



Critical temperatures and pressures of ethylene glycols

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ABSTRACT

The critical temperatures and pressures of di-, tri-, tetra-, penta-, and hexaethylene glycols have been measured using the pulse-heating method applicable to thermally unstable compounds. The results obtained have been compared with the data of previous measurements and the results of computer simulations. The recommended values of the critical temperatures and pressures of the homologous series of ethylene glycols have been given.

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1. Introduction

Ethylene glycols $H(OCH_2CH_2)_nOH$ form a homologous series all the members of which decompose at their critical points. The critical temperatures and pressures of mono-, di-, tri-, and tetraethylene glycols and polyethylene glycols PEG (300), PEG (400), and PEG (600) were measured by us using the pulse-heating technique applicable to thermally unstable compounds [1,2]. The critical properties of ethylene glycols were also measured by Lyons [3], Teja and Anselme [4], Teja and Rosenthal [5], VonNiederhausern et al. [6], Anselme and Teja [7]. Steele and co-workers measured the vapor pressure of diethylene glycol [8] and triethylene glycol [9] and represented the results of the measurements by the Wagner-Ambrose equation. Then they calculated the critical pressure of diethylene glycol taking the critical temperature to be equal to our value [2]. For triethylene glycol, they took the critical temperature $T_c = 770$ K and calculated the critical pressure. The data of all the work mentioned above are given in Table 2. The critical properties of ethylene glycol and its homologues were also the subject of a considerable number of computer simulation studies [10–15]. The results of simulations are listed in Table 2 too.

Analysis of our paper [2] shows that the critical properties of tri- and tetraethylene glycols are suspiciously close to each other. In

addition, in that paper we used a rather complex method of extrapolating the dependences of the apparent values of the critical temperature and the critical pressure on the duration of a heating pulse to a zero duration to obtain the critical properties of undecomposed glycols. Later we developed a new method of such extrapolation, which we considered to be better [16]. In this paper, we measured the critical temperatures and pressures of di-, tri-, tetra-, penta-, and hexaethylene glycols by the same pulse-heating method we used in Refs.1 and 2.

2. Experimental

2.1. Materials

The samples of ethylene glycols were purchased from Sigma-Aldrich and used without any additional purification; the Chemical Abstracts Service Registry Numbers (CASRN's) of the compounds studied and the purities of the samples according to the suppliers' certificates of analysis are given in Table 1.

2.2. Method

The pulse-heating method for the measurement of the critical temperatures and pressures of thermally unstable compounds has been described in detail in previous papers [1,17–20]. The method is based on the phenomenon of the superheat of liquids [21,22] and consists in measuring the pressure dependence of the temperature of the attainable superheat (the line of the attainable superheat)

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Table 1

Purities of compounds used in critical point measurement (Sigma-Aldrich, GC, suppliers' certificates of analysis).

Compound	CASRN ^a	Purity (mol. %)
Diethylene glycol	111-46-6	99.5
Triethylene glycol	112-27-6	99.7
Tetraethylene glycol	112-60-7	99.1
Pentaethylene glycol	4792-15-8	97.8
Hexaethylene glycol	2615-15-8	98.1

^a Chemical abstracts service registry number.

with the help of a wire probe heated by electric current pulses with durations from 0.03 to 1.0 ms. Short durations of the heating pulses provide small decomposition of thermally unstable compounds in the course of measuring the critical properties. The line of the attainable superheat ends at the critical point. As an example, the line of the attainable superheat for triethylene glycole is shown in Fig. 1. The last point on this line corresponds to the measured values of the critical pressure p_c^m and temperature T_c^m .

Pulse-heating experiments on compounds the critical properties of which are well studied show that, as a rule, the values of p_c^m and T_c^m are somewhat lesser than the true critical parameters. The true critical pressure p_c and temperature T_c of stable compounds are calculated by the following equations:

$$p_c = p_c^m / \pi_0, \quad T_c = T_c^m / \tau_0, \quad (1)$$

where $1/\pi_0$ and $1/\tau_0$ are correction factors. The procedure of the calculation of the correction factors was given in detail in our previous papers [20,23]. It was shown on a large number of compounds that the use of the procedure led to values of the critical properties which coincided with reliable literature data within the uncertainties of the measurement [20].

