

# *Low Electrical Conductivity Glycol Coolants as Alternative to Perfluorinated Fluids for Electronics Cooling Applications*

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**Abstract**— Per- and polyfluoroalkyl substances (PFAS/PFOS) are being phased out due to environmental and health concerns. Low electrical conductivity ethylene glycol-water solutions were studied to understand if these coolants can be a viable alternative to PFAS/PFOS. Glycol-water fluids demonstrate excellent thermo-physical properties, but ions from various sources can cause the electrical conductivity to rise continuously. A deionizer containing mixed bed (MB) resin particles can maintain low electrical conductivity, but limited studies have been done to understand the effect of a glycol solution on the ion exchange capacity and performance of the MB resin.

In our research, MB resin was exposed to Dynamene low electrical conductivity ethylene glycol-water 50 wt% solution (LCEG 50 wt%) as well as ultrapure deionized water (UPW) at different temperatures and time intervals up to 12 weeks. Results demonstrated that the MB resin has a continuous usage temperature range from -25°C to 93°C in LCEG 50 wt%, with the fastest ion exchange occurring between 22.8°C to 70°C. There was a minor loss (less than 7%) in ion exchange capacity for LCEG 50 wt% and UPW at room temperature after 12 weeks, while a notable reduction in capacity was observed at 93°C after the same timeframe: 68% loss for LCEG 50 wt% and 47% loss for UPW. It was also observed that the anionic resin degradation in LCEG 50 wt% was 2.5 times higher on average compared to degradation in UPW. Results show that resin performs better in UPW than in LCEG 50 wt% but can still be used to effectively maintain low electrical conductivity in glycols.

**Keywords**—electronics cooling, PFAS, low electrical conductivity, glycol-water coolant, ion-exchange resin

## I. INTRODUCTION

With the increase in demand for small and critical electronic and semiconductor components, there is an urgency for developing cooling liquids that provide efficient thermal management. Several commercial electronic coolants are available for both direct and indirect cooling of electronic and semiconductor processes and applications [1] [2]. Among the most common are Per- and polyfluoroalkyl coolants (PFAS/PFOS) due to their excellent chemical and physical properties. They were introduced before 1940 and are currently used in more than 200 industries and 1400 products [3] [4].

These organofluoro compounds do not degrade easily in the human body or the environment and are often referred to as “forever chemicals.” These chemicals have been shown to cause harmful effects to human health [3] [5]. As a result, major suppliers and the EPA are slowly trying to eradicate the use of PFAS chemicals by 2025 [3] [6] [7]. A large amount of PFAS chemicals are used as heat transfer and dielectric fluids in the electronics and semiconductor industry [3]. These long-chain organofluoro coolants are non-flammable, dielectric, have high heat capacities and wide temperature ranges. Short-chain PFAS molecules have been considered as substitutes, and though they do not bioaccumulate for as long as their long-chain counterparts, these molecules can be found in aquatic systems. More research needs to be done to understand their long-term effects [8] [9]. Silicone and other hydrocarbons are also considered as possible replacements, but these fluids have high viscosity and high flammability. These undesirable properties pose challenges such as sticking to the material surface, low pumpability, and safety concerns.

Glycol-water blends are commonly used as antifreeze and coolants in various heating and cooling applications due to their low-temperature freeze protection, high boiling point, wide working temperature range, and excellent thermo-physical properties. Table I compares some important thermophysical properties of Dynamene low electrical conductivity 50 wt% ethylene glycol-water (LCEG 50 wt%) to common PFAS heat transfer fluids, including 3M Fluorinert Electronic Liquid FC-770 and 3M Novec 7100. Although both PFAS fluids have higher density and lower viscosity compared to LCEG 50 wt%, which are favorable for heat transfer, they both exhibit lower specific heat and thermal conductivity, which are unfavorable for heat transfer. For example, the Novec 7100 has an absolute viscosity of 0.58cP compared to 3.38cP for LCEG 50 wt%, but the Novec 7100 has a thermal conductivity of 0.069 W m<sup>-1</sup> °C<sup>-1</sup> compared to 0.392 W m<sup>-1</sup> °C<sup>-1</sup> for LCEG 50 wt% [10] [11]. This tradeoff of having either high density and low viscosity or high specific heat and high thermal conductivity makes both glycol-water and PFAS effective coolants. Glycol-water blends also offer the advantages of being non-flammable and low cost. These coolants have higher surface tension than the PFAS

**Table I.**

Thermophysical Properties of Dynalene LCEG 55 wt% compared to 3M Fluorinert Electronic Liquid FC-770 and 3M Novec 7100 (all properties at 25°C) [8] [9].

