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Boiling points of the propylene glycol + glycerol system at 1 atmosphere pressure: 188.6–292 °C without and with added water or nicotine

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Abstract

In electronic cigarettes (“electronic nicotine delivery systems”, ENDS), 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). The use of ENDS is increasing rapidly worldwide, yet the BP characteristics of the PG + GL system have been characterized as the mixtures; here we re-do this, but significantly, also study the effects of added water and nicotine. 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). BPs of PG + GL mixtures were then tested in the presence of additives such as water (2.5 and 5 mol% added) and nicotine (3 mol%). Water was found to decrease the BP of PG + GL mixtures significantly at all compositions tested, and nicotine was found to decrease the BP of PG + GL mixtures containing ~75 GL: 25 PG (by moles) or more. The effect of added water (5, 10, and 15 mol% added) on electronic cigarette degradation production (some aldehydes and formaldehyde hemiacetals) was examined and found to have no significant impact on solvent (PG or GL) degradation for the particular device used.

Keywords

E-Cigarette liquid; Electronic cigarette; Electronic nicotine delivery system (ENDS); Glycerol; Heat exchanger fluid; Propylene glycol

Introduction

Propylene glycol (PG) and glycerol (GL) are high production volume (HPV) chemicals used in numerous industrial and consumer applications (Pendergrass, 1999; Teschke et al., 2005). First, they serve as heat exchanging fluids in solar hot water and geothermal energy systems,

including as PG + GL mixtures. Second, they are main ingredients in the nicotine-containing liquids (e-liquids) used in electronic cigarettes (aka “e-cigarettes”, “electronic nicotine delivery systems”, “ENDSs”) either individually or as a mixture. The dependence of boiling point (BP) temperature on composition is of interest in heat exchangers, e-cigarette applications, and for separations by distillation (Chen et al., 2015). Boiling is very unwelcome in heat exchange applications, but essential in the e-cigarettes (boiling must occur if the desired subsequent condensation aerosol is to form (Zhang et al., 2013; Glycerine as a heat transfer fluid and antifreeze, 2016). Globally, from 2014 to 2015, solar hot water capacity grew 6.4% from 409 to 435 gigawatts (Renewables 2016 Global status report, 2016; Mickle, 2015). For the e-cigarette industry, global growth was 58% in 2014 (Market Research on Vapour Devices, 2016). The number of regular adult e-cigarette users in the US in 2014 has been estimated at 11.8 million, with the number of “ever-users” estimated at 40.2 million (Schoenborn and Gindi, 2015).

Remarkably, BP behavior in the binary PG + GL system has received little direct study (Talib et al., 2017). For heat exchange applications, such information is needed during design to avoid vapor formation, and in e-cigarette applications, the information reveals the minimum temperatures that the ingredient chemicals (which may include flavor chemicals) will experience. Also, it is now well known that heating of “e-liquids” can lead to degradation products, some of which are toxic (formaldehyde (Jensen et al., 2015), acrolein and other aldehydes, and aromatic hydrocarbons (Hahn et al., 2014)). In a mixture, boiling occurs when the vapor pressure contributions from all components combine to become at least somewhat greater than the system pressure. It is thus useful to know how BP varies with composition in the PG + GL system.

Antoine equation parameterizations for the temperature-dependent vapor pressures of pure PG (p_{PG}^0) and pure GL (p_{GL}^0) are available (Table 1). By assuming ideal liquid mixtures (i.e., applicability of Raoult’s Law), one can use these parameterizations to predict the BP values for the full range of compositions for PG + GL mixtures according to

$$p_{TOT} = x_{PG}p_{PG}^0 + x_{GL}p_{GL}^0 \quad (1)$$

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

Materials and methods

Materials

Boiling point and ^1H NMR testing—United States Pharmacopeia grade PG and GL were obtained from Sigma-Aldrich (St. Louis, MO). Upon each opening and resealing, caps were wrapped with paraffin film to reduce hygroscopic absorption of water from the atmosphere. Reagents were 99.9+% pure, which was verified by nuclear magnetic resonance spectroscopy (NMR). (S)-(-)-nicotine (99%) was acquired from Alfa Aesar (Haverhill, MA). Deuterium oxide (99.9% ^2H , 0.1% ^1H) and dimethyl sulfoxide- d_6 (99.9% ^2H , 0.1% ^1H) were from Cambridge Isotope Laboratories (Tewksbury, MA), respectively.

