at T=(274.15 to 323.15) K (Fig. 1). A metal cell was applied at the temperatures T= (323.15 to 473.15) K (Fig. 2). The glass-cell installation included the absolute and differential parts. They have internal and external volumes. Distilled water pumped from Lauda Gold R-415, Germany (21) was flowing between them. Figure 1shows the water connections of the stabilization of measuring cells and pressure head sensors in blue, electric heaters in red, and temperature measurement circuit in green. The internal volume of every measuring cell was approximately 80 cm^3 for both glass and steel cells.

The glass-cell apparatus consists of a bolted-top cell (27) in a water bath kept at constant temperature (ΔT= ±0.01 K) using a thermostat (21). The measuring cell is equipped with an injection port. The vapor pressure is measured using a calibrated high-accuracy sensor head (23) [Type 615A connected (15) to the signal conditioner Type 670A (14), MKS Baratron, USA] attached to the top of the cell. The experimental uncertainty of the pressure in the absolute vapor pressure measurement part with glass cell is ΔP = ±(10 to 30) Pa (MKS Baratron pressure sensor). The temperature inside the cell was measured by a platinum resistance thermometer PT-100 (35), connected to the signal conditioner Omega PT-104A (19), with an accuracy of ΔT = ±0.001 K.

If the vapor pressure of substance is the smaller than ±(10 to 30) Pa (uncertainty of measurements), the measurements can be carried out using other cells in the differential part of the system. In this part two cells contained in one external reservoir. The both glass cells of differential method (3, 4) kept at constant temperature (ΔT = ±0.01 K) using a Lauda Gold R-415 thermostat, Germany (21). The temperature inside the cells was measured by a platinum resistance thermometer PT-100 (6), connected to a signal conditioner Omega PT-104A (19), with an accuracy of $T \pm 0.001$ K. The measuring cells are equipped with injection ports. The vapor pressure was measured using a calibrated high-accuracy sensor head (10) [Type 616A connected (12) to a signal conditioner Type 670A (13), MKS Baratron, USA] attached to the top of the cell. The experimental uncertainty of the vapor pressure in the differential part with glass cell is $\Delta P = \pm(1 \text{ to } 3)$ Pa (MKS Baratron pressure sensor).

Both sensor heads of static and differential parts (10, 23) were placed inside of air reservoirs (11, 22) with temperature T=333.15±0.01 K having internal and external walls, between which hot water was pumped from the thermostat (16) produced by Haaki (Germany).

The received pressure signal from signal conditioners (13, 14) and temperature signals from Omega PT-104A (19) were sent to PC (34), and all system was controlled using LabVIEW programme.

Because the vapor pressure of 1-butanol is higher than the uncertainties of measurements in all temperatures, the differential part of this installation was not used during this investigation.

Before the experiments, the measuring cell was washed with the water and acetone. All fluid parts removed from cells using the vacuum system (31, 32) with TRIVAC® (Germany) rotary vane vacuum pump (33). These procedure continue appr. 3-5 hours up to reach the pressure less than 1 Pa. All measuring cells were dried and became ready for the experiments.

Prior to injection into the measuring cell, 1-butanol is degassed in the special designed cell using magnetic stirrer (29, 30). A known quantity of 1-butanol were injected into the equilibrium cells (4, 27) from connections (7, 20) (appr. 50 % of the volume) and valves (7, 26) were closed. Some part of pure 1-butanol separated from the measured sample, moved to the vapor phase under vacuum conditions inside of the cell, and vapor-liquid phase equilibrium between the vapor and liquid phases of 1-butanol was reached by stirring of the two phases using magnetic stirrers (1,28) and a Teflon coated magnets (2, 36) inside the cells.

The measuring glass cell and metal tube connection of signal conditioner MKS Baratron (measuring cell - signal conditioner connection) was impossible to connect directly. In this case a special “glass-metal” adapter was connected to the measuring glass cell. The flange connections DN 10 short (VAT Deutschland GmbH, Germany) were set to the end of metal side of the “glass-metal” adapter and to the metal tube connection site of signal conditioner MKS Baratron. The clamping ring and centering ring were used for the connection of both side of flange connection. The cells and signal conditioners

