



# Critical temperatures and pressures of straight-chain alkanediols (C<sub>3</sub> to C<sub>12</sub>)



Eugene D. Nikitin<sup>a,\*</sup>, Alexander P. Popov<sup>a</sup>,  
Nataliya S. Bogatishcheva<sup>a</sup>, Vasily A. Kuznetsov<sup>b</sup>

<sup>a</sup> Institute of Thermophysics, Ural Branch of the Russian Academy of Sciences, Amundsena Street, 106, 620016 Ekaterinburg, Russia

<sup>b</sup> Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, Sof'i Kovalevskoi Street, 20, 620219 Ekaterinburg, Russia

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## ABSTRACT

The critical pressures  $p_c$  and the critical temperatures  $T_c$  of diols with straight alkylchains  $\text{HO}(\text{CH}_2)_n\text{OH}$  and  $n = 3, 4, 5, 6, 8, 9, 10, 12$  have been measured. All the alkanediols studied decompose at near-critical temperatures. A pulse-heating method which allows measuring the critical properties of thermally unstable compounds has been used. The times of heating from the beginning of a pulse to the moment of reaching the critical temperature were from (0.03 to 0.46) ms. The short residence times provided little degradation of the substances in the course of the experiments. The uncertainties of the measurement of the critical properties of alkanediols are  $0.04 p_c$  and  $0.015 T_c$ , where  $T_c$  is the absolute temperature. The critical properties obtained have been compared with the values measured earlier by various techniques. The experimental critical constants of alkanediols have also been compared with those calculated using the group-contribution methods of Lydersen, Wilson and Jasperson, and Marrero and Gani.

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## 1. Introduction

Diols with straight-chain alkyl radicals  $\text{HO}(\text{CH}_2)_n\text{OH}$  are an important family of organic compounds. They are of industrial importance as well. For instance, the first member of this homologous series, 1,2-ethanediol (ethylene glycol) is widely used as an antifreeze, a coolant and heat transfer agent, a precursor for polymers, a desiccant. Other alkanediols are employed in cosmetics and so forth [1]. All the alkanediols decompose at their critical points. The critical properties of some alkanediols have been measured using various methods applicable to thermally unstable compounds. Lyons has measured the critical temperature of 1,2-ethanediol using a sealed tube method, he has determined the critical pressure by the extrapolation of the vapor pressure curve to the critical temperature [2]. A modified sealed ampoule method have been used to measure the critical temperature of 1,2-ethanediol [4], a visual flow method and a non-visual flow method have been employed to determine the critical constants of 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol [5–8]. The critical properties of 1,2-ethanediol have been measured by us by the pulse-heating method [9]. This method is also used in

this work to measure the critical temperatures and pressures of alkanediols  $\text{HO}(\text{CH}_2)_n\text{OH}$  with  $n = 3, 4, 5, 6, 8, 9, 10, 12$ .

We failed to find in the literature any information about decomposition products and the rate of decomposition of diols in the liquid phase at near-critical temperatures. Indirectly, one can judge about the thermal stability of diols using the dependence of the apparent critical properties on the residence time. Von Niederhausern et al. [6] in measuring the critical properties of 1,2-ethanediol by a visual flow method found that increasing the residence time from 0.35 min to 1.05 min led to the decrease of the critical temperature from 713.5 K to 705.5 K and the increase of the critical pressure from 9.6 MPa to 10.9 MPa. For 1,4-butanediol, they observed the fall of the critical temperature from 723.5 K to 717.5 K and the rise of the critical pressure from 6.8 MPa to 7.8 MPa when the residence time increased from 0.9 min to 2.4 min [5].

## 2. Experimental

### 2.1. Materials

The samples of diols were of commercial origin (Aldrich, Alfa Aesar). The sources, purities, and Chemical Abstract Service Registry Numbers (CASRN) of the samples are given in Table 1. Before and after the measurements of the critical properties, the purities of the samples were determined by a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector and a fused silica capillary column ZB-5 (30 m, 0.25 mm,  $0.25 \times 10^{-3}$  mm). The

\* Corresponding author. Tel.: +7 343 2678810; fax: +7 343 2678800.

E-mail addresses: [e-nikitin@mail.ru](mailto:e-nikitin@mail.ru), [nikitin@itp.uran.ru](mailto:nikitin@itp.uran.ru) (E.D. Nikitin), [popov@itp.uran.ru](mailto:popov@itp.uran.ru) (A.P. Popov), [bogatishcheva@mail.ru](mailto:bogatishcheva@mail.ru) (N.S. Bogatishcheva), [basilkv@yandex.ru](mailto:basilkv@yandex.ru) (V.A. Kuznetsov).

**Table 1**  
Purities of compounds used in critical point measurement (GH<sup>a</sup>).

| Compound          | CASRN <sup>b</sup> | Supplier   | Mole fraction purity                |                                    |
|-------------------|--------------------|------------|-------------------------------------|------------------------------------|
|                   |                    |            | Before measuring critical constants | After measuring critical constants |
| 1,3-Propanediol   | 504-63-2           | Aldrich    | 99.9                                | 99.9                               |
| 1,4-Butanediol    | 110-63-4           | Alfa Aesar | 99.9                                | 99.9                               |
| 1,5-Pentanediol   | 111-29-5           | Alfa Aesar | 99.9                                | 99.9                               |
| 1,6-hexanediol    | 629-11-8           | Aldrich    | 99.9                                | 99.9                               |
| 1,8-Octanediol    | 629-41-4           | Alfa Aesar | 99.9                                | 99.9                               |
| 1,9-Nonanediol    | 3937-56-2          | Aldrich    | 99.9                                | 99.9                               |
| 1,10-Decanediol   | 112-47-0           | Aldrich    | 99.8                                | 99.8                               |
| 1,12-Dodecanediol | 5675-51-4          | Aldrich    | 99.9                                | 99.9                               |

<sup>a</sup> Gas–liquid chromatography.