Disposable capillary tubes (25 μL) were obtained from Drummond Scientific (Broomall, PA). Outer boiling point capillaries and an MP80 Melting Point System were obtained from Mettler Toledo (Columbus, OH). Graphite carbon powder (“–20 + 60 mesh”) was from Alfa Products (Danvers, MA).

Vaporized e-liquid collection—An NE-1660 model syringe pump (New Era Pump Systems Incorporated; Farmingdale, NY) was equipped with Monoject™ 140 mL syringes (Covidien; Dublin, Ireland), a valve control box (New Era Pump Systems Incorporated), and a 3-port solenoid valve (12 VDC; Humphrey; Kalamazoo, MI) with barbed brass fittings (McMaster-Carr; Elmhurst, IL) in order to collect vaporized e-liquid samples. Nylon Luer lock fittings (Cole-Parmer; Vernon Hills, IL) were used to connect silicone rubber laboratory tubing (Cole-Parmer; 0.125” I.D., 0.250” O.D., wall thickness 0.0625”) to BD (Franklin Lakes, NJ) PrecisionGlide™ Needles (18 gauge, 1.2 mm $\times$ 25 mm), which entered and exited the 2 mL sample collection vials (screw thread autosampler vials; Fisher Scientific; Pittsburgh, PA). Vials were equipped with 8 mm screw thread autosampler rubber septum caps (Fisher Scientific). A KangerTech KBOX Mini (Shenzhen KangerTech Technology Co., Ltd; Guangdong, China) was equipped with a 18650 Sony (Tokyo, Japan) 2100 mAh High Discharge Flat Top battery, KangerTech Subtank Mini tank, and KangerTech 1.2 Ω OCC (“Organic Cotton Coil”). A custom stainless-steel mouthpiece was developed to securely connect the mouth of the e-cigarette to the tubing.

Sample preparation

Large-scale boiling point determinations—Mixtures of PG and GL were prepared in triplicate at room temperature using 40 mL brown glass vials. The mixtures ranged from 0 to 100% by mass GL in increments of 10% by weight, for a total of 33 individually prepared ~20 mL samples.

Micro-scale boiling point determinations—Mixtures of PG and GL were prepared in batch sizes ranging from 5 to 10 mL in 40 mL brown glass vials. Five sets of mixtures were prepared. Each set of mixtures ranged from 0 to 100% by mols GL in increments of 25% by mol. To each set, water or nicotine was added to prepare one of the following: 2.5 mol% water, 5 mol% water, or 3 mol% nicotine (equivalent to 64.2–64.3 mg/mL nicotine, depending on whether pure PG or GL is used), for a total of 25 individually prepared mixtures.

All boiling point samples—Mass fractions were used as the basis of the preparations rather than volume fractions because of greater ease, with viscous liquids, in measuring mass versus volume amounts delivered. Vial caps were wrapped with paraffin film. Each sample was mixed by shaking for five minutes then stored in the dark for no more than 24 h before testing.

E-liquids for vaporization—PG and GL were combined in equal molar quantities and prepared gravimetrically to produce a stock mixture (“no added water”; ~125 g, ~109 mL) for vaporization experiments. After this PG:GL stock was confirmed to be approximately equimolar by ^1H NMR, three additional mixtures were prepared by taking aliquots of the stock mixture (by mass; ~22 g/sample) and adding deionized distilled water (by volume) to produce 5, 10, and 15 mol%-added water samples. These prepared e-liquids were evaluated by NMR and found to contain approximately 0, 7, 11, and 14 mol% water. Samples were stored in brown bottles, wrapped with paraffin film to reduce hygroscopic water absorption from the air, and used for experimentation within 8 h of preparation.