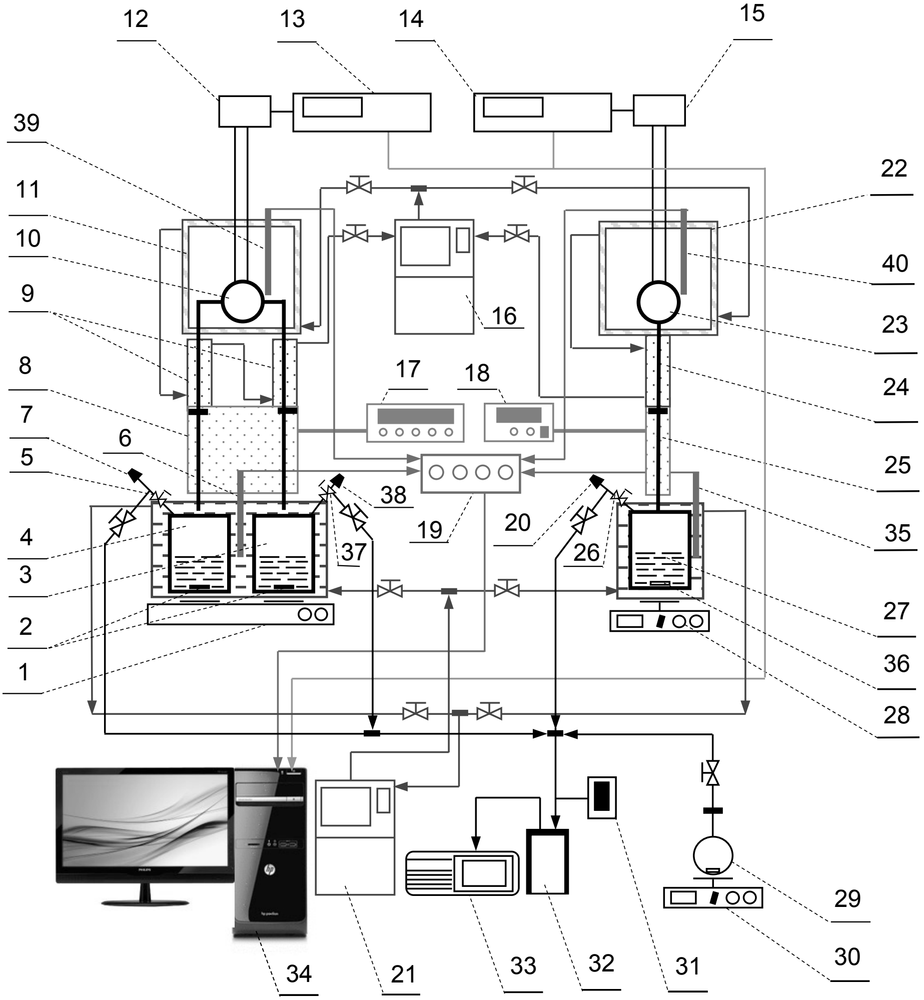

Figure 1. The experimental installation for the vapor pressures at T=(274.15 to 323.15) K: (1), (28), (30) magnetic stirrer; (2), (36) magnet, (3) cell for water of the difference method; (4) cell for measuring sample of the difference method; (5), (37) valves for closing of cell for measuring sample of the difference method and (26) of the static cell; (6), (35), (39), (40) platinum resistance thermometers with temperature signal conditioner Omega PT-104A (19); (7), (20), (38) injection ports of measuring sample; (8), (25) electric heating; (9), (24) water heat exchange system; (10) pressure sensor head of the difference method and (23) of static cell; (11) pressure sensor reservoir of the difference method and (22) of the static method cell; (12) pressure signal connection of the difference method cell and (15) of the static method cell; (13) pressure signal conditioner of the difference method and (14) of the static method cell; (16) Thermostat HAAKE F5; (17), (18) electric heater control systems; (21) Thermostat Lauda Gold RE-630 G; (27) static cell; (29) injection cell; (31) vacuum indicator; (32) liquid nitrogen trap with cold finger; (33) vacuum pump; (34) PC.

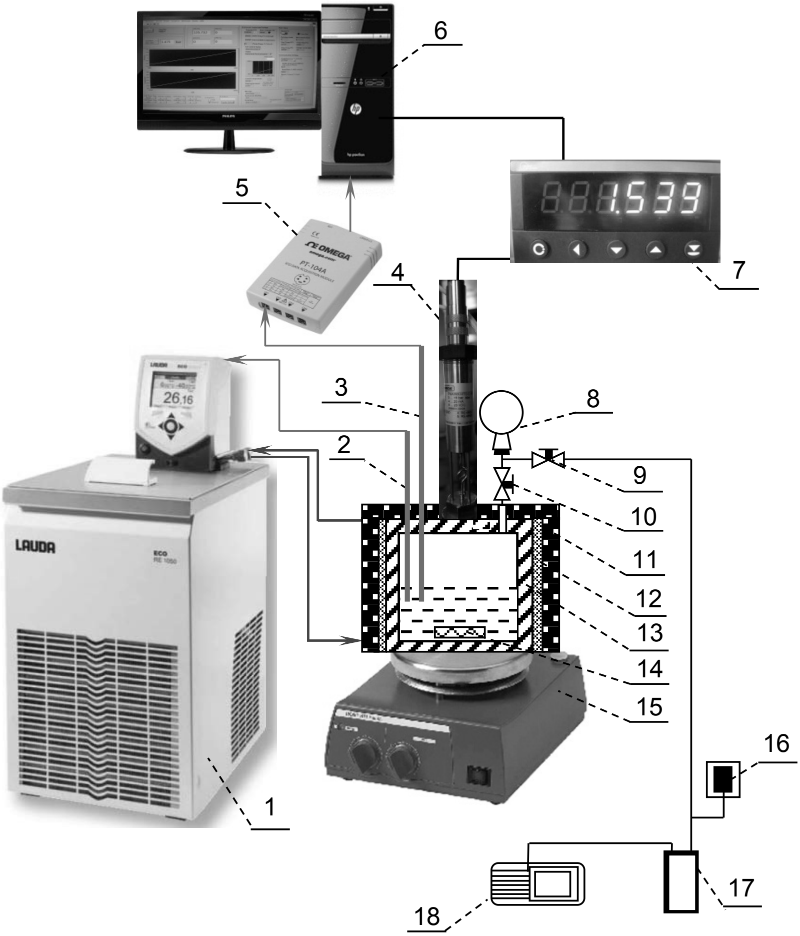

Figure 2. The experimental installation for the vapor pressures at T=(333.15 to 468.15) K: (1) Thermostat Lauda Gold RE-415 G; (2) platinum resistance thermometers PT-100 for the control of the measuring cell temperature by the thermostat; (3) platinum resistance thermometer PT-100 for the control of temperature of the measuring cell; (4) Pressure transmitter 35 X HTC Omega GmbH and Co.; (5) Omega PT-104A Channel RTD Input Data Acquisition Module for the measuring of temperature; (6) PC; (7) Manual pressure signal conditioner; (8) Flask for the sample; (9), (10) valves; (11) insulation of measuring cell; (12) heat transfer reservoir; (13) measuring cell; (14) magnet; (15) magnetic stirrer; (16) vacuum indicator; (17) liquid nitrogen trap with cold finger; (18) vacuum pump.

located appr. 40 cm from each other. The connections between them are "glass-metal" adapter and metal tube with 3.5 mm inside diameter. The metal tube part of the measuring cell - signal conditioner connection were stabilized using a water heat exchanger (9, 24), where water flowed from reservoirs (11, 22) with a constant temperature T=333.15±0.01 K. However, it was impossible to make the same isolation using water flow in the other side of this connection, where ring and centering ring were clamped. In this case, the electric heating (8, 25) with isolation were used. The heating was controlled during all experimental procedures using the electric regulators (17,18). In both cases (absolute and difference methods) vapor pressure of reference substances (water, methanol, acetone, ethanol, toluene, various substances with small vapor pressures) were tested many times for regulation of electric heating power at every measured temperature, and these functional dependence were included to the LabVIEW control programme. In this case, PC added the necessary power to the electric heaters during the measurements.