Properties	3M Fluorinert Electronic Liquid FC-770	3M Novec 7100	Dynalene LCEG 50 wt%
Density	1793 kg/m <sup>3</sup>	1510 kg/m <sup>3</sup>	1079 kg/m <sup>3</sup>
Absolute Viscosity	1.359 cP	0.58 cP	3.38 cP
Specific Heat	1038 J kg <sup>-1</sup> °C <sup>-1</sup>	1183 J kg <sup>-1</sup> °C <sup>-1</sup>	3267 J kg <sup>-1</sup> °C <sup>-1</sup>
Thermal Conductivity	0.063 W m <sup>-1</sup> °C <sup>-1</sup>	0.069 W m <sup>-1</sup> °C <sup>-1</sup>	0.392 W m <sup>-1</sup> °C <sup>-1</sup>

coolants [3] and are less likely to cause spills and leaks. Due to the presence of ionic inhibitors, traditional heat transfer fluids have high electrical conductivities greater than 2,000  $\mu\text{S}/\text{cm}$  and will likely cause short circuits and failure if they contact electronics. Therefore, low electrical conductivity (LC) coolants are crucial for preserving the integrity of electrical components in the event of a spill. Such LC glycol-water based coolants are desirable for battery and fuel cell cooling [12] [13]. They provide excellent thermal management when used to replace PFAS coolants in the indirect cooling of electronic components. Unfortunately, ion leaching of materials and thermal oxidative induced glycol breakdown contribute to the increase in electrical conductivity of glycol-water mixtures [13] [14] [15] [16]. Thus, it is imperative to maintain low electrical conductivity (less than 5  $\mu\text{S}/\text{cm}$ ) in these coolants especially when they are used near semiconductor and electronic components.

Mixed bed (MB) ion-exchange resins are commonly used to deionize water in various applications, such as medical, pharmaceutical, power generation, and automotive. MB resins can remove both cations and anions from the feed water and offer improved water quality over placing the individual resin counterparts in series [17]. These MB resins help to maintain neutral pH and provide high ion exchange capacity [18]. However, they are not widely used in conjunction with LC glycol coolants. Though desalination of contaminated glycols had been attempted [19], few companies provide these low conductivity glycol coolants in combination with an ion-exchange resin deionizer. Limited research has been done regarding the effect of glycol on the performance and integrity of these resin media [20][21][22]. Kamo, K., & Miyashita, M. discussed how the capacity reduction of ion exchange resin in the presence of glycol can be determined considering temperature and the organic acids produced by degrading glycol but did not quantify the thermal degradation of the anionic resin [20].

The resin used in this study consists of a divinylbenzene-(DVB) crosslinked polystyrene gel matrix, which serves as the backbone [23] [24]. It is then functionalized through sulfonation to form strong acid cation (SAC) resin containing stationary sulfonic acid functional groups and mobile  $\text{H}^+$  ions or through chloromethylation and amination with trimethylamine (TMA) to form type 1 strong base anion (SBA) resin containing stationary quaternary ammonium functional groups and mobile  $\text{OH}^-$  ions [23] [24]. The resulting MB resin is 1:1 (equivalent basis) SAC and Type 1 SBA resins. During ion exchange, a counter ion from

the solution diffuses into the resin bead and displaces the mobile ion part of the functional group. SBA resins are less stable compared to SAC and the maximum operating temperature reflects this. The SAC resin can handle up to 140°C while Type 1 SBA is only rated for 60°C [17]. TMA groups in the SBA resins are stripped at the carbon-nitrogen bond when subjected to high temperatures and this can be measured.

