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Full title:

Boiling Points of the Propylene Glycol + Glycerol System
at 1 Atmosphere Pressure: 188.6 to 292 °C

Short title:

Boiling Points: Propylene Glycol + Glycerol

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Abstract

In electronic cigarettes (“electronic nicotine delivery systems”, ENDSs), mixtures of propylene glycol (PG) and/or glycerol (GL; aka “vegetable glycerin”, VG) with nicotine are vaporized to create a nicotine-containing aerosol. For a given composition, the temperature required to boil the liquid at 1 atmosphere must be at least somewhat greater than the boiling point (BP). Use of ENDS is increasing rapidly worldwide, yet the BP characteristics of the PG+GL system had not yet been experimentally investigated. BP values at 1 atmosphere pressure were measured over the full binary composition range. Fits based on the Gibbs-Konovalov theorem provide BP as a function of composition (by mole-percent, by weight-percent, and by volume-percent).

Keywords

propylene glycol; glycerol; heat exchanger fluid; electronic cigarette; e-cigarette liquid; electronic nicotine delivery system (ENDS); e-cigarette.

29 **1. Introduction**

30 Propylene glycol (PG) and glycerol (GL) are high production volume (HPV) chemicals
31 used in numerous industrial and consumer applications (Pendergrass, 1999; Teschke, 2005).
32 First, they serve as heat exchanging fluids in solar hot water and geothermal energy systems,
33 including as PG+GL mixtures. Second, they are main ingredients in the nicotine-containing
34 liquids (e-liquids) used in electronic cigarettes (aka “e-cigarettes”, “electronic nicotine delivery
35 systems”, “ENDSs”) either individually or as a mixture. The dependence of boiling point (BP)
36 temperature on composition is of interest in heat exchanger, e-cigarette applications, and for
37 separations by distillation (Chen et al., 2015). Boiling is very unwelcome in heat exchange
38 applications, but essential in the e-cigarettes (boiling must occur if the desired subsequent
39 condensation aerosol is to form (Zhang et al., 2013; Glycerine as a heat transfer fluid and
40 antifreeze, 2016). Globally, from 2014 to 2015, solar hot water capacity grew 6.4% from 409 to
41 435 to gigawatts (Renewables 2016 Global status report, 2016; Mickle, 2015). For the e-cigarette
42 industry, global growth was 58% in 2014 (Market Research on Vapour Devices, 2016). The
43 number of regular adult e-cigarette users in the U.S. in 2014 has been estimated at 11.8 million,
44 with the number of “ever-users” estimated at 40.2 million (Schoenborn and Gindi, 2015).

45 Remarkably, BP behavior in the binary PG+GL system has received little direct study.
46 For heat exchange applications, such information is needed during design to avoid vapor
47 formation, and in e-cigarette applications, the information reveals the minimum temperatures
48 that the ingredient chemicals (which may include flavor chemicals) will experience. Also, it is
49 now well known that heating of “e-liquids” can lead to degradation products, some of which are
50 toxic (formaldehyde (Jensen et al., 2015), acrolein and other aldehydes, and aromatic
51 hydrocarbons (Hahn et al., 2014)). In a mixture, boiling occurs when the vapor pressure

52 contributions from all components combine to become at least somewhat greater than the system
53 pressure. It is thus useful to know how BP varies with composition in the PG+GL system.

54 Antoine equation parameterizations for the temperature-dependent vapor pressures of
55 pure PG (p_{PG}°) and pure GL (p_{GL}°) are available (Table 1). By assuming ideal liquid mixtures
56 (i.e., applicability of Raoult's Law), one can use these parameterizations to predict the BP values
57 for the full range of compositions for PG+GL mixtures according to

$$58 \quad p_{TOT} = x_{PG} p_{PG}^{\circ} + x_{GL} p_{GL}^{\circ} \quad (1)$$

59 For each value of x_{PG} (with $x_{GL} = 1 - x_{PG}$), Equation 1 can be solved to obtain the normal BP as
60 the value of T that gives $p_{TOT} = 1$ atm. The predicted BP values thereby obtained in Table 2 are
61 largely within the reported applicability range for the Antoine fit for GL, but are above the
62 applicability range for PG: the applicability range for PG only extends to the BP of PG, which is
63 below the BP for every mixture of PG and GL. The goal of this work was to carry out BP
64 measurements for the full range of PG and GL mixtures.