Equilibration in the cells is a rapid process and the constancy of pressure in the stationary regime is reached within 15 min. Equilibrium pressure readings are performed in triplets with approximate 10-20 min intervals. PC received the vapor pressure signal every minute and tracked the stabilization of pressure in the cell. After these the temperature was changed automatically using the LabVIEW programme. The measurements were carried out from the low temperature (T=274.15 K) to high (T=323.15 K) with required temperature steps. After the reaching of maximal temperature the thermostat was stopped automatically. Then the measurements from high temperature (T=323.15 K) to low (T=274.15 K) were done in the same way. Manually-controlled measurements were also possible.

Vapor pressures of the water, methanol, acetone, toluene *etc.* as reference substances were measured for testing of both installations. The vapor pressure results of pure water and comparison of them with calculated results from (Wagner & Pruß, 2002) are given in Table 2. The experimental vapor pressure P/Pa results are assessed to be reliable to within $\Delta P = \pm$ (10 to 30) Pa average uncertainty according to test measurements.

The experiments to determine vapor pressure of 1-butanol at temperatures T=(323.15 to 468.67) K were performed in a metal cell by using the static method (Fig. 2). In the Fig. 2, the connections for heat transfer fluid between the thermostat (1) and measuring cell (13) are shown in blue. The connections for the temperature measurements are shown in green and for the pressure measurements in black.

The installation consists of a stainless-steel DIN 1.4571 (V4A) measuring cell (13) in a stainless-steel KORASILON oil M50 (Kurt Obermeier GmbH & Co. KG, Germany) reservoir. The internal volume of the measuring cell is appr. 140 cm^3 together with the connected tube, hole of the pressure transmitter and ½ volume of the valve (10). The volume of platinum resistance thermometers PT-100 (2, 3) in the inside of measuring cell is calculated as a volume difference.

The temperature of the measuring cell and heat transfer reservoir (12) with KORASILON oil M50 (Kurt Obermeier GmbH & Co. KG, Germany) is stabilized using the thermostat (1) (LAUDA ECO RE 415 G, Germany) with the accuracy ΔT=±0.01 K. This temperature are measured using two different platinum resistance thermometers PT-100 (1/10 DIN Class B, Temperatur Messelemente Hettstedt GmbH, Germany) (2, 3). One from them is connected a directly to the thermostat via PT-100 Libus Modul. This thermometer transfers information directly from the measuring cell. Using this thermometer, the thermostat maintains the temperature directly in the measuring cell, not in the thermostat itself. This is a very important point, because it enables stabilization and measuring the experimental temperature with high accuracy directly in the studied medium.

The second platinum resistance thermometers PT-100 transfers the measured temperature in the computer via Omega PT-104A Channel RTD Input Data Acquisition Module (Omega Engineering, inc., USA) for the measuring of temperature (5), with an accuracy of ΔT=±0.001 K.

The vapor pressure was measured using the two various Omega-Keller pressure transmitters (4) with max. 3 and 10 bar measured pressures (Model: SERIE 35 X HTC, Omega GmbH & Co., Germany) with the uncertainty 1.5 kPa for pressures up to P=300 kPa and ΔP = ±5 kPa and at P = (300 to 1000) kPa. These high-temperature transmitters are suitable for media temperatures up to T=573.15 K. The pressure, acting onto the flush diaphragm, is transferred over an oil-filled capillary to the silicon measuring cell. The capillary has the function of a cooling spiral, allowing media temperatures of up to T=573.15 K. The temperature of the electronics, which can be read out with the PROG30 software, may not exceed T=393.15 K. For this purpose two air fans were installed in the pressure transmitter area.

Before the experiments the measuring cell was washed. All fluid parts were removed from the measuring cells using the TRIVAC® rotary vane vacuum pump (18) and the vacuum system (16, 17). The measuring cell was dried up to a pressure P=(10 to 30) Pa and became ready for the experiments. The valve (9) was closed. A known quantity of 1-butanol (appr. ½ part of volume of the measuring cell) was injected in the measuring cell using a flask of sample (8) and after that the valve (10) was closed. Phase equilibrium is reached by stirring of the two phases using a magnetic stirrer (15) and a Teflon coated magnet (14) inside the measuring cell. Equilibration in the measuring cell is a rapid process, and the constancy of pressure is reached within appr. 50-70 min. Equilibrium pressure readings are performed with 1 min intervals and transferred to the computer system controlled using the LabView program. Experiments were carried out starting from small temperature (T=333.15 K) to high temperature T=468.67 K with ΔT=10 K intervals. After stabilization of the pressure within the system and measuring of vapor pressure at the given temperature the PC (6) with LabView programme increases the temperature using the pre-defined step. The new vapor pressure of sample is measured. This procedure continues up to the last measured temperature T=468.67 K, after which the PC (6) stops the thermostat (1) and the measurements at T=(333.15 to 468. 67) K is finished. The total measurements at T=(333.15 to 468.67) K take approximately 10 hours. After scanning the temperature range, the measurements were continued from the high T=468.67 K to the low T=333.15 K using the cooling process in the thermostat for verification.

Table 1. Summary of the vapor pressure measurements for 1-butanol over wide range of temperatures