To replace PFAS products with a sustainable option such as glycol-water heat transfer coolant, it is essential that ion-exchange resin deionizers maintain a low electrically conductive coolant with superior thermo-physical and corrosion properties. In this study, the performance and integrity of the resin in low electrical conductivity ethylene glycol-water solution (Dynalene LCEG 50 wt%) was compared to that in ultrapure deionized water (UPW). Ion exchange capacity, ion exchange rate, and the concentration of TMA (anionic resin degradation product) were determined to assess the viability of using deionized LC coolants as PFAS substitutes.

## II. MATERIALS & METHODS

To evaluate a deionizer's ability to quickly remove ions in practice, 40L of Dynalene LCEG 50 wt% was heated to 85°C, enriched with Emprove® Essential USP Sodium Chloride to a conductivity of 100  $\mu\text{S}/\text{cm}$ , and circulated at 15 LPM through a Dynalene IC-093-08H deionizing cartridge filled with 900 milliequivalents of chloride (mEq Cl) mixed bed resin (60% SBA and 40% SAC resins in the  $\text{OH}^-$  and  $\text{H}^+$  forms). Electrical conductivity was plotted versus time using a data acquisition system to identify the times where conductivity dropped to 5  $\mu\text{S}/\text{cm}$  and 1  $\mu\text{S}/\text{cm}$ .

Further investigation into resin ion exchange rate was performed. 5g sodium chloride was dissolved in 300g LCEG 50 wt% at -25°C, 22.8°C, 70°C, or 90°C. Upon addition of 60g mixed bed resin at the same temperature, chloride concentration was measured at different time intervals using Hach® Chloride QuanTab® Test Strips (certified to  $\pm 10\%$  accuracy). The ion exchange rate was determined as the slope after 30 seconds, 1 minute, or 2 minutes of stirring.

Resin capacity was measured with time and temperature. Teflon jars containing 10g mixed bed resin and 100g Dynalene LCEG 50 wt% or 100g Ultra-pure deionized water (UPW) were placed at 22.8°C, 50°C, 70°C, 80°C, 93°C, or 100°C and remained closed without agitation for 1 week, 2 weeks, 4 weeks, 6 weeks, 8 weeks, or 12 weeks. Jars were then transferred to

hotplates to maintain their respective temperatures while stirring, save for another set of jars with LCEG 50 wt% stored at 100°C that were cooled to 22.8°C. Sodium chloride was added in 0.1g or 0.01g additions and the solution's conductivity was allowed to drop below 5 μS/cm before subsequent additions until the conductivity did not drop below 5 μS/cm after 3 hours. Using the total amount of chloride added the resin capacity in mEq Cl was found:

$$mEq\ Cl = \frac{mg_{Cl} \times Valence}{AW} \quad (1)$$

where  $mg_{Cl}$  is the total amount of chloride added in mg and  $AW$  is the atomic weight of chloride. Resin capacity was then expressed in mEq Cl/g resin and plotted versus time.

To examine the effect of thermal degradation on the removal of amine functional groups from the anionic resin, 100g mixed bed resin was added to 750g Dynalene LCEG 50 wt% or 750g UPW and kept statically at 22.8°C, 70°C, or 100°C. 100g of sample was removed after 1 week and 2 weeks, and a total neutralizing amine titration was performed using AquaPhoenix Scientific Total Alkalinity Indicator (Al6925) as the indicator and AquaPhoenix Scientific Neutralizing Amine Titrating Solution as the titrant.

### III. RESULTS & DISCUSSION

When circulated through ion-exchange resin, low electrical conductivity glycol-water solutions may be suitable replacements for PFAS coolants in indirect liquid cooling applications. A mixed bed of SBA and SAC resins in the OH<sup>-</sup> and H<sup>+</sup> forms removes charge-carrying ions from glycol-water coolant that may jeopardize the performance of electronic components in the event of a spill. To maintain low conductivity, it is crucial that the resin remove ions efficiently while resisting degradation due to time and temperature.