65

66 **[Place Table I here]**

67

68

69

[Place Table II here]

70

71 **2. Materials and Methods**

72 **2.1 Materials**

73 United States Pharmacopeia grade PG and GL were obtained from Sigma-Aldrich (St.
74 Louis, MO). Upon each opening and resealing, caps were wrapped with paraffin film to reduce
75 hygroscopic absorption of water from the atmosphere. Reagents were 99.9+% pure, which was
76 verified by nuclear magnetic resonance spectroscopy (NMR). Deuterium oxide (99.9% ^2H , 0.1%
77 ^1H) was obtained from Cambridge Isotope Laboratories (Tewksbury, MA).

78 **2.2 Sample preparation**

79 Mixtures of PG and GL were prepared in triplicate at room temperature using 40 mL
80 brown glass vials. The mixtures ranged from 0 to 100% by mass GL in increments of 10% by
81 weight, for a total of 33 individually prepared ~20 mL samples. Mass fractions were used as the
82 basis of the preparations rather than volume fractions because of greater ease, with viscous
83 liquids, in measuring mass vs. volume amounts delivered. Vial caps were wrapped with paraffin
84 film. Each sample was mixed by shaking for five minutes then stored in the dark for no more
85 than 24 hours before testing.

86 **2.3 Boiling point determinations**

87 Prior to heating, a “pre-boiling” 10 μL aliquot of each sample was mixed with 600 μL
88 D_2O for analysis by NMR. The BP of the remaining ~20 mL of sample was determined using the
89 apparatus represented in Fig 1. A three-necked round bottom flask was fitted with two reflux
90 condensers that allowed nitrogen gas (N_2) to enter the boiling chamber, then exit via an oil
91 bubbler (not shown); this permitted N_2 gas to flow freely through the system while maintaining
92 an anoxic environment at ambient pressure. An HH12B digital thermometer and a KTSS-HH

93 temperature probe from Omega (Stamford, CT) were fitted in the third flask opening. The digital
94 temperature probe accuracy was reported by the manufacturer as ≤ 1.3 °C, and this was verified
95 by measuring the BP values of three liquids at 1 atm pressure: water (BP: 100.0 °C),
96 acetophenone (BP: 204 °C), and ethyl benzoate (BP: 214 °C). Standard deviation (SD) values for
97 the triplicate PG and GL mixtures were found to be at most 0.5 °C, which is smaller than the
98 probe accuracy (as reported by the manufacturer). Below 200 °C, the probe displayed four
99 significant figures, including one decimal; above 200 °C, only three significant figures were
100 displayed. The flask was held in a rheostat-regulated heating mantle; mixing was provided using
101 a stir plate. The system was thoroughly flushed with N₂ gas prior to heating. Samples were
102 gradually heated over 30 to 90 minutes while stirring continuously until boiling was observed.
103 Boiling temperatures were determined as the stable temperature at which each sample exhibited
104 a steady rolling boil for at least five minutes. Each system was then allowed to return to room
105 temperature under N₂ gas. A “post-boiling” aliquot (10 μ L) was taken for analysis by NMR. The
106 pre- and post-boiling NMR samples were collected to ensure that the boiling process did not
107 considerably alter composition.