<sup>b</sup> Chemical abstracts service registry number.

temperature program of the GC was  $T=313\text{ K}$  for 3 min followed by a heating rate of  $10\text{ K min}^{-1}$  to  $T=553\text{ K}$  (storage for 30 min). The temperature of the evaporator was  $523\text{ K}$ , the detector temperature was  $573\text{ K}$ . The split ratio was 1:30, and the carrier gas (nitrogen) flow through the column was  $1.0\text{ mL min}^{-1}$ . The purities of the samples did not change in the course of measuring the critical properties.

## 2.2. Method

The pulse-heating method used for the measurement of the critical temperatures and pressures of alkanediols has been discussed in detail in previous papers [9–13]. Briefly, the method is based on the phenomenon of liquid superheat [14–16]. In the course of the experiments, the pressure dependence of the temperature of the attainable superheat (spontaneous boiling-up) of liquid is measured. The critical point is not only the end point on the vapor–liquid equilibrium line, but the end point on the line of the attainable superheat as well. Thus, when the pressure in the liquid approaches the critical pressure, the temperature of the attainable superheat approaches the critical temperature.

The temperature of the attainable superheat at a given pressure is measured with the help of a wire probe heated by electric current pulses. The probe is made of platinum, has a diameter of  $2 \times 10^{-3}\text{ cm}$  and a length of 1–3 cm. The probe serves simultaneously as a heater and a resistance thermometer. The probe is heated by electric pulses in such a way that the probe temperature reaches the temperature of spontaneous boiling-up by the end of a pulse. The time from the beginning of a pulse to the moment of boiling-up  $t^*$  in various experiments is from 0.03 to 1.0 ms. At the moment of boiling-up a probe temperature perturbation takes place because the conditions of heat transfer from the probe to the liquid change sharply. The temperature perturbation is uniquely connected with a voltage perturbation on the probe. The voltage perturbation is observed on the screen of a digital oscilloscope or a personal computer. The temperature of the probe at the beginning of the temperature perturbation, that is, at the beginning of boiling-up is determined from the resistance of the probe.

The probe temperature perturbation may be negative or positive. The sign of the perturbation depends on the thermophysical properties of a substance under study and the time  $t^*$ . For comparatively low-molar-mass compounds (nonpolymers) at near-critical pressures the temperature perturbation is negative. When the pressure approaches the critical pressure, the properties of the liquid and vapor phases come closer and the amplitude of the temperature perturbation drops. The pressure in the chamber with a substance under investigation increases step by step until the negative temperature perturbation decreases to the level of the apparatus sensitivity ( $1 \times 10^{-3}\text{ K}$ ). This pressure and the temperature of boiling-up at this pressure are considered as the measured values of the critical pressure  $p_c^m$  and the critical temperature  $T_c^m$ .

The values of  $p_c^m$  and  $T_c^m$  are always lesser than the true critical properties and should be corrected. The true critical pressure  $p_c$  and temperature  $T_c$  of a stable substance or the apparent critical parameters of an unstable compound are calculated using the following equations:

$$p_c = \frac{p_c^m}{\pi_0}, \quad T_c = \frac{T_c^m}{\tau_0} \quad (1)$$

where  $1/\pi_0$  and  $1/\tau_0$  are correction factors [9,13]. For the estimation of the correction factors some properties of a compound under investigation at near-critical states are required. These properties are as follows: density, thermal conductivity, heat capacity of the liquid phase, density of the vapour phase, enthalpy of vaporization, boiling temperature, and the temperature of the attainable superheat. The properties are calculated using the formulas [17] obtained by the principle of corresponding states. The formulas contain the similarity parameter of the compound under study suggested by Filippov [18]:

$$A = 100 \frac{p_{vp}(T/T_c = 0.625)}{p_c} \quad (2)$$

Here  $p_{vp}$  is the vapor pressure at reduced temperatures equal to 0.625. The sense of the Filippov parameter is close to that of the well-known Pitzer acentric factor. The relation between the Filippov parameter and the acentric factor can be established with the help of an equation for the dependence of the vapor pressure on the temperature. Filippov, using the equation by Riedel [19], obtained the following formula:

$$\omega = 0.401 - 0.664 \log_{10} A \quad (3)$$

The Filippov parameters and the critical properties were calculated by an iteration method. The measured values of the critical parameters,  $p_c^m$  and  $T_c^m$ , were employed as the critical constants for the first iteration. The vapor pressure at the reduced temperature  $T/T_c = 0.625$  was estimated using an equation suggested by Filippov [18]:

$$\log_{10} \frac{P^*}{p_{vp}} = 3.9726 \log_{10} \frac{T^*}{T} + \left( \frac{T^*}{T} - 1 \right) \left( 0.3252 + 0.40529 \frac{T^*}{T} \right) \quad (4)$$

This equation gives the dependence of vapor pressure on temperature from the triple to the critical point. Here  $P^*$  and  $T^*$  are the characteristic pressure and temperature. They were calculated using  $p_c^m$ ,  $T_c^m$ , and the values of the boiling temperature  $T_b$  at a given pressure mostly at atmospheric pressure (see Table 2). If there were a few values of the boiling temperature at various pressures we preferred to use the normal boiling temperature. However, for 1,8-octanediol one can find the normal boiling temperature [20] but the origin of this value is unknown and we used the boiling temperature at a reduced pressure as more reliable [21]. Then the Filippov parameters were estimated by Eq. (2). Thereafter the correction factors and the critical constants were calculated; these values were

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