Boiling point determinations

Large-scale—Prior to heating, a “pre-boiling” 10 μL aliquot of each sample was mixed with 600 μL D_2O for analysis by NMR. The BP of the remaining ~20 mL of sample was determined using the apparatus represented in Figure 1. A three-necked round bottom flask was fitted with two reflux condensers that allowed nitrogen gas (N_2) to enter the boiling chamber, then exit via an oil bubbler (not shown); this permitted N_2 gas to flow freely through the system while maintaining an anoxic environment at ambient pressure. An HH12B digital thermometer and a KTSS-HH temperature probe from Omega (Stamford, CT) were fitted in the third flask opening. The digital temperature probe accuracy was reported by the manufacturer as $\pm 1.3^\circ\text{C}$, and this was verified by measuring the BP values of three liquids at 1 atm pressure: water (BP: 100.0°C), acetophenone (BP: 204°C), and ethyl benzoate (BP: 214°C). Standard deviation (SD) values for the triplicate PG and GL mixtures were found to be at most 0.5°C , which is smaller than the probe accuracy (as reported by the manufacturer). Below 200°C , the probe displayed four significant figures, including one decimal; above 200°C , only three significant figures were displayed. The flask was held in a rheostat-regulated heating mantle; mixing was provided using a stir plate. The system was thoroughly flushed with N_2 gas prior to heating. Samples were gradually heated over 30–90 min while stirring continuously until boiling was observed. Boiling temperatures were determined as the stable temperature at which each sample exhibited a steady rolling boil for at least five minutes. Each system was then allowed to return to room temperature under N_2 gas. A “post-boiling” aliquot (10 μL) was taken for analysis by NMR. The pre- and post-boiling NMR samples were collected to ensure that the boiling process did not considerably alter composition.

Micro-scale—The Mettler-Toledo MP80 Melting Point System was used to conduct all micro-scale boiling point trials. The system was operated using the manufacturer’s instructions, with some minor modifications that were required due to the high mixture viscosities. Each external boiling point capillary tube was loaded with 100–200 μL of sample, ~1 mg of graphite carbon powder, and a disposable 25 μL capillary tube. The 25 μL

capillary tube was fractured at the sample end prior to insertion in the outer capillary tube in order to serve as a surface for bubble nucleation.

Boiling point trials were conducted in triplicate. Preliminary trials were conducted prior to trials in order to determine an appropriate temperature range to test for each sample. The temperature range tested for each sample (ending temperature – starting temperature) varied and was as small as 25° and as large as 55°, and was centered around a potential boiling point. Variation in temperature range size was due to the inconsistent behavior of mixtures. The brightness was set to 40% and samples were heated at a rate of 10 °C/min within the selected range.

The boiling point of each sample was initially determined two different ways. (1) During a boiling point trial, the MP80 system attempted to report the boiling point by measuring the bubble rate as recorded by the instrument; once the bubble rate surpassed a certain threshold, the instrument reported the current temperature as the boiling point (“instrument-determined”). (2) The instrument recorded a video of the boiling point trial, which was magnified and viewed on the instrument screen during the trial, as well as reviewed after each trial (“visual determination”). Because of the viscous nature of the mixtures, precise “instrument-determined” boiling points were not reliable; while “visual determination” was concluded to be the most reliable and reproducible method of the two boiling point measurement methods, and so was used to determine the boiling points reported herein.

1D ¹H NMR analyses

Large-scale boiling point samples—The NMR analyses conducted on each pre- and post-boiling 10 µL aliquot (as diluted in 600 µL of D₂O) were carried out using a Bruker (Billerica, MA) Avance III spectrometer (599.90 MHz) with a 5 mm TXI probe. A pulse sequence of zg30 was used to acquire the data, with the relaxation delay value (d1) set to 5 s, in combination with the 30°-observation pulse of the zg30 experiment to allow for full relaxation, and so give reliable integrations.

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

Micro-scale boiling point samples—Each stock mixture was tested by ^1H NMR as in section Large-scale boiling point samples (above), within 1 h of BP evaluation, by combining 100 μL of sample with 400 μL of $\text{DMSO-}d_6$ and mixing. In this case, the relaxation delay (D1) was set to 3 s, because this value was determined to be sufficient for accurate integration of the peaks resulting from these mixtures. Despite gravimetric sample preparation, NMR was used to assess and report composition due to the presence of water in all samples and the hygroscopic nature of PG and GL.