108

109

[Place Figure 1 here]

110

111

112 **2.4 1D ¹H NMR analyses**

113 The NMR analyses conducted on each pre- and post-boiling 10 μ L aliquot (as diluted in
114 600 μ L of D₂O) were carried out using a Bruker (Billerica, MA) Avance III spectrometer
115 (599.90 MHz) with a 5 mm TXI probe. A pulse sequence of zg30 was used to acquire the data,

116 with the relaxation delay value (d1) set to 5 seconds, in combination with the 30°-observation
117 pulse of the zg30 experiment to allow for full relaxation, and so reliable integrations.

118 All NMR spectra were processed using the software package MestReNova 9.0 (Santiago
119 de Compostela, Spain; Mnova, 2016). Spectra were auto-phase corrected (but with manual
120 adjustment as needed), followed by auto-baseline correction. Integral values were verified by
121 manually correcting some spectra; the results of which were found to agree with the values from
122 the corresponding auto-corrected spectrum values, to within 0.5%. Satellite peaks caused by the
123 1.1% natural abundance of ^{13}C overlapped with some peaks of interest, thereby potentially
124 introducing error to the mole ratio calculation. This error was minimized by integrating peaks of
125 interest and adjusting for the natural abundance of ^{13}C , allowing for more accurate measurements
126 of mole ratios. This produced mole ratio measurements that were within 1.4 mol% of values
127 based on the mass preparation method. The difference between the NMR-determined and
128 predicted mol% GL (based on initial masses) was calculated; the absolute values of the
129 differences were averaged for all trials to determine the average difference ($\pm\text{SD}$), which is $0.3 \pm$
130 0.3 mol% GL. Despite gravimetric sample preparation, NMR was used to assess post-boiling
131 composition for analysis because these results were most closely associated in time with
132 observed boiling.

133

134 **3. Results and Discussion**

135 The overall precision of this BP determination technique was established for each method
136 by calculating the standard deviation of triplicate boiling point ($^{\circ}\text{C}$) values (Table 3). Standard
137 deviation in terms of %GL for each method results in $\leq 0.2\%$ for wt% GL (based on initial

138 mixture masses), $\leq 0.4\%$ for the mol%, and $\leq 0.5\%$ for the vol% (calculated using the mol%
139 determined by NMR).

140 **[Place Table III here]**

141 BP values of PG and GL mixtures (t_b , °C) shown in Fig 2 as BP vs. mol percent were fit
142 with a Gibbs-Konovalov parameterization (Al-Jiboury, 2007; Malesiński, 1965)

$$143 \quad t_b \text{ (}^\circ\text{C)} = x_{\text{PG}}t_{\text{b,PG}} + x_{\text{GL}}t_{\text{b,GL}} + x_{\text{PG}}x_{\text{GL}} \left(A + B(x_{\text{PG}} - x_{\text{GL}}) - C(x_{\text{PG}} - x_{\text{GL}})^2 + D(x_{\text{PG}} - x_{\text{GL}})^3 \right) \quad (2)$$

144 where $t_{\text{b,PG}}$ and $t_{\text{b,GL}}$ (°C) are the measured boiling points of pure PG and GL, respectively. Fit
145 values of the coefficients A , B , C , and D for Equation 2 (i.e., using mol fraction composition)
146 were obtained by minimizing the sum of the residuals using the Microsoft Excel *Solver*
147 (Frontline Systems Inc., Incline Village, NV) add-in. Fit values were similarly obtained using
148 volume and weight fraction values. Coefficients A - D are presented in Table 4. Corresponding
149 calculated BP values are given in Table 5. Gibbs-Konovalov calculated values (Table 5) were
150 compared to the Antoine equation values (Table 2) and found to differ by up to 6.7 °C at the
151 upper range (beginning >230 °C), with an average difference (\pm SD) of 1.8 ± 1.9 °C over the
152 entire range.