First author	Year	Method	Properties	Temperature, T/K	Uncertainty, $\pm \Delta P$/Pa	Fitted equation	Purity	Company of Purchase
Butler	1935	IM	P,T	293.13 to 383.35	6.67	Antoine type		
Kay	1955		P,T	463.15 to 562.89	appr. 138		h.p.	
Shemilt	1959		P,ρ,T	273.15 to 560.15		Clapeyron	c.p.grade	
Brown	1959		P,T	318.15				
Ambrose	1963	GA	P,ρ,T	419.34 to 562.98		Frost and Kalkwarf		
Biddiscombe	1963	CE	P,ρ,T	362.36 to 398.84	13.3	Antoine	w>99.9%	
Efremov	1969	CA	P,ρ,T	353.15 to 553.15			c.p.	CSFCR
Kemme	1969	DTA	P,T	295.75 to 390.95		Antoine		
Ambrose	1970	CE	P,T	351.708 to 398.836		Antoine, Cragoe		
Munday	1980	SM	P,T	273.15 to 323.31		CCT		
Krestov	1983	SM	P,T	298.15 to 368.15		Antoine type		
Gregorowicz	1987	SE	P,T	360.766 to 390.542	6.67	Antoine	w>99.95%	CHEMIPAN
Tsymarniy	1990	CVP	P,T	298.2 to 323.2	0.6 %	Mayer-Bogolyubov	c.p.	CSFCR
Shahverdieyev	1992	CVP	P,ρ,T	398.15 to 548.15	0.5 %		c.p.	CSFCR
Gracia	1992	SM	P,T	283.10 to 323.12	10	Antoine	w>99.33%	Fluka
Deák	1995	CA	P,T	412.76 to 502.25	1000		w>99.9%	Baker
Gimeno	2011	SM	P,ρ,T	278.15 to 323.15	10	Antoine	w>99.99%	Aldrich
Safarov	2014	SM	p,T	274.15 to 323.15	10 to 30	CCT	w>99.995%	Merck AG
Safarov	2014	SM	p,T	333.15 to 468.67	1000 to 8000	CCT	w>99.995%	Merck AG

IM, the isotensiscope method; *P*, vapor pressure; *T*, temperature; h.p., high purity; GA, glass apparatus; CE, comparative ebulliometry; CA, capillary ampoule; CASM, Cailletet apparatus; DTA, differential thermal analysis; SM, static method; CCT, Clausius-Clapeyron type; SE, Swietoslawski ebulliometer; CVP, constant volume piezometer; CSFCR , Cherkassiy state factory of chemical reagents; *w*, weight percent; c.p., chemical pure; t.w., this work.

Table 2. Experimental and calculated literature values (Wagner & Pruß, 2002) of vapor pressure p of pure water

T/K	P_{exp}/Pa	P_{lit}/Pa	(P_{exp}- P_{lit})/Pa	T/K	P_{exp}/Pa	P_{lit}/Pa	(P_{exp}- P_{lit})/Pa
274.15	661	657	4	328.14	15748	15754	-6
279.48	953	961	-8	328.14	15746	15754	-8
286.16	1508	1502	6	328.88	16312	16321	-9
291.39	2094	2096	-2	333.15	20056	19946	110
293.14	2337	2338	-1	343.15	31279	31201	78
296.32	2834	2840	-6	353.15	47450	47414	36
296.31	2839	2838	1	363.15	70210	70182	28
298.81	3288	3297	-9	373.15	101425	101418	7
301.37	3827	3832	-5	383.15	143287	143379	-92
303.57	4360	4351	9	393.15	198752	198674	78
307.73	5507	5500	7	403.15	270216	270280	-64
308.26	5666	5664	2	413.15	361642	361539	103
312.87	7275	7276	-1	423.15	476334	476165	169
313.07	7345	7354	-9	433.15	618336	618235	101
314.62	7977	7984	-7	443.15	792154	792187	-33
318.13	9585	9585	0	453.15	1002713	1002811	-98
318.13	9578	9585	-7	463.15	1255226	1255236	-10
322.99	12260	12254	6	468.15	1398871	1398820	51
323.10	12320	12321	-1	470.15	1459748	1459719	29
323.17	12362	12364	-2	471.15	1490952	1490935	17

Results and discussion

The measured experimental vapor pressures p of 1-butanol at T=(274.15 to 468.67) K are listed in Table 3, also shown in Fig. 3. The temperature steps were ΔT=(5 to 10) K. The obtained experimental works are fitted to two different equations. Firstly, the experimental vapor pressure p results of 1-butanol were fit to the Antoine equation:

$$\ln(P/\text{Pa}) = A - B/\{(T/\text{K}) + C\} \qquad (1)$$

The evaluated constants *A, B* and *C* are tabulated in Table 4 together with the standard mean deviation as:

$$\Delta P/P = 100/n \cdot \sum_{i=1}^{n} \left[(P_{\text{exp.}} - P_{\text{cal.}})/P_{\text{exp.}} \right] \qquad (2)$$

During the fitting of experimental values, we have seen, that Antoine equation fit the experimental values with not high accuracy. The uncertainty of fitting is $\Delta P = \pm 1297$ Pa. But, use of the extended version of Clausius–Clapeyron equation for fitting of the vapor pressure data for 1-butanol reduced the fitting error:

$$\ln P = \mathrm{A} + \frac{\mathrm{B}}{T} + \mathrm{C} \ln T + \mathrm{D}, \qquad (3)$$

where P is vapor pressure, Pa; T is the absolute temperature in K; A, B, C and D are the coefficients of equation. The uncertainty of fitting is decreased up to $\Delta P = \pm 38$ Pa. If the last coefficient D will be equal to zero (D=0), the uncertainty of fitting increasing up to $\Delta P = \pm 199$ Pa. That is why the Clausius–Clapeyron type equation with four coefficients (A, B, C, D) was selected as the final fitting equation for the vapor pressure of 1-butanol. The coefficients of Eq. (3) are tabulated in Table 5. The fitting line also shown in the Fig. 3b.

Table 3. Experimental and calculated by Clausius-Clapeyron equation values of vapor pressure *p* of 1-butanol

T/K	P_{exp}/Pa	P_{cal}/Pa	(P_{exp}- P_{cal})/Pa	T/K	P_{exp}/Pa	P_{cal}/Pa	(P_{exp}- P_{cal})/Pa
274.15	133	133	0	373.15	51825	51787	38
278.15	188	188	0	383.15	76225	76210	15
283.15	285	286	-1	393.15	109178	109219	-41
293.15	624	625	-1	403.15	152632	152774	-142
303.15	1281	1284	-3	413.15	208708	208994	-286
313.15	2483	2487	-4	423.15	279656	280108	-452
323.15	4571	4573	-2	433.15	367818	368407	-589
333.15	8030	8027	3	443.15	475581	476185	-604
343.15	13517	13504	13	453.15	605332	605682	-350
353.15	21890	21864	26	463.15	759418	759025	393
363.15	34224	34187	37	468.67	855726	854610	1116

