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Abstract: *The necessity of antifreeze additives connected to climate conditions in automotive is a non-changing fact. For decades two substances, ethane-1,2-diol and propane-1,2-diol, are dominating the market with all of their advantages and disadvantages. In this paper is presented new potential antifreeze additive from the same family of polyols with different structural formula of propane-1,3-diol. Though similar to propane-1,2-diol the position of hydroxyl groups at the ends of the carbon parent chain gives this substance some unique properties that are distinguishable from its predecessors. Important physical properties for use as an antifreeze additive in automotive and solar heat systems were measured in controlled conditions and compared to the current additives such as propane-1,2-diol. Propane-1,3-diol shows especially favourable values for viscosity in wide ranges of temperatures and dilutions which lowers the needs for pump power and subsequently energy demands on the systems, alongside the advantage of being completely produced from renewable sources.*

Keywords: Antifreeze, Propane-1,3-diol, Heat Transfer Fluid, Automotive, Solar Thermal

1. INTRODUCTION

For low-temperature systems (typically from -20 °C to 150 °C) water is usually the first choice as it is efficient and highly cost-effective fluid for transferring heat. Unfortunately, the basic properties of water and its typical behaviour at temperatures below 0 °C bring the necessity for antifreeze protection in form of additives to avoid damages to the system. The antifreeze additives are common in many industrial, home and automotive applications when there is a possibility for the temperatures to drop below freezing point of plain water. The protection against freezing is particularly used in outdoor systems like combustion engine cooling in vehicles or solar thermal systems and the extent of utilisation is usually connected to the specific climate conditions. Furthermore, thanks to profound standardisation in materials production and manufacturing processes, the antifreeze additives are also quite common in warm climate regions mostly in automotive.

1.1 State of art

The antifreeze additives for water are primarily selected on their compatibly with it and the freezing protection. Good antifreeze additive is fully miscible with water, has small or minimal effect on the heat transfer properties, it is cheap and easy to produce and it has, needless to say, good freezing protection. There is also number of other selected properties like compatibility with sealing, low toxicity or low corrosivity. Also, with the emphases on environment protection and sustainable development, the environmental friendly production and easy recycling or biodegradability are common requirements for modern systems.

Historically the first antifreeze additives were simple alcohols like methanol and ethanol as they were abundant, cheap and easy to produce, and naturally, were offering a sufficient freezing protection. But because of their high flammability and volatility, not mentioning the very high toxicity of methanol, they were soon replaced by ethane-1,2-diol (ethylene glycol or EG) and later on by propane-1,2-diol (propylene glycol or PEG) [1].
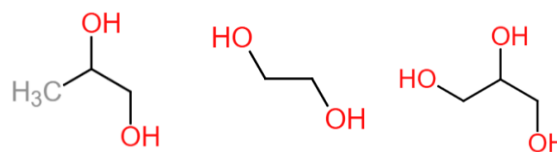

Fig. 1. Left: Propane-1,2-diol, middle: Ethane-1,2-diol, right: Propane-1,2,3-triol
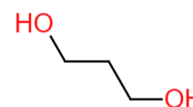

Fig. 2. Propane-1,3-diol

The ethane-1,2-diol and propane-1,2-diol belong to the diols (glycols) group and the presence of vicinal hydroxyl group and sufficiently short hydrocarbon part is allowing for them to be fully miscible with water with strong freezing point depression. Furthermore, the advantage of the glycol additives does not lie only on freezing protection but also on significantly enhancement of boiling point at the standard pressure and antifreeze dilutions (30-50 wt.%) to 110 - 115 °C.

At the present the propane-1,2-diol and ethane-1,2-diol are the most exploited antifreeze additives for water though most of their production is actually used on production of polyesters and polyurethanes[2]. Ethane-1,2-diol is used for producing PET and propane-1,2-diol is important part for producing polyester resins and polyurethane. Thanks to non-toxic properties of propane-1,2-diole[3] the substance has also wide range of other applications in food industry, pharmaceuticals and it is main part of the liquid for so-called e-cigarettes