153 **[Place Figure 2 here]**

154 **[Place Table IV here]**

155 **[Place Table V here]**

156 **4. Conclusions**

157 The data obtained provide the BP values of PG+GL mixtures at 1 atmosphere pressure
158 and smooth fitting allows prediction of BP for any composition (e.g., Table 5). Depending on
159 composition, the minimum temperature required to produce an e-cigarette aerosol from a
160 PG+GL liquid ranges from 188.6 to 292.0 °C; some effects from dissolved nicotine, flavor
161 chemicals, and water will be operative.

162 **Acknowledgements**

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165 parameterization; Michael Lethin and Astrid Woodall for assistance with the boiling point
166 measurements.

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Table I. Antoine Equation Parameters for Vapor Pressure p° (bar) of the Pure Liquids Propylene Glycol (PG) and Glycerol (GL), with Applicable Temperature Ranges, $\log_{10}(p^{\circ}) = A - B/(T + C)$. (1 atm = 1.01325 bar.) <http://webbook.nist.gov/chemistry/>

	<u>t ($^{\circ}\text{C}$) range</u>	<u>T (K) range</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>Reference</u>
PG	45.6 – 188.3	318.7 - 461.4	6.07936	2692.2	-17.94	Richardson, 1886
GL	183.3 - 260.5	456.4 - 533.6	3.9374	1411.5	-200.566	Stull, 1947

Table II. Boiling Point Values 211
Assuming Raoult's Law (Ideal 212
Mixtures).

$p_{\text{TOT}}(T) = x_{\text{PG}}p_{\text{PG}}^{\circ} + x_{\text{GL}}p_{\text{GL}}^{\circ} =$ 213
1.01325 bar (=1 atm) For Antoine
Equation Parameters in Table 1.

<i>Boiling Point</i>			
x_{PG}	x_{GL}	t (°C)	T (K)
1.00	0.00	188.0	461.2
0.95	0.05	189.6	462.8
0.90	0.10	191.3	464.4
0.85	0.15	193.1	466.2
0.80	0.20	194.9	468.1
0.75	0.25	196.9	470.1
0.70	0.30	199.1	472.2
0.65	0.35	201.4	474.6
0.60	0.40	203.9	477.1
0.55	0.45	206.7	479.8
0.50	0.50	209.6	482.8
0.45	0.55	212.9	486.1
0.40	0.60	216.6	489.8
0.35	0.65	220.7	493.9
0.30	0.70	225.4	498.6
0.25	0.75	230.9	504.0
0.20	0.80	237.3	510.4
0.15	0.85	245.1	518.2
0.10	0.90	254.8	528.0
0.05	0.95	267.8	540.9
0.00	1.00	286.4	559.6

214 **Table III. Measured Boiling Point (BP) Values of Propylene Glycol (PG) and Glycerol**
 215 **(GL) Mixtures With Volume %, Weight %, and Mol % (N=3).**

216

BP average \pm SD ($^{\circ}$ C)	% Glycerol (Average \pm 1 SD)		
	volume %	weight %	mol %
188.6 \pm 0.6	0 \pm 0	0.0 \pm 0.0	0.0 \pm 0
191.6 \pm 0.2	8.3 \pm 0.1	10.0 \pm 0.0	8.3 \pm 0.1
194.7 \pm 0.4	17.3 \pm 0.2	20.1 \pm 0.0	17.3 \pm 0.2
198.6 \pm 0.2	26.1 \pm 0.2	30.0 \pm 0.0	26.2 \pm 0.2
203 \pm 0.0	35.8 \pm 0.2	40.1 \pm 0.1	35.8 \pm 0.2
208 \pm 0.6	45.5 \pm 0.1	49.9 \pm 0.0	45.6 \pm 0.1
214 \pm 0.0	55.8 \pm 0.4	60.0 \pm 0.0	55.9 \pm 0.4
223 \pm 0.6	66.4 \pm 0.4	69.9 \pm 0.0	66.4 \pm 0.4
236 \pm 0.0	77.6 \pm 0.5	80.0 \pm 0.0	77.6 \pm 0.4
258 \pm 0.6	89.2 \pm 0.2	90.0 \pm 0.2	89.2 \pm 0.2
292 \pm 0.0	99.9 \pm 0.1	100.0 \pm 0.0	99.9 \pm 0.1