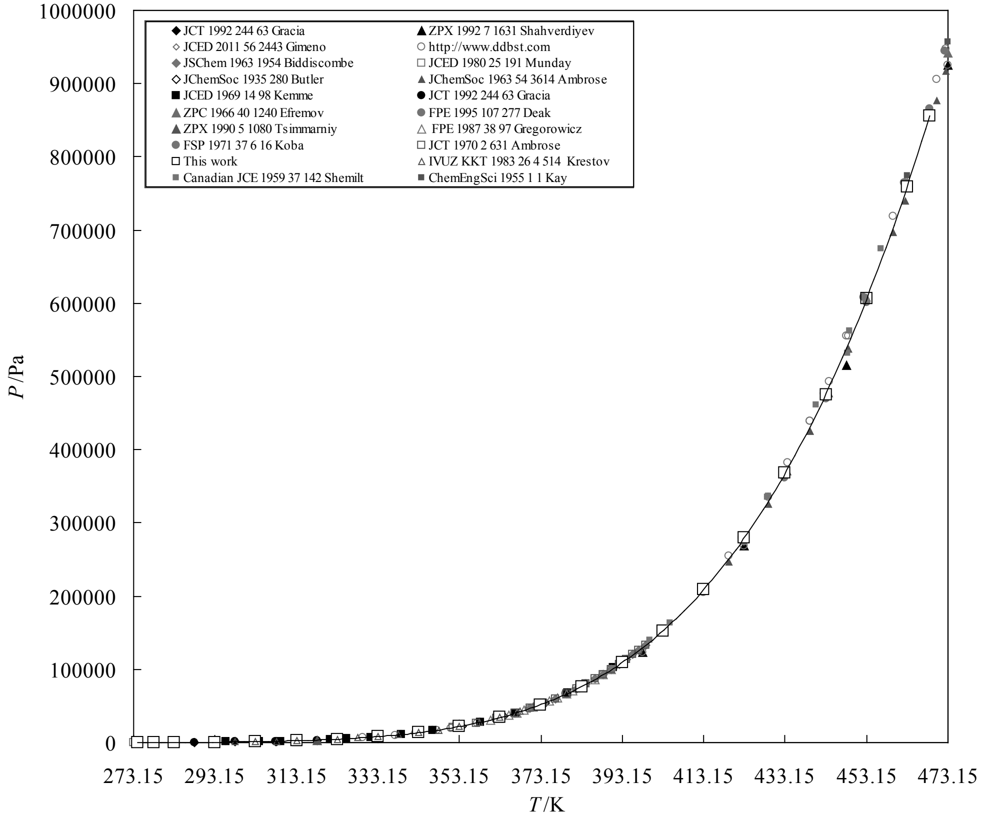

Figure 3. Plot of vapor pressure P/Pa of 1-butanol versus temperature T/K together with the literature values: a) in P-T coordinates; solid line: Clausius–Clapeyron type Eq. (3); b) in ln(P) - (1/(T-85.0376)) coordinates. solid line: Clausius–Clapeyron type Eq.(3)

Table 4. Antoine parameters A, B, C and standard deviations $\delta P/P$ of 1-butanol

A	B	C	$(\Delta P/P)/\%$
22.26	3289.71	-85.0376	±1.34

Table 5. Clasius - Clapeyron equation fitting parameters A, B, C and D

A	B	C	D	$(\Delta P/P)/\%$
125.277	-10321.5	-15.043	0.00622461	±0.114

The Clausius–Clapeyron type equation constructed in this work, was used for the analysing of literature values. The results of this analysis are discussed in the below and shown in Figure 4.

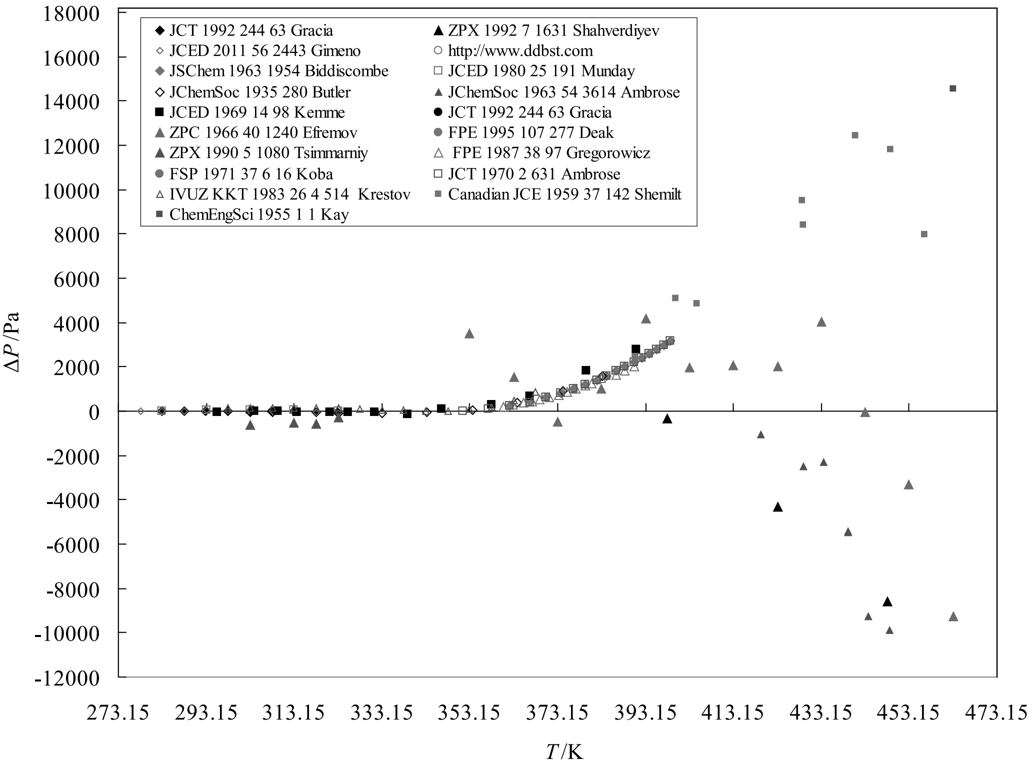

Figure 4. Plot of absolute deviation of experimental $P_{\text{exp.}}$ and literature $P_{\text{lit.}}$ vapor pressure values of 1-butanol *versus* temperatures *T*/K.