#### A. Ion Exchange Efficiency with LCEG 50 wt% in Practice

Ion exchange efficiency reflects a resin's ability to maintain conductivity levels below a desired threshold such as the characteristically low 5 μS/cm used for fuel cell cooling. After heating LCEG 50 wt% to 85°C, raising the conductivity to 100 μS/cm, and circulating through a deionizing cartridge, the resulting conductivity versus time was plotted (see Fig. 1. for experimental setup). Results indicate the conductivity was reduced to 5 μS/cm in 8.2 minutes and 1 μS/cm in 13.2 minutes. A drop in conductivity from a relatively high conductivity threshold and temperature to acceptable levels of less than 5 μS/cm in under 10 minutes supports the use of glycol-water in high temperature applications sensitive to changes in conductivity. The ability to maintain low conductivity while resisting large fluctuations is important for minimizing corrosion and ion leaching which hinder system performance.

#### B. Resin Ion exchange Rate in LCEG 50 wt%

Resin's effectiveness in glycol-water was investigated further by measuring ion exchange rate in LCEG 50 wt% at -25°C, 22.8°C, 70°C, and 90°C. Ion exchange rate was determined by measuring the mEq Cl removed over time. The resin was saturated with an excess concentration of sodium chloride and chloride concentration was plotted against time in

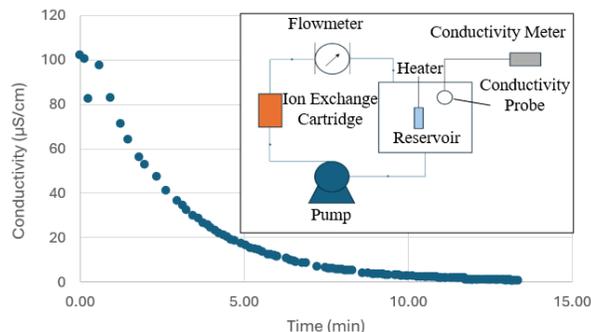


Fig. 1. Electrical conductivity was measured versus time for 40L LCEG 50 wt% circulated through an IC-093-08H mixed bed resin deionizing cartridge at 85°C and 15LPM. Inset shows the set-up where a pump circulates glycol through a cartridge and flowmeter back to the reservoir, and a conductivity meter indicates conductivity and temperature in the reservoir.

Fig. 2. The ion exchange rates at each temperature followed the increasing order -25°C < 90°C < 70°C < 22.8°C and were equal to  $2.5 \times 10^{-3}$ ,  $1.4 \times 10^{-2}$ ,  $2.6 \times 10^{-2}$ , and  $2.9 \times 10^{-2}$  mEq Cl · g resin<sup>-1</sup> · s<sup>-1</sup>. The significantly lower resin ion exchange rate at -25°C compared to 22.8°C (11.6 times less), 70°C (10.4 times less), and 90°C (5.6 times less) was due to greater ion diffusion rates at higher temperatures [25]. However, a drop-off in ion exchange rate was observed at 70°C and continued up to 90°C. This decrease is likely caused by cleavage of the trimethylamine (TMA) functional groups from the anionic resin [26]. After 2 minutes, resin capacity had plateaued for 22.8°C, 70°C, and 90°C at 0.96, 0.89, and 0.84 mEq Cl/g resin respectively while capacity at -25°C continued to increase another 2.2 times up to a maximum of 0.97 mEq Cl/g resin after 2 hours, providing further evidence that ion exchange is not preferred at colder temperatures where glycol is commonly used for freeze protection.