Vaporized e-liquid samples—Samples were produced by vaporizing e-liquid and having the vapor pass through a 2 mL autosampler vial containing 500 μL of $\text{DMSO-}d_6$. The resulting sample-containing $\text{DMSO-}d_6$ was transferred to a NMR tube and tested by ^1H NMR methods described in section Large-scale boiling point samples (above) but with a relaxation delay (D1) of 3 s. Samples were tested within 24 h of being produced.

Vaporized e-liquid sample collection: the effect of added water

E-cigarette preparation—The method for e-cigarette vaping and NMR sample collection was adapted from Jensen et al. (2017). A KangerTech KBOX Mini equipped with a 2100 mAh battery was fully charged prior to sample generation. KangerTech 1.2 Ω organic cotton coils were inserted into three KangerTech Subtank Minis. Coils used in this experiment were “conditioned” by vaporizing 10–20 puffs (see section E-cigarette “puff” protocol for puff methods) of PG + GL e-liquid (50 mol% of each) at 26 W and were used to generate samples at 24 W or lower to determine if they resulted in e-liquid degradation. Only coils that showed significant e-liquid degradation, as indicated by the production of aldehydes and formaldehyde hemiacetals, were chosen for this experiment. We hypothesized that since the addition of water (2.5 and 5 mol%) to PG + GL mixtures decreased the BP, then the vaporized e-liquids containing more water could result in less degradation due to the lower vaporization temperature required. Since we hypothesized that more water in the e-liquid would produce less degradation, we wanted to ensure that significant degradation could be seen prior to the addition of more water. For the “no added water” condition, tanks were filled with 4.6–5.1 g of e-liquid and the coil was thoroughly wetted with e-liquid. After samples were collected for this condition, tanks were drained of e-liquid and dried with lint-free tissues. Tanks were then rinsed with ~ 1 mL of the next refill liquid, which was discarded, and then tanks were refilled for testing with the same e-liquid condition. This process was repeated for each testing condition for each tank. For the 5, 10, and 15 mol% added water conditions, 4.3–4.7 g, 4.0–4.6 g, and 4.1–4.4 g of e-liquid was added to tanks, respectively.

E-cigarette vapor collection setup—The charged KangerTech KBOX Mini, attached to the e-liquid-filled Subtank Mini, was vertically positioned and a custom-made stainless-steel mouthpiece was inserted into the tank opening using a rubber O-ring to provide a seal. A nylon Luer lock fitting was screwed into the stainless-steel mouthpiece connecting it to ~ 9 cm of silicone tubing. At the other end of the tubing, was a barbed Luer lock fitting attached to an 18 gauge needle. The tubing and needle arced $\sim 180^\circ$ from the mouthpiece of the e-cigarette. This first needle was inserted fully through the rubber septum of the cap on the 2 mL sample vial (containing 500 μL $\text{DMSO-}d_6$), such that the tip of the needle was touching

the side of the vial above the solvent line. A second (exit) needle was also inserted through the same rubber septum, but just far enough that the needle opening was inside the vial. This exit needle was also connected to a Luer lock fitting that securely attached to a second piece of silicone tubing (~9 cm). This final piece of tubing connected the sample collection system to a 3-port solenoid valve. The solenoid valve allowed the pump to withdraw the sample from the e-cigarette through one opening during the withdrawal time-period, and eject the remaining puff into the fume hood. The final opening on the solenoid valve connected with tubing to the sample collection system to a 140 mL syringe (controlled by the pump). The solenoid valve was controlled by the valve control box, which was wired to the pump. The pump was programmed according to section, E-cigarette “puff” protocol (below).

E-cigarette “puff” protocol—Samples were generated using the puffing parameters set forth by CORESTA (Cooperation Centre for Scientific Research Relative to Tobacco) for e-cigarette aerosol sample production (CORESTA, 2015). The puff duration was 3 s, the puff volume was 55 mL, and the puff frequency was 2 puffs/minute (one puff started every 30 s). The power button on the e-cigarette was activated one second prior to the start of sample collection (syringe withdrawal), and held for a total of 4 s (including the 3 s puff). The interpuff interval (distance between the end of one puff and the start of the next) was thus 27 s.