The earliest vapor pressure values presented by Butler on 1935 up to ambient pressure were compared with our results in 10 measured points. The middle deviation of the compared values is ΔP = 69 Pa. These values have a good deviation from our results. They are increasing up to ΔP = 361 Pa at T = 383.35 K.

The ten values from next measured twenty three vapor pressure values of 1-butanol of (Shemilt et al., 1959) above the ambient pressure systematically higher than our values. This is the first literature results at high temperatures. The deviation at the first measured point (T = 383.35 K) is ΔP = 640 Pa and at the last (T = 456.76 K) is ΔP = 16340 Pa. The mean deviation of all values in this reference from our values is ΔP = ± 7015 Pa.

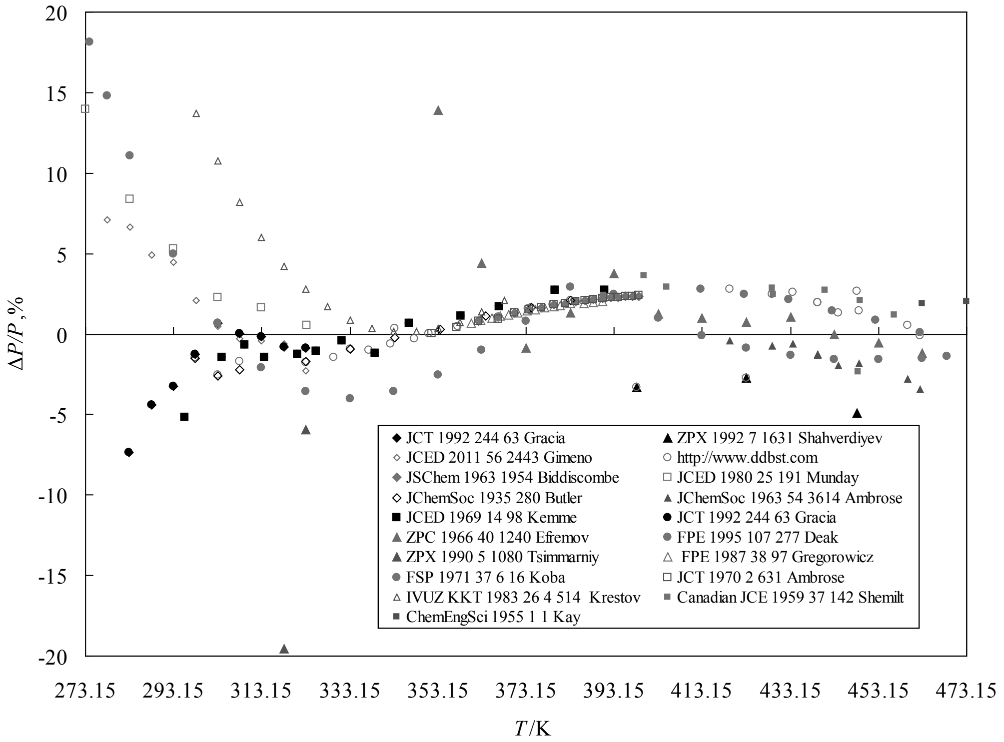

Figure 5. Plot of per cent deviation of experimental $P_{\text{exp.}}$ and literature $P_{\text{lit.}}$ vapor pressure values of 1-butanol *versus* temperatures T/K

Our vapor pressure values of 1-butanol above the ambient pressure are systematically lower than the values of (Ambrose & Townsend, 1963) and the mean deviation is $\Delta P = \pm 7005$ Pa. The deviation increasing with the increasing of temperature and the maximum deviation is $\Delta P = 11823$ Pa at $T = 462.64$ K. These deviations can be discussion on the base of uncertainties of pressure sensors in both works.

The eleven values below the ambient pressure and five above the ambient pressure of (Biddiscombe et al., 1963) are higher than our values with the mean deviation $\Delta P = \pm 342$ Pa. The deviations slowly increasing with the increasing of temperature and the maximum deviation is $\Delta P = 764$ Pa at $T = 398.84$ K.

The twelve vapor pressure values of 1-butanol from twenty one presented by Efremov (1966) also compared in our experimental temperature interval. The deviations of our results from that source are both negative and positive. The mean deviation of both measurements is $\Delta P = \pm 1797$ Pa. The maximum deviation is $\Delta P = 5978$ Pa at $T = 463.15$ K.

Thirteen vapor pressure values of 1-butanol of (Kemme & Kreps, 1969) below the ambient pressure compared with our values and Δ*P* = ±202 Pa middle deviation was obtained. The deviations slowly increasing with the increasing of temperature and the maximum deviation is Δ*P* = 1002 Pa at *T* = 390.95 K.

The comparison of experimental vapor pressure values of (Ambrose & Sprake, 1970) (mostly below the ambient pressure) with our results gives us Δ*P* = ±307 Pa mean and Δ*P* = 765 Pa as maximum deviation at *T* = 398.836 K. Mostly these values are higher than our results.

The twenty two calculated values of (Koba & Polishchuk, 1971) in all experimental temperature interval of our work also were compared. These results have positive or negative deviations from our results, but the deviation in absolute value increasing with increasing of temperature. The middle uncertainty is Δ*P* = ±2200 Pa and maximum (in *T*=468.67 K) is Δ*P* = 11163 Pa. As the same with previous literature results, the uncertainty of comparison is increasing with increasing of temperature.

Four vapor pressure values of (Munday et al., 1980) below the ambient pressure are higher than our results with the mean deviation Δ*P* = ±56 Pa. The maximum deviation is Δ*P* = 102 Pa at *T* = 323.31 K.

Fifteen vapor pressure values measured by Krestov et al. (1983) below the ambient pressure have Δ*P* = ±164 Pa mean deviation from our results. These values are higher than our results and the maximum deviation is Δ*P* = 435 Pa at *T* = 368.15 K.

Fifteen vapor pressure values by Gregorowicz et al. (1987) below ambient pressure have Δ*P* = ±110 Pa mean deviation with the maximum Δ*P* = 279 Pa at *T*=390.542 K. These values are the higher than our results.