#### C. Resin Capacity in LCEG 50 wt% compared to UPW

Since the ion exchange process is controlled by equilibrium, resin reaches its full capacity once there is no net displacement of ions under a given set of conditions. To explore the ion exchange capacity with glycol under different conditions, resin ion exchange capacity was compared amongst LCEG 50 wt%

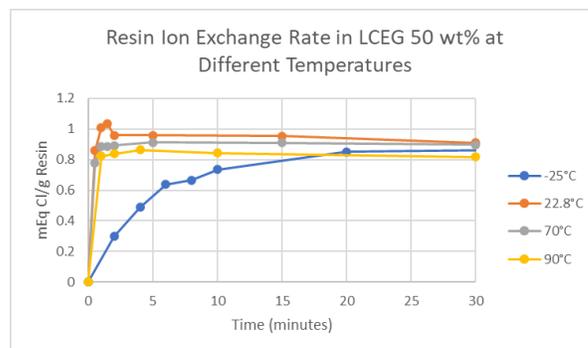


Fig. 2. Resin capacity versus time for LCEG 50 wt% showed an increase in ion exchange rate from -25°C to 22.8°C and a decrease from 22.8°C to 70°C and from 70°C to 90°C. The chloride measurement has an accuracy of ±10%.

and UPW after being stored at 22.8°C, 50°C, 70°C, 80°C, 93°C, or 100°C for 12 weeks. Total resin capacity in mEq Cl/ g resin was measured at 1, 2, 4, 6, 8, and 12 weeks and was defined as the point where a conductivity less than 5 μS/cm could no longer be maintained. The resulting capacities were lower with higher temperature, longer time, and in LCEG 50 wt% compared to UPW. Fig. 3(a) and Fig. 3(b) present these differences clearly. Ion exchange capacity did not change significantly after 12 weeks at 22.8°C for resin in LCEG 50 wt% (6.3% reduction) or resin in UPW (5.1% reduction). Resin experienced a 50% decrease in mEq Cl/g resin after 12 weeks in LCEG 50 wt% at 70°C while a similar decrease of 47% was achieved by resin stored in water after 12 weeks at 93°C. Not accounting for LCEG 50 wt% 100°C data, the capacity reduction after 12 weeks was nearly 2 times greater for resin in LCEG 50 wt% (53% average reduction) compared to resin in UPW (26% average reduction). The greater mEq Cl/g resin reduction with temperature for LCEG 50 wt% compared to UPW may be in part attributed to a combination of the amine degradation products given off by the resin and the acidic degradation products generated by the glycol during heating, which a portion of the resin’s capacity is used to remove. The mEq Cl/g resin reduction was linear overtime for both fluids as seen in Fig. 4. Slopes of the linear trends for LCEG 50 wt% and UPW were only 1.9% different from each other, which shows that temperature alone had a similar effect on the resin in both liquids. Resin in LCEG 50 wt% was tested last at 100°C to determine the maximum temperature where ion exchange would occur. The resin lost 89% capacity by the seventh week and did not remove any salt at the 12-week mark. Findings suggest a continuous usage temperature range from -25°C (possibly lower) and up to 93°C for resin in LCEG 50 wt%.

In a similar study, jars of resin in LCEG 50 wt% were stored at 100°C for different periods of time, removed from storage, and their capacities tested at 100°C or after cooling from 100°C to 22.8°C. Table II demonstrates that at 1 week, the ion exchange capacity was the same at 100°C and 100°C cooled to 22.8°C, as the time wasn’t long enough to cause an appreciable amount of irreversible degradation. Conversely, a complete loss

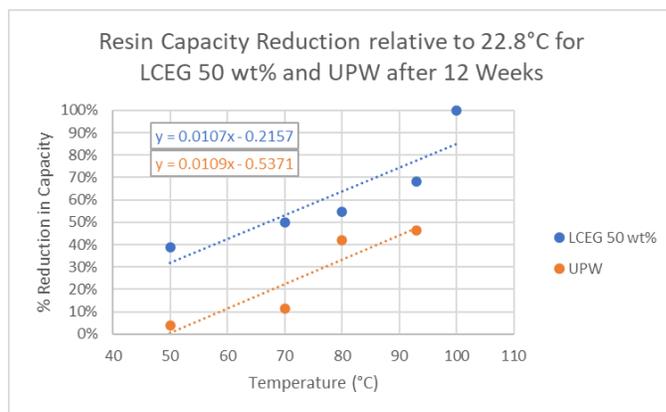


Fig. 4. Resin capacity loss relative to 22.8°C was twice as great in LCEG 50 wt% compared to UPW, and their slopes very similar, being 0.0107 for LCEG 50 wt% ( $R^2 = 0.7965$ ) and 0.0109 for UPW ( $R^2 = 0.8461$ ). The expected error was  $\pm 5\%$ .