E-cigarette vapor collection at 22 W—The coils used for this experiment were previously conditioned and analyzed by NMR in terms of degradation production (section E-cigarette preparation). The same KangerTech KBOX Mini and battery were used for all samples and was set to 22 W (these coils are rated for up to 26 W); the device was charged between conditions. Tanks and vials were weighed before and after sample collection so that the fraction of aerosol that was trapped in the sample vial (%-trapped) could be calculated for each sample. The mouthpiece of each tank was cleaned after the generation of each sample prior to weighing. After tanks were filled with new e-liquids, 10 “wicking puffs” were collected into a vial and discarded. Approximately 1–5 min elapsed between the end of the final wicking puff and the collection of a sample collected for NMR (three puffs); one of each was collected from each tank per water condition, for a total of 24 samples.

Results and discussion

Large-scale boiling point determinations

The overall precision of the large-scale BP determination technique was established for each method by calculating the standard deviation of triplicate boiling point (°C) values (Table 3). Standard deviation in terms of %GL for each large-scale method resulted in 0.2% for wt% GL (based on initial mixture masses), 0.4% for the mol%, and 0.5% for the vol% (calculated using the mol% determined by NMR). The similarities between the volume % and mol % at each temperature are simply a consequence of the density/molecular mass ratio being nearly the same for both PG and GL.

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

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

where $t_{b,\text{PG}}$ and $t_{b,\text{GL}}$ ($^{\circ}\text{C}$) are the measured boiling points of pure PG and GL, respectively. Fit values of the coefficients A , B , C , and D for Equation (2) (i.e., using mol fraction composition) were found by minimizing the sum of the residuals using the Microsoft Excel *Solver* (Frontline Systems Inc., Incline Village, NV) add-in. Fit values were similarly obtained using volume and weight fraction values. Coefficients A – D are presented in Table 4. Corresponding calculated BP values are given in Table 5. Gibbs-Konovalov calculated values (Table 5) were compared with the Antoine equation values (Table 2) and found to differ by up to 6.7 $^{\circ}\text{C}$ at the upper range (beginning >230 $^{\circ}\text{C}$), with an average difference ($\pm\text{SD}$) of 1.8 ± 1.9 $^{\circ}\text{C}$ over the entire range (Table S3).

Micro-scale boiling point trials

Large-scale boiling was possible and reliable for PG + GL mixtures, but additives such as water or nicotine made such determinations difficult. Determining the BPs for PG + GL mixtures with additives was made possible using the micro-scale BP method. Mixtures of PG + GL were tested using the micro-scale method (0, 25, 50, 75, and 100 mol% GL) and found to agree with the previously determined/calculated BPs (Table 5) within 3 $^{\circ}$. The absolute differences between the large-and micro-scale BPs (data not shown) were averaged and found to be 1.5 ± 1.0 $^{\circ}\text{C}$ (SD).

Samples analyzed using the micro-scale boiling point system were tested by NMR to verify composition because PG and GL are hygroscopic. NMR results were used to ensure that similar amounts of water were present in samples within each condition. Although gravimetric methods were used to prepare samples, NMR composition results were used to determine the mole %GL in relation to only PG for comparison with BPs. NMR composition results produced mole ratio measurements that were within 3.1 mol% of values based on the mass preparation method. The largest uncertainty, which was associated with the 3 mol% nicotine sample in ~75 GL: 25 PG (by mol%), was attributed to the mol% water, and is due to the hygroscopic nature of the mixture. All other values differed from the expected composition by less than 2.1 mol%. The absolute difference between the actual (NMR-determined) and predicted mol% GL (based on gravimetric preparation of the samples) was calculated for each sample; the average ($\pm\text{SD}$) of the absolute difference for each component was 0.7 ± 0.7 mol% for GL, 0.9 ± 0.6 mol% for PG, 1.4 ± 0.7 mol% for water, and 0.1 ± 0.1 mol% for nicotine. Water was the largest source of uncertainty for all samples.