217

218

219 **Table IV. Coefficients Determined for Gibbs-Konovalov Parameterization of Propylene**
220 **Glycol (PG) and Glycerol (GL) Boiling Point Data.**

	<i>coefficient</i>			
	A	B	C	D
vol %	-119.9	-87.3	55.8	-22.6
wt %	-130.3	-100.8	66.9	-10.6
mol %	-119.9	-87.3	55.9	-22.5

221

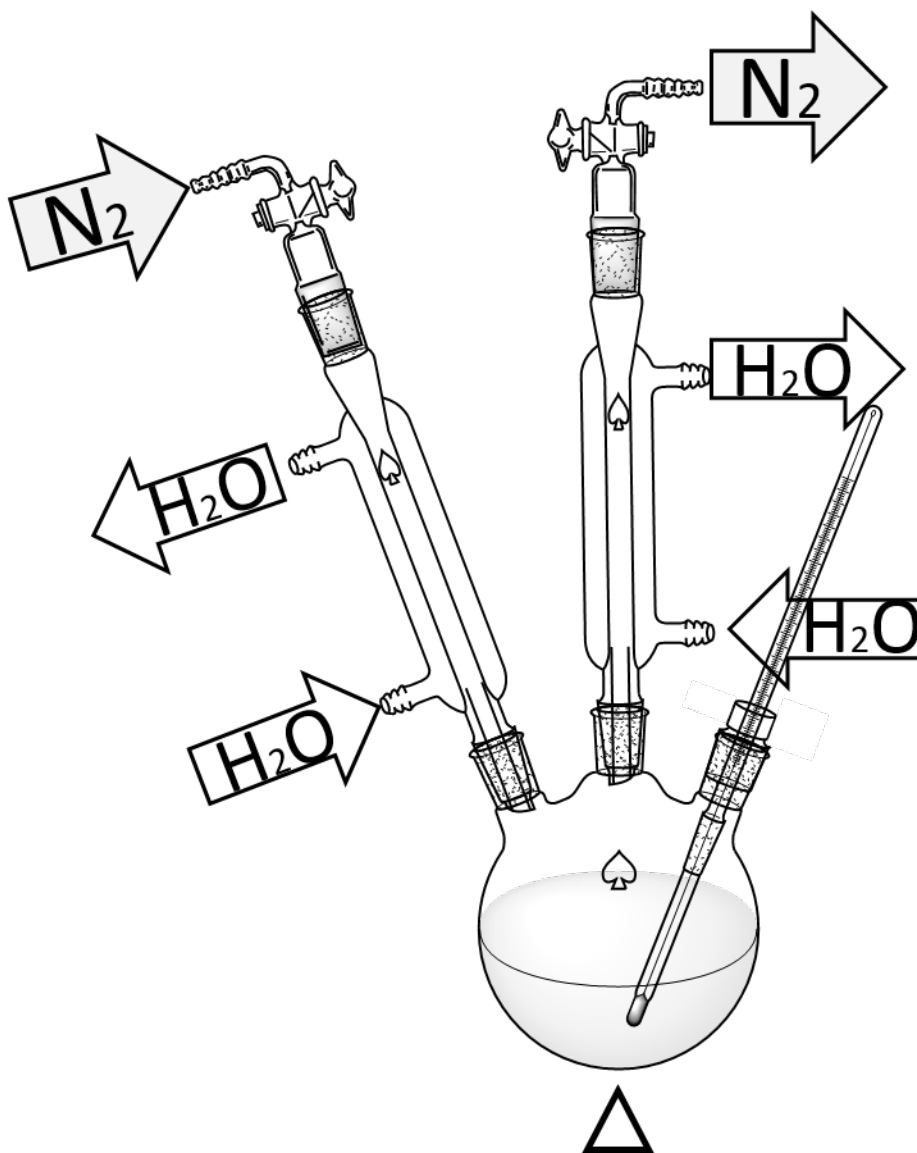
222

223 **Table V. Calculated Boiling Point (BP) Values (°C) for Propylene Glycol and Glycerol (GL)**
 224 **Mixtures by Volume, Weight, and Mole Percent GL using Coefficients A-D in Table 4, and**
 225 **Equation 2.**