Four vapor pressure values of below the ambient pressure measured by Tsimmarniy & Palaguta (1990) are smaller than our values and have Δ*P* = ±443 Pa mean deviation. The deviations are not characteristic below ambient pressure. The problem can be in the uncertainties (0.6%) of experimental method in this work.

Three vapor pressure values obtained from (p,ρ,T) measurements at saturation pressure at high temperatures by our group (Shahverdiyev et al., 1992) have Δ*P* = ±4407 Pa middle deviation.

We also analysed the nine experimental vapor pressure values of Gracia et al. (1992) below the ambient pressure and found a very good agreement. The mean deviation between the both results is Δ*P* = ±27 Pa with the maximum Δ*P* = ±46 Pa at *T*=313.08 K.

Six above-ambient vapor pressure measured by Deák et al. (1995) showed Δ*P* = ±7240 Pa mean deviation from our values. The deviations increase with increasing temperature, and the maximum deviation is Δ*P* = 1002 Pa at *T* = 462.53 K. These literature values are higher than our results.

The last ten literature values of Gimeno et al. (2011) below ambient pressure are in a very good agreement with our values. The mean deviation is Δ*P* = ±31 Pa with the maximum Δ*P* = ±42 Pa at *T*=313.15 K. These literature values are higher than our values.

Form these comparison, it is seen that the vapor pressure values for 1-butanol at temperatures up to *T*=391.01 K (normal boiling temperature at 101325 Pa obtained in this work by interpolation) have good agreement with most literature values within Δ*P*=±200 Pa. The large deviation between the experimental vapor pressure values of 1-butanol and values obtained in the literature were obtained above normal boiling point of 1-butanol. Sometimes the deviations are up to Δ*P* = ±18 kPa. This fact have many reasons for the discussion. First, it is difficult to measure pressures much higher than the ambient pressure with high accuracy, unlike MKS Baratron pressure sensors for lower pressures (Δ*P* = ±10 to 30 Pa). Modern pressure transmitters with mechanic membranes are used in such experiments. They have uncertainties 0.1%, sometimes 0.05 % of the maximal measured pressure. There are five experimental and one calculated values at high temperatures up to *T*=468.67 K. The results of Shemilt et al. (1959), Efremov (1966), Ambrose & Townsend (1963) have no information about the uncertainties of measurements. These works were carried out more than 40 years ago using of older pressure transmitters and thermometers. Our present results obtained with modern pressure transmitters and thermometers have the uncertainties up to Δ*P* = ±5 Pa. In this case, the uncertainties approximately Δ=±(0.05 to 0.1) % of the measured vapor pressures above normal boiling point must be reasonable. It is impossible to obtain higher accuracy measurements in this region.

Conclusion

The vapor pressure of 1-butanol at temperatures *T*=(274.15 K to 468.15) K experimentally measured in two modern automatic installations based on the static method. The investigations in the such wide range and high quality was carried out for the first time. The obtained experimental results were fitted by two different equations. The Clausius-Clapeyron type equation with four parameters showed the best fit. All available literature on vapor pressure of 1-butanol was analysed, and our experimental results were compared to that.

REFERENCES

Ambrose, D. & Townsend, R. (1963). Thermodynamic properties of organic oxygen compounds, part IX: the critical properties and vapor pressures, above five atmospheres, of six aliphatic alcohols. *J. Chem. Soc., 54*, 3614-3625.

Ambrose, D. & Sprake, C.H.S. (1970). Thermodynamic properties of organic oxygen compounds, XXV: vapor pressures and normal boiling temperatures of aliphatic alcohols. *J. Chem. Therm., 2,* 631-645.

Bernardes, M.A.S. (Ed.). (2011). *Biofuel production – recent developments and prospects*. Rijeka: InTech.

Biddiscombe, D.P., Collerson, R.R., Handley, R., Herington, E.F.G., Martin, J.F. & Sprake, C.H.S. (1963). Thermodynamic properties of organic oxygen compounds, VIII: purification and vapor pressures of the propyl and butyl alcohols. *J. Chem. Soc. (Resumed)*, 1954-1957.

Brown, I. & Smith, F. (1959). Liquid-vapor equilibria. IX: the systems propanol + benzene and butanol + benzene at 45 °C. *Australian J. Chem., 12*, 407–412.

Butler, J.A.V., Ramchandi, N. & Thomson, D.W. (1935). The solubility of non-electrolytes; part I: the free energy of hydration of some aliphatic alcohols *J. Chem. Soc.,* 280-285.

Calvar, N., Gómez, E., Domínguez, Á. & Macedo, E.A. (2010). Vapor pressures, osmotic and activity coefficients for binary mixtures containing (1-ethylpyridinium ethylsulfate + several alcohols) at T = 323.15 K. *J. Chem. Therm., 42*, 625-630.

Deák, A., Victorov, A.I. & de Loos, Th.W. (1995). High pressure VLE in alkanol + alkane mixtures: experimental results for n-butane + ethanol, + 1-propanol, + 1-butanol systems and calculations with three EOS methods. *Fluid Phase Equilibria, 107*, 277-301.

Duncan, A.M., Ahosseini, A., McHenry, R., Depcik, C.D., Stagg-Williams, S.M. & Scurto, S.M. (2010). High-pressure viscosity of biodiesel from soybean, canola, and coconut oils. *Energy Fuels*, *24*, 5708–5716.

Efremov, Y.V. (1966). Density, surface tension, saturated vapor pressures, and critical parameters of alcohols. *Zhur. Fiz. Khim., 40,* 1240-1247.

Geiseler, G., Stühnel, K. & Quitzsch, K. (1973). Excess behaviours of binary mixtures from isomeric butanols, *Z. physik. Chemie*, *254*, 261-270.

Gimeno, B., Torcal, M., Mainar, A.M. & Perez, P. (2011). Isothermal vapor-liquid equilibrium of (1-butanol þ 1,8-cineole) at 10 Temperatures between (278.15 and 323.15). *J. Chem. & Eng. Data*, *56*, 2443–2448.

Gracia, M., Sanchez, F., Perez, P., Valero, J. & Gutierrez Losa, C. (1992). Vapor pressures of (butan-1-ol + hexane) at temperatures between 283.10 K and 323.12 K. *J. Chem. Thermod., 24*, 463-471.