[4]. The ethane-1,2-diol and propane-1,2-diol are mainly produced from ethylene and propylene oxide respectively, when both precursors are derived from crude oil. However, there are some significant differences between these two-abovementioned species. Though the pure glycols themselves have the freezing point quite high, see Table 1., after mixing with water, the strong interaction between the two hydroxyl group and water molecules cause rapid drop of the freezing temperature far below the individual's pure states with the minimum around 60-80 wt.% as pictured on Fig. 3. Only exception is propane-1,2-diol, which is not equipped with terminal hydroxyl groups and has short hydrocarbon "tail" hindering interaction with water molecules and acts differently

1.2 New trends
Because of the environmental issues and toxicity connected to using of ethane-1,2-diol [5] most of the antifreeze is currently under pressure to be substituted by propane-1,2-diol [6]. Especially modern technologies using antifreeze on a large scale, like the solar thermal systems or HVAC, are utilizing preferably the non-toxic propane-1,2-diol which is also connected to different standards and material use. In this context new antifreeze coolant based on propane-1,3-diol was introduced several years ago [7] to be added as potentially more stable and environmental friendly substitute together with propane-1,2-diol.
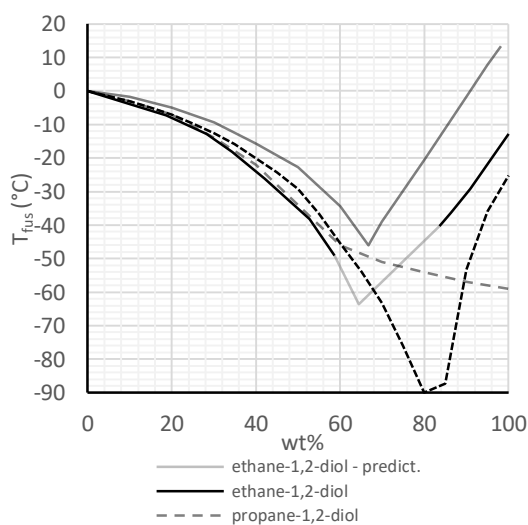

Fig. 3. Freezing points of common antifreeze additives in comparison to propane-1,3-diol[9].

Table 1. Physical properties of antifreeze additives in pure state [22][23]

Additives (20 °C)	Ethane-1,2-diol	Propane-1,2-diol	Propane-1,2,3-triol	Propane-1,3-diol
Density	1.1132 g·cm^{-3}	1.036 g·cm^{-3}	1.261 g·cm^{-3}	1.053 g·cm^{-3}
Heat capacity	148.1 J·mol^{-1}K^{-1}	189.9 J·mol^{-1}K^{-1}	221.2 J·mol^{-1}K^{-1}	173.4 J·mol^{-1}K^{-1}
Boiling point	197.3 °C	188.2 °C	290 °C	217 °C
Melting point	-12.9 °C	−59.0 °C	17.8 °C	−27.0 °C
Dynamic viscosity	0.016 Pa·s	0.0581 Pa·s	1.412 Pa·s	0.052 Pa·s

As was reported by Eaton [7] the newly proposed coolant employing propane-1,3-diol as its base has higher thermal stability then other glycols and together

with its environmental-friendly bio-based [8] production has high potential to fully substitute propane-1,2-diol and possibly replace the toxic ethane-1,2-diol. But after this first study, the propane-1,3-diol was investigated only scarcely and adequate literal sources further studying its physical properties are missing.

1.3 Propane-1,3-diol production
Most of the propane-1,3-diol produced at the moment is used for producing of poly (trimethylene terephthalate), also known as PTT [10]. This versatile polymer is mostly used in carpet production [11] but thanks to its unique properties it is considered for many other applications like clothes and functional sportswear [11][12].
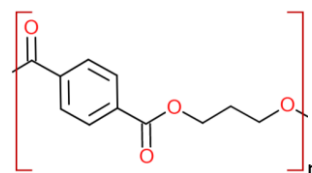

Fig. 4. Polyester - Poly (trimethylene terephthalate)