An additional source of uncertainty arises from the water content of the samples, as it was difficult to calculate using NMR integrations due to overlap between the water peak and resonances from PG and GL. In most samples, the water peak was located under the PG and/or GL peaks, and so was determined by peak subtraction. Despite careful phasing, baseline correction, and processing, this could contribute to the uncertainty in the

determination of the water content in mixtures by NMR. However, since samples within a batch were prepared at the same time and based on mass data, they are fairly similar in terms of content. The average added water content determined by mass for the 5 mol% water samples was 4.9 ± 0.2 mol% and 2.6 ± 0.2 mol% water for the “2.5 mol% added water samples”. By NMR, the average water content in the “5 mol% added water” samples was 5.6 ± 1.6 (SD), and 3.9 ± 0.6 for “2.5 mol% added water” samples. The average nicotine content in the 3 mol% nicotine mixtures was found to be 2.9 ± 0.2 mol% (as calculated from gravimetric data) and 2.7 ± 0.2 mol% by NMR.

The boiling points of PG GL mixtures with additives (Table 6) indicate + that water at molar concentrations of 2.5 and 5 mol% of the total mixture decrease the BP of PG GL mixtures ranging from 0% to 100% GL. Nicotine (3 mol% of the total mixture) was found to decrease the BP, but the only significant changes involved ~75 GL: 25 PG and 100 GL: 0 PG (by mol %). Water as an additive altered the BP of PG + GL mixtures by up to ~60° for 5 mol% water (in 100% GL), and up to ~30° for 2.5 mol% water (in 100% GL); see Figure 3. Nicotine (3 mol%) lowered the BP by up to ~15° (100% GL), but lowered the BP for 0 GL: 100 PG to 50 GL: 50 PG (by mol%) by less than one degree. One mol% added nicotine was also evaluated, and the BP values were found not to be significantly perturbed across the entire range of PG + GL mixtures (data not shown).

The effect of water on degradation in e-cigarettes

¹H NMR spectroscopy has been shown to be useful for evaluating PG + GL e-liquid degradation during e-cigarette vaping (Jensen et al., 2015, 2017). Samples vaporized using a KangerTech KBOX Mini in combination with a KangerTech Subtank Mini were analyzed by NMR and degradation was examined as a function of added water. Degradation was considered by examining aldehyde peaks (propanal, acetaldehyde, glyceraldehyde, glycolaldehyde, lactaldehyde, and acrolein) and PG and/or GL formaldehyde hemiacetal peaks and were identified based on chemical shifts and splitting patterns (Jensen et al., 2017). Based on the micro-scale BP trials (section Micro-scale boiling point trials), the “2.5” and “5 mol% added water” conditions would lower the BPs by ~10° and ~20°, respectively. We hypothesized that lowering the BP could decrease degradation production because a lower temperature would be required for aerosolization. Spectra were normalized using the PG and GL peaks so that degradation could be compared between samples. However, no significant and reproducible effect on degradation quantities was seen upon the addition of 5, 10, or 15 mol% water (equivalent to 1.2, 2.4, and 3.6 vol% added water) to equimolar PG + GL (Figure S1). We found that up to 15 mol% added water had no significant impact on degradation production. The %-trapped aerosol ((absolute value of the change in the vial mass/absolute value of the change in tank mass)*100) was determined for each of the four conditions per tank and averaged. Samples from tank 1 contained $54 \pm 7\%$ of the total aerosol produced. Samples from tanks 2 and 3 contained $37 \pm 4\%$ and $44 \pm 2\%$ of the total aerosol, respectively.