of ion exchange capacity was observed for both after 12 weeks. Hence, the recovered capacity was 0% in both cases. Recovered capacity was highest after 2 weeks at 8.83%, and decreased linearly down to 0% by 12 weeks, indicating a reversible process occurred that diminished with time as anionic resin became increasingly damaged from the irreversible effects of thermal degradation. These results open the possibility of resin being used intermittently at temperatures of 100°C and above, though more testing is needed to identify acceptable time intervals in a temperature cycling case.

#### D. TMA Concentration in LCEG 50 wt% compared to UPW

Breakdown of anionic resin in LCEG 50 wt% was compared to that in water for a mixed bed over 2 weeks. process in anionic resin breakdown and was quantified for anionic resin at 22.8°C, 70°C, and 100°C [23]. LCEG 50 wt% controls without resin showed no TMA at 22.8°C and comparable TMA at 70°C and 100°C for both weeks as seen in Fig. 5. Similar to the controls, resin in LCEG 50 wt% and UPW at 22.8°C had no TMA after 1 week and 2 weeks. Compared to samples containing UPW and resin at 70°C, TMA concentrations in LCEG 50 wt% with

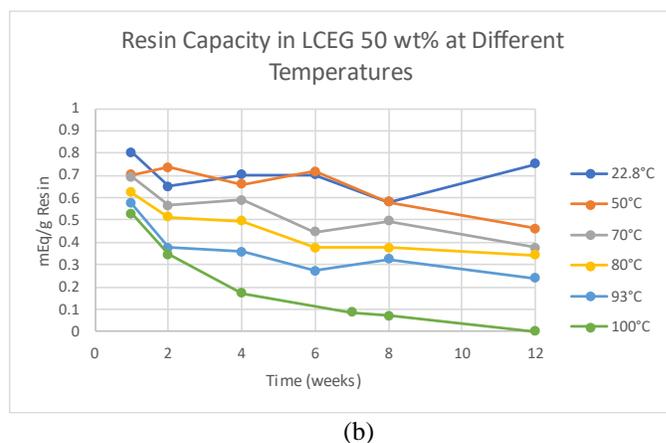
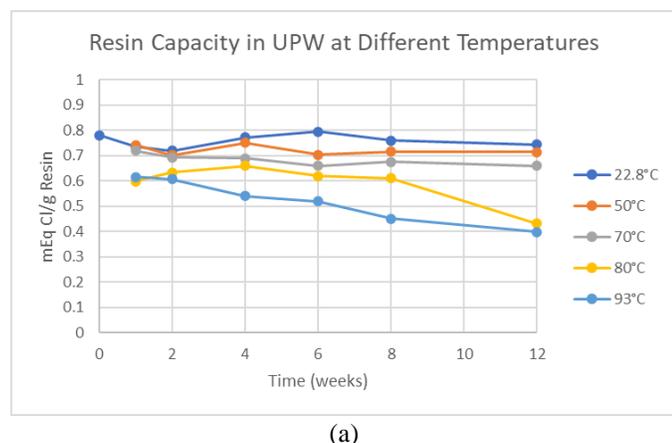


Fig. 3. Resin capacity over 12 weeks at 22.8°C, 50°C, 70°C, 80°C, 93°C, and 100°C. (a) UPW resin exhibited a 26% average drop in capacity after 12 weeks, with a 5.1% decrease at 22.8°C and 47% at 93°C. (b) LCEG 50 wt% resin experienced a 68% average drop in capacity after 12 weeks, with a 6.3% decrease at 22.8°C and 68% at 93°C. The expected error was 5%.

**TABLE II.**

Recovered Capacity for Resin Cooled from 100°C to 22.8°C relative to Resin at 100°C, expressed as a Percentage of Original Capacity.