The basic main synthesis routes for producing propane-1,3-diole are hydroformylation from ethylene oxide and hydrolysis followed by hydrogenation of acrolein. These two techniques are the most used at the current production [11] but the raw source of material for the synthesis is crude oil. Another synthetic route was also developed from now abundantly available glycerol produced as a by-product from bio-fuel/bio-diesel production [13]. Together with the classical synthetic routes, new bio-approaches are investigated to answer the global demand for clean and environment-friendly technologies. The bio-transformation through bacterial of glycerol was thoroughly investigated by several researches [14][15] and are still under investigation. Though, this simple bio-transformation route employs common and glycerol available from bio-fuel production [16], other more direct approaches of bio-production of propane-1,3-diol are also investigated. Some of the processes are patented and are were already commercialized [12], like the DuPont's Bio-PDO™ for Sorona® PTT production by its own corn sugar fermentation method. Other big producer of propane-1,3-diol, the Shell company, is producing propane-1,3-diol mainly from the oil-based ethylene oxide for production of its PTT's polyester version Corterra™. Except from the fermentation process of corn sugar by DuPont, other processes of biomass fermentation are investigated like in the case of two-stage fermentation of wheat-based thin stillage reported by Ratanapariyanuch in 2017 [17]. Many other methods are then summarised in the microbial production of propane-1,3-diol review put together by Saxena [8].

2. EXAMINATION OF PHYSICAL PARAMETERS OF THE PROPANE-1,3-DIOL/WATER MIXTURE

2.1 Viscosity
Because propane-1,3-diol and its aqueous form is considered as a Newtonian fluid, for defining the viscosity we use the Newton's Law of Viscosity. The Eq. 1. defines the Newtonian fluid as shear stress τ

inside the fluid as a function of viscosity η and shear rate or shear local velocity $d\mu/dx$.

$$\tau = \eta \frac{d\mu}{dx}$$
Eq. 1

The viscosity itself is then usually acquired by measuring dynamic or kinematic viscosity directly by viscometers by various principles of working. In this article the dynamic viscosity of aqueous propane-1,3-diole was measured by automatic vibrational viscometer Anton Paar Stabinger SVM 3000 with cryostat Julabo and standard Ubbelohde U-type viscometer as a referential method according to standard method ASTM D445 [18]. The temperature range for measuring was defined for the most used range from -20 °C to 80 °C. The aqueous solutions were selected for the most usual range of antifreeze dilution between 30% and 70%. The used propane-1,3-diol was Zemea™ Propanediol made from corn sugar acquired from DuPont Tate&Lyle BioProducts™ in the purity of 99.8%.

2.2 Density
The values of density and kinematic viscosity are important for calculating the hydraulic properties of the fluid and are also necessary for calculating the Reynolds number. Viscosity and density directly affect the pump performance, efficiency of the pumping and consequently power consumption.

To recalculate the dynamic viscosity to kinematic viscosity we use the known relation between kinematic and dynamic viscosity and density of fluid for different dilutions:

$$\upsilon = \frac{\eta}{\rho}$$
Eq. 2

For this purpose it is necessary to measure the density, too. Density was measured by the Anton Paar Stabinger SVM 3000. The viscosities were measured for the same temperature range and dilutions as in case of dynamic viscosity.

2.3 Freezing point
Even with accurate measuring methods, the freezing point of water-glycol mixtures tends to be unreliable around the eutectic mixture ratio. As was shown by Corday [9] in the case of ethane-1,2-diol/water system, to find the exact values for the glycol/water mixture is very hard and can vary significantly by used standard. The problem is connected to special properties of glycol/water mixtures and their tendencies to form quasi-stable eutectic mixtures. The mixtures do not freeze completely in the beginning but rather form an aggregation of water crystals in the glycol/water solution and practically forming a slush with high viscosity. For these reasons in case of glycol antifreeze, we can distinguish talk about freezing protection and burst protection. The freezing point was measured manually according to the international standard ASTM D1177 for measuring antifreeze [19].

3. RESULTS AND DISCUSSION
For system design, the viscosity is an important parameter. The Reynolds number and hydrodynamic parameters of the fluids are directly connected to the viscosity and greatly influence the power demands and capacity of circulating pump. But partially because propane-1,3-diol was initially used for producing PTT, the important physical data on aqueous solutions