The values of the correction factors mainly depend on a similarity parameter of a compound under study: the acentric factor or the Filippov parameter [24]:

$$A = 100 \frac{p_{vp}(T_r = 0.625)}{p_c}, \quad (2)$$

where p_{vp} is the vapour pressure, and $T_r = T/T_c$ is the reduced temperature. The Filippov parameter is related to the Pitzer acentric factor

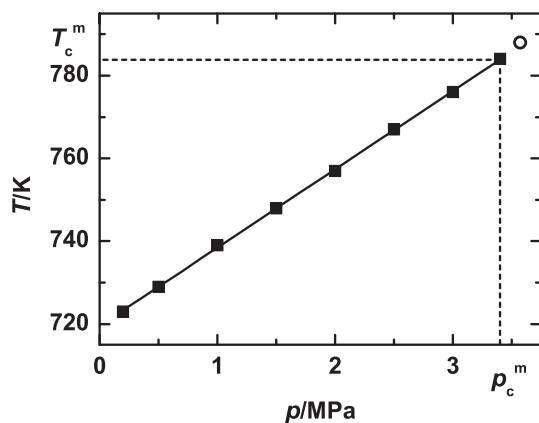


Fig. 1. Temperature of the attainable superheat of triethylene glycol (■) against the pressure; ○, critical point; p_c^m and T_c^m are the measured values of the critical pressure and temperature. The time from the beginning of a heating pulse to the moment of boiling-up is 0.035 ms.

$$\omega = \log \left(\frac{p_c}{p_{vp}(T_r = 0.7)} \right) - 1 \quad (3)$$

by the equation [24]:

$$\log_{10} A = 0.604 - 1.505\omega. \quad (4)$$

An iteration method was used to calculate the Filippov parameters and the critical properties. For the first iteration, p_c^m and T_c^m were taken as the critical constants. The vapor pressures at a reduced temperature $T_r = 0.625$ were calculated for di- and triethylene glycols by equations suggested by Steele et al. [8,9], and for tetraethylene glycol by the Antoine equation [25]. According to Alfa Aesar Company, now a part of Fisher Scientific, the normal boiling temperature of pentaethylene glycol is 611–613 K [26]. However, Steele and co-workers point out that the onset of decomposition of diethylene glycol is about 540 K [8] and for triethylene glycol is approximately 560 K [9]. One may suggest that pentaethylene glycol begins to degrade at approximately the same temperature so that the normal boiling temperature given by Alfa Aesar cannot be used to determine the Filippov parameter. Gallagher and Hibbert measured the boiling points of some ethylene glycols from monoethylene glycol to heptaethylene glycol at reduced pressures [27]. Their data for penta- and hexaethylene glycols are given in Table 2. The vapor pressures of these glycols at reduced temperature $T_r = 0.625$ were calculated using the following equation [24]:

$$\log_{10} \frac{P^*}{p_{vp}} = 3.9726 \log_{10} \frac{T^*}{T} + \left(\frac{T^*}{T} - 1 \right) \left(0.3252 + 0.40529 \frac{T^*}{T} \right) \quad (5)$$

here P^* and T^* are the pressure and temperature characteristic of the compound. The values of P^* and T^* were calculated from Eq. (5) using p_c^m , T_c^m , and the data by Gallagher and Hibbert. Then the Filippov parameters of penta- and hexaethylene glycols were calculated by Eq. (2). The results of such an estimation are given in Table 2. This table shows that the Filippov parameters of penta- and hexaethylene glycols calculated from the data by Gallagher and Hibbert are unrealistically low.

We estimated the acentric factors of ethylene glycols from monoethylene glycol to hexaethylene glycol using the method of Constantinou and Gani as presented by Poling et al. [29] and calculated the Filippov parameters of these glycols using Eq. (4). The estimates are listed in Table 2. For completeness we also estimate the Filippov parameters of monoethylene glycol from experimental data. The vapor pressures of this glycol at $T_r = 0.625$ were calculated using the Antoine equation [25]; the recommended values from Table 2 were taken as the critical properties. The results of such an estimation are given in Table 2 as well. One can see from Table 2 that the experimental and estimated Filippov parameters of mono- to tetraethylene glycols do not differ considerably so that we used the Filippov parameters estimated from the method of Constantinou and Gani to calculate the correction factors for penta- and hexaethylene glycols.

As the Filippov parameters were determined, the correction factors and the critical parameters were calculated; these values were used in the second iteration. The iterative process ended after two iterations because the correction factors are little sensitive to the variation of the Filippov parameter (the acentric factor). In general, the greater is the acentric factor, the greater are the correction factors. For ethylene glycols studied, the correction factors lie in the following ranges: $1/\pi_0 = 1.044$ and $1/\tau_0 = 1.005$ (diethylene glycol) to $1/\pi_0 = 1.072$ and $1/\tau_0 = 1.006$

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