% GI	0	5	10	15	20	25	30	35	40	45	50	%GL
BP (°C)	189	190	192	194	196	198	200	202	205	207	210	vol %
	189	190	191	193	195	197	199	201	203	205	208	wt %
	189	190	192	194	196	198	200	202	205	207	210	mol %
% GI	55	60	65	70	75	80	85	90	95	100		%GL
BP (°C)	213	217	221	226	232	240	249	260	274	292		vol %
	211	214	218	223	229	237	246	258	273	292		wt %
	213	217	221	226	232	240	249	260	274	292		mol %

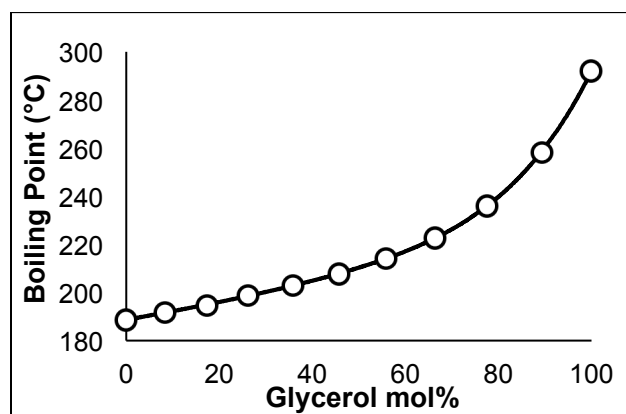
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228 **Figure 1. Schematic of Boiling Point (BP) Setup.** Thermometer in third port represents a
229 digital thermometer.



230

231 **Figure 2. Averages of Triplicate Boiling Point Measurements for Mixtures Composed of**
232 **Propylene Glycol (PG) and Glycerol (GL).** Mole percent GL post-boiling was determined by
233 NMR analysis. Error bars as ± 1 SD are too small to be seen.



234

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240 **Propylene Glycol (PG) and Glycerol (GL).** Mole percent GL post-boiling was determined by
241 NMR analysis. Error bars as ± 1 SD are too small to be seen.

242

243 **Supporting information**

244
 245 **S1 Figure. Comparison Between Pre- and Post-Boiling Compositions in terms of Percent**
 246 **Glycerol (GL) for Propylene Glycol (PG) + GL Mixtures. Average Percent GL, N=3, as**
 247 **Determined by NMR (%PG = 100% - %GL).**

248

<i>mol % glycercol</i>		
pre-boiling	post-boiling	ldifference
0.0	0.0	0.0
8.3	8.3	0.0
16.8	17.3	0.5
25.8	26.2	0.4
35.2	35.8	0.6
44.7	45.6	0.9
55.0	55.9	0.9
65.4	66.4	1.0
76.3	77.6	1.3
87.7	89.2	1.5
99.9	99.9	0.0

249 PG+GL mixtures were prepared by mass; however, due to differences between pre- and post-
 250 boiling composition, the post-boiling molar quantities were used to relate boiling point and
 251 (mol% and vol%) compositions. The values for 0, 8.3, and 99.9 mol% GL (0,10, and 100 wt%
 252 GL) remained constant with respect to pre- and post-boiling composition, while the 16.8-87.7
 253 mol% GL (20-90 wt% GL) increased by 0.4 – 1.5 mol% with respect to mol% GL. This effect is
 254 likely due to the lower vapor pressure of PG.