necessary for system design and application are missing. In the literature most of the current finding is focused almost solely on the propane-1,3-diol production and the available data on other properties through investigation of its possible use as an antifreeze are strongly limited only to absolute necessary examples of dilution.
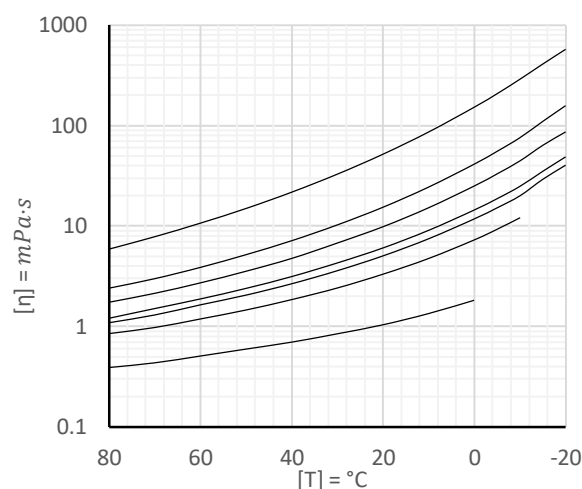
Fig. 5. Dynamic viscosity for aqueous propane-1,3-diol. The lines from top: 100wt%, 72wt%, 61wt%, 50wt%, 45wt%, 33wt%, water.
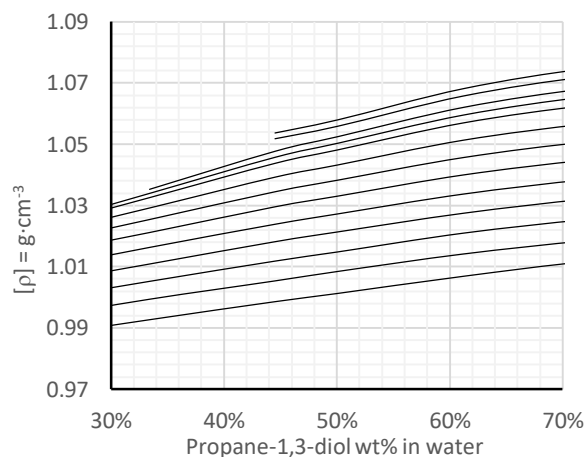
Fig. 6. Density for aqueous propane-1,3-diol. The lines from top: -20 °C, -15 °C, -10 °C, -5 °C, 0 °C, 10 °C, 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C.

Through presented results is apparent that the physical properties are on par with propane-1,2-diol as presented in many studies and are part of standard physical and chemical tables[20]. As the base hydrocarbon chain is of the same length, the differences in viscosity and freezing point are caused by the position of the second hydroxyl group in case of propane-1,3-diol. Instead of vicinal position in case of propane-1,2-diol, the propane-1,3-diol has both groups in terminal positions on each end of the hydrocarbon chain. Therefore, the interaction with water molecules is significantly altered which causes several different aberrations from other glycols. Most visible is comparison of pure glycols and their aqueous solutions. In case of comparing propane-1,2-diol and propane-1,3-diol this effect is primarily on viscosity at low temperatures. As the pure substances has almost the same viscosity at 20 °C the 50% dilutions of propane-1,2-diol are nearly twice more viscous then with same dilution of propane-1,3-diol.

Though the viscosity is better than in case of propane-1,2-diol, the viscosity of ethane-1,2-diol is still significantly lower especially in lower temperatures. That is caused by the shorter hydrocarbon chain and it is hardly to be overcome by any other glycol. Ethane-1,2-diol has also better properties for freezing protection at lower dilutions, which means that for the same protection effect it is not necessary to use as much of it as other glycols, which makes the final product cheaper. But the propane-1,3-diol has strong advantage over ethan-1,2-diol, and respectively over propane-1,2-diol, too, because it is non-toxic [21] and the modern method of bio-production are fully sustainable. The lingering problem, at this moment, are still high price and problematic supply as the biggest producers are consuming most of the propane-1,3-diol for their PTT production.

4. CONCLUSION

Propane-1,3-diol has lower viscosity then propane-1,2-diol in the key water ratios mostly used as an antifreeze, but is showing slightly less depression of freezing point at the same dilutions.

On the other hand this antifreeze mixture based on propane-1,3-diol offers a fully environmental friendly option for the modern systems requiring higher endurance.

Nonetheless, the price for the mixture is still high and the utilisation will be limited for high-end devices requiring lover viscosity over price. But with rapid improvement of bio-transformation methods of producing, the propane-1,3-diol has potential to become significant player in the antifreeze/coolant industry.

5. ACKNOWLEDGEMENT

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