Gregorowicz, J., Kiciak, K. & Malanowski, S. (1987). Vapor pressure data for 1-butanol, cumene, n-octane and n-decane and their statistically consistent reduction with the Antoine equation. *Fluid Phase Equilibria*, *38*, 97-107.

Hauschild, T., Wu, S. & Sandler, S.I. (1987). Vapor-liquid equilibrium of the mixtures 2-furaldehyde/1-butanol and 2-furaldehyde/4-methyl-2-pentanone. *J. Chem. & Eng. Data*, *32*, 226–229.

Hiaki, T., Taniguchi, A., Tsuji, T. & Hongo, M. (1998). Isothermal vapor-liquid equilibria of octane with 1-butanol, 2-butanol, or 2-methyl-2-propanol. *Fluid Phase Equilibria*, *144*, 145–155.

Kay, W.B. & Donham, W.E. (1955). Liquid-vapor equilibria in the iso-butanol - n-butanol, methanol - n-butanol and diethyl ether - n-butanol systems. *Chem. Eng. Sci., 4*, 1-16.

Kemme, H.R. & Kreps, S.I. (1969). Vapor pressure of primary n-alkyl chlorides and alcohols. *J. Chem. & Eng. Data*, *14*, 98-102.

Koba, K.A. & Polishchuk, A.G. (1971). Temperature dependence of the pressure of alcohol vapors. *Fermentnaya i Spirtovaya Promyshlennost, 37*(6), 16-17.

Krestov, A. G., Klopov, V. I. & Pirogov, A. I. (1983). Saturated vapor pressure in the cholesterol tridecylate-n-butanol system at 298-368 K. *Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya*, *26*(4), 514-517.

Luis, A., Forero, G., Jorge, A. & Velásquez J. (2011). Wagner liquid–vapor pressure equation constants from a simple methodology. *J. Chem. Therm., 43*, 1235–1251.

Munday, E.B., Mullins, J.C. & Edie, D.D. (1980). Vapor pressure data for toluene, 1-pentanol, 1-butanol, water, and 1-propanol and for the water and 1-propanol system from 273.15 to 323.15. *J. Chem. & Eng. Data*, *25*(3), 191-194.

Oracz, P. & Kolasinska, G. (1987). Vapor-liquid equilibria – III: total vapor pressure measurements for binary mixtures of methanol, ethanol, 1-propanol and 1-butanol with benzene, methylbenzene and p-xylene at 313.15 K. *Fluid Phase Equilibria*, *35*, 253-278.

Polishchuk, A.G. & Koba, K.A. (1972). Equations for the saturated vapor pressure of lower aliphatic alcohols. *Vestnik L'vovskogo Politekhnicheskogo Instituta*, *71*, 10-15.

Sachek, A.I., Peshchenko, A.D., Markovnik, V.S., Ral'ko, O.V., Andreevskii, D.N. & Leont'eva, A.A. (1982). Temperature dependence of vapor pressure of butyl alcohols. *Termodinamika Organicheskikh Soedinenii*, 94-98.

Safarov, J., Hamidova, R., Zepik, S., Schmidt, H., Kul, I., Shahverdiyev, A. & Hassel, E. (2013). Thermophysical properties of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide at high temperatures and pressures, *J. Mol. Liquids*, *187,* 137-156.

Schmeling, T. & Strey, R. (1983). Equilibrium vapor pressure measurements for the n-alcohols in the temperature range from -30 °C to +30 °C. *Ber. Bunsen-Gesellschaft*, *87*, 871-874.

Shahverdiyev, A.N., Naziev, Y..M. & Safarov, J.T. (1992). Thermal properties of various aliphatic alcohols near the line of phase-change "liquid-vapor". *Russian J. Applied Chem., 7,* 1631-1637.

Shemilt, L.W., Esplen, R.W. & Singh Mann, R. (1959). Thermodynamic properties of some organic compounds: I. PVT relationships and calculated thermodynamic properties for normal butanol. *Canadian J. Chem. Enging., 37*(4), 142–152.

Sundberg, A.T., Laavi, H., Kim, Y., Uusi-Kyyny, P., Pokki, J.-P. & Alopaeus, V. (2012). Vapor-liquid equilibria, excess enthalpy, and excess volume of binary mixtures

[TRC]. (1973). *Thermodynamic tables - non hydrocarbons: vapor pressures*. College Station: Texas A&M University.

containing an alcohol (1-butanol, 2-butanol, or 2-methyl-2-butanol) and 2-ethoxy-2-methylbutane. *J. Chem. & Eng. Data*, *57*, 3502-3509.

Tsymarniy, V. A. & Palaguta, V. M. (1990). Saturation pressure and density of vaporous aliphatic alcohols. *Zhur. Prikl. Khimii*, *63*, 1080-1084.

Wagner, W. & Pruß, A. (2002). The IAPWS Formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Physical Chemistry Reference Data*, *31*, 387-535.

✉ **Dr. Javid Safarov** (corresponding author)
Institute of Technical Thermodynamics, University of Rostock,
Albert-Einstein-Str. 2, D-18059 Rostock, Germany
E-mail: javid.safarov@uni-rostock.de

Mr. Bahruz Ahmadov
Department of Industrial ecology and safety of habitability,
Azerbaijan Technical University,
Huseyn Javid Avn.25, AZ1073 Baku, Azerbaijan
E-mail: ahmedov_bahruz@mail.ru

Dr. Saleh Mirzayev
Department of Industrial ecology and safety of habitability,
Azerbaijan Technical University,
Huseyn Javid Avn.25, AZ1073 Baku, Azerbaijan
E-mail: ahmedov_bahruz@mail.ru

Prof. Astan Shahverdiyev
Department of Heat and Refrigeration Techniques,
Azerbaijan Technical University,
Huseyn Javid Avn.25, AZ1073 Baku, Azerbaijan
E-mail: ozone@azdata.net

Prof. Dr. habil, h.c. Egon Hassel
Institute of Technical Thermodynamics, University of Rostock,
Albert-Einstein-Str. 2, D-18059 Rostock, Germany
E-mail: egon.hassel@uni-rostock.de