Conclusions

The data obtained herein provide BP values of PG + GL mixtures at 1 atmosphere pressure, and smooth fitting allows prediction of BP for any composition (e.g., Table 5). Depending on composition, the minimum temperature required to produce an e-cigarette aerosol from a PG GL liquid ranges from 188.6 °C to 292 °C. Water, as an additive, was found to decrease the BP of PG + GL mixtures for all tested mixtures. Nicotine (3 mol%) was found to only significantly impact PG + GL mixtures containing at least ~75 mol% GL. The nicotine level tested (3 mol%) was equivalent to ~64 mg/mL; this exceeds common levels found in commercial e-liquids, which are often under 50 mg/mL. In order to test the impact of BP lowering, a KangerTech KBOX Mini was tested at 22 watts using three different 1.2 Ω coils in three different KangerTech Subtank Minis at four different water conditions: 0, 5, 10, and 15 mol% added water. PG + GL degradation was monitored by ^1H NMR in terms of aldehydes and PG and/or GL formaldehyde hemiacetal production (Jensen et al., 2017, and Figure S1 herein). No significant differences in degradation were observed for the various added water conditions. Despite the ~20° BP lowering of PG + GL due to 5 mol% water as determined using the micro-scale method, and likely an even greater BP decrease due to adding up to 15 mol% water, these concentrations did not have a significant effect on solvent degradation. Larger amounts of water could reduce the BP of the solvent mixtures even more, and may then reduce solvent degradation; this set of studies is planned for other devices as well as varying the solvent mixtures beyond 50 PG: 50 GL (by mol%).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Schematic of boiling point (BP) setup. Thermometer in third port represents a digital thermometer.

Figure 2.

Averages of triplicate boiling point measurements for mixtures composed of propylene glycol (PG) and glycerol (GL). Mole percent GL post-boiling was determined by NMR analysis. Error bars as ± 1 SD are too small to be seen; the largest SD is 0.6° .

Figure 3.

Averages of triplicate boiling point measurements for mixtures composed of propylene glycol (PG) and glycerol (GL). The boiling points of propylene glycol + glycerol mixtures were determined in the absence of additives (“Large-scale boiling: no additives”), as well as in the presence of 3 mol% nicotine, 2.5 mol% added water, and 5 mol% added water. Fits are included to guide the eye, rather than allow extrapolated boiling points. Error (± 1 SD) is provided for all data points ($N = 3$).

Table 1.

Antoine equation parameters for vapor pressure p° (bar) of the pure liquids propylene glycol (PG) and glycerol (GL), with applicable temperature ranges, $\log_{10}(p^\circ) = A - B/(T(K) + C)$. (1 atm = 1.01325 bar.) <http://webbook.nist.gov/chemistry/>

	t (°C) range	T (K) range	A	B	C	Reference
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 2.

Boiling point values at 1 atm pressure assuming Raoult's law (ideal mixtures).

$p_{\text{TOT}}(T) = x_{\text{PG}}p_{\text{PG}}^0 + x_{\text{GL}}p_{\text{GL}}^0 = 1.01325 \text{ bar} (= 1 \text{ atm})$ for Antoine equation parameters in Table 1.

		Boiling point	
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

Table 3.

Measured boiling point (BP) values of propylene glycol (PG) and glycerol (GL) mixtures with volume %, weight %, and mol % ($N=3$)

% Glycerol (average ± 1 SD)			
BP average $\pm$ SD ($^{\circ}\text{C}$)	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

Table 4.

Coefficients determined for Gibbs–Konovalov parameterization of propylene glycol (PG) and glycerol (GL) boiling point data.

	Coefficient			
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
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

Table 5.

Calculated boiling point (BP) values (°C) for propylene glycol and glycerol (GL) mixtures by volume, weight, and mole percent GL using coefficients A – D in Table 4, and Equation (2).

%GL	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 %
	55	60	65	70	75	80	85	90	95	100		
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 %

Table 6.

Micro-scale boiling points (BP) of propylene glycol (PG) + glycerol (GL) mixtures with additives in relation to mol% GL (relative to moles PG only).

5 mol% water		2.5 mol% water		3 mol% nicotine	
mol% GL	BP (°C)	mol% GL	BP (°C)	mol% GL	BP (°C)
100	230.7 ± 0.6	100	261 ± 1.0	100	277 ± 0.0
75	203.3 ± 2.5	76	212.5 ± 0.9	76	229.5 ± 1.3
50	191.7 ± 1.5	50	199.7 ± 0.2	50	210.1 ± 0.4
26	185 ± 0.0	26	191.0 ± 0.9	26	198.3 ± 0.6
0	173.3 ± 1.2	0	183.3 ± 1.2	0	188.2 ± 0.3