Time (weeks)	Recovered Capacity
1	0.00%
2	8.83%
4	6.38%
6	5.74%
8	3.62%
12	0.00%

resin were almost 2.5 times greater on average at 70°C and 7.5 times greater on average at 100°C. This gap in TMA concentrations between glycol-water and UPW may result from glycol degradation acids having an amplified effect on anionic resin breakdown. TMA concentrations increased significantly more from 70°C to 100°C than they did from 22.8°C to 70°C as the resin exceeded its optimal temperature range. For example, TMA for resin in LCEG 50 wt% increased 25 times more from 70°C to 100°C than it did from 22.8°C to 70°C after 2 weeks.

#### IV. CONCLUSION

Testing of ion exchange capacity, ion exchange rate, and degradation of anionic resin was employed to demonstrate that ion exchanged LC glycol-water solutions can maintain acceptable conductivity levels in industries where PFAS may normally be used. Notable conclusions of this study include the following:

- 1) Mixed bed deionizing cartridges keep conductivity levels below 5  $\mu\text{S}/\text{cm}$  in an LCEG 50 wt% glycol-water solution, a threshold adhered to in multiple industries.
- 2) Ion exchange occurs faster from 22.8°C to 70°C, after which thermal degradation of anionic resin reduces capacity to a point that reverses the efficiency benefits of increased temperature.

- 3) Mixed bed resin has a continuous usage temperature range from -25°C to 93°C in LCEG 50 wt%, which extends lower than -25°C.
- 4) Resin regains a portion of its capacity when ion exchanged at 22.8°C after being stored at 100°C for a period of time, where the fraction of recovered capacity decreases with storage time. Resin can potentially be used intermittently at temperatures of 100°C or above, but additional studies are needed to confirm.
- 5) Resin capacity decreases with increasing time and temperature. After 12 weeks, there was no significant reduction in resin capacity at 22.8°C for resin in LCEG 50 wt% and resin in UPW, but there was a 47% and 68% loss in capacity for each respective fluid at 93°C.
- 6) Resin capacity varies by fluid. On average, resin capacity in LCEG 50 wt% was about half that of UPW.
- 7) Loss of resin capacity in glycol-water, especially at temperatures above 70°C, can be caused by the formation of acidic breakdown products upon thermal degradation of the glycol. Resin ion exchange capacity is reduced as it removes these acidic ions.
- 8) Anionic resin degradation is greater for resin in LCEG 50 wt% compared to resin in UPW. After 2 weeks at 70°C, TMA concentrations for resin in LCEG 50 wt% were almost 2.5 times greater on average than for resin in UPW.

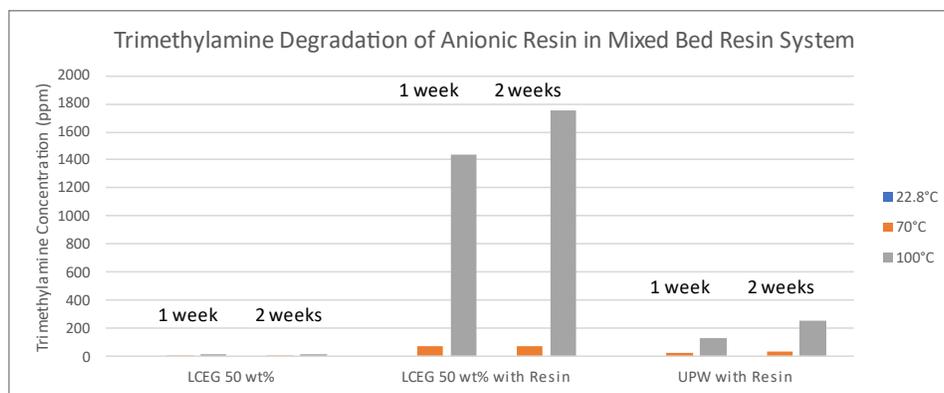


Fig. 5. TMA degradation of anionic resin in LCEG 50 wt%, LCEG 50 wt% with resin, and UPW with resin at 22.8°C, 70°C, and 100°C. Data shows elevated TMA levels in samples containing LCEG 50 wt% and resin, especially at 100°C.

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