BRNO UNIVERSITY OF TECHNOLOGY

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

FACULTY OF CHEMISTRY

FAKULTA CHEMICKÁ

INSTITUTE OF CHEMISTRY AND TECHNOLOGY OF ENVIRONMENTAL PROTECTION

ÚSTAV CHEMIE A TECHNOLOGIE OCHRANY ŽIVOTNÍHO PROSTŘEDÍ

DEGRADATION OF HEAT TRANSFER FLUIDS IN THERMAL SOLAR SYSTEMS AND PROPANE-1,3-DIOL AS A NEW OPTION

STÁRNUTÍ TEPLONOSNÝCH KAPALIN V TERMICKÝCH SOLÁRNÍCH SYSTÉMECH A PROPAN-1,3-DIOL JAKO NOVÁ MOŽNOST

DOCTORAL THESIS

DIZERTAČNÍ PRÁCE

AUTHOR — Ing. František Mikšík

AUTOR PRÁCE

SUPERVISOR — prof. Ing. Josef Čáslavský, CSc.

ŠKOLITEL

BRNO 2018

ABSTRAKT

Stárnutí teplonosných kapalin na organické bázi je dlouhodobým problémem, který je znám od počátku jejich používání. První část této disertační práce je tak věnována případové studii funkčního experimentálního systému, který byl jako nový naplněn teplonosnou kapalinou na bázi propan-1,2-diol a pozorován po období 7 let. Pro analýzu stárnutí kapaliny v tomto systému byly sledovány základní provozní vlastnosti kapaliny jako jsou hustota, viskozita, teplota tuhnutí, pH a obsah kovů. Skrze tyto vlastnosti tak bylo sledováno stárnutí kapaliny nepřímo. Přímé sledování stárnutí bylo posléze provedeno analýzou degradačních produktů, jako jsou organické kyseliny a změny ve složení směsi pomocí izotachoforézy a hmotnostní spektrometrie. Pro srovnání byly taktéž analyzovány vybrané vzorky z několik dalších systémů plněných identickou kapalinou s prokazatelně pokročilou formou degradace. V druhé části práce jsou představeny základní fyzikálně-chemické vlastnosti směsí propan-1,3-diolu s vodou a jejich analytické hodnocení a matematické modelování pro universální použití jakožto nového základu pro nemrznoucí teplonosné kapaliny. Na základě dostupných informací je pak hodnocena použitelnost této směsi. Výhoda propan-1,3-diolu je spatřována především ve výrobě z obnovitelných zdrojů a v některých fyzikálních a chemických vlastnostech, které dle dosavadních poznatků předčívají doposud používané glykolové směsi.

ABSTRACT

Degradation of heat transfer fluids on an organic basis is a long-standing problem known since the beginning of their use. The first part of this dissertation is devoted to a case study of a functional experimental system that was filled with a propan-1,2-diol based heat transfer fluid upon construction and had been observed for a period of 7 years. Analysis of the fluid aging in this system was conducted by following the basic operating characteristics of the fluid, such as density, viscosity, freezing temperature, pH and metals content. Through these properties, the aging of the fluid was tracked indirectly. Direct observation of the degradation process was then performed by analysis of degradation products such as organic acids formation and changes in the composition of the mixture by isotachophoresis and mass spectrometry. For comparison, selected samples from several other systems filled with identical liquid with an evidently advanced form of degradation were also analysed. The second part of this thesis presents the basic physicochemical properties of aqueous propane-1,3-diol mixtures and their analytical evaluation and mathematical modelling for universal use as a new basis for antifreeze heat transfer fluid. Based on available information, the usability of this mixture is assessed. The advantage of propane-1,3-diol is seen mainly in the renewable production and certain physical and chemical properties, which outweigh the glycols used up to now in several areas.

KLÍČOVÁ SLOVA

Teplonosná kapalina; Nemrznoucí kapalina; Degradace; Termický solární systém; Propan-1,3-diol; Fyzikálně-chemické vlastnosti

KEYWORDS

Heat transfer fluid; Antifreeze; Degradation; Thermal solar system; Propane-1,3-diol; Physicochemical properties

CONTENT

1 INTRODUCTION

Renewable energy sources (RES) continuously increase their share of primary energy sources due to the known limitations associated with exhaustible quantities of fossil fuels. The goal of developed countries thus largely lies in a diversification of basic energy sources and a gradual transition to renewable energy sources which will be able to ensure energy stability and self-sufficiency in the long run. This progress is further enhanced by social awareness and social pressure that places more and more emphasis on the environmental aspects of energy production and its use.

Similarly to fossil fuels, individual countries have limited prerequisites for the use of various RES, and of course, the Czech Republic is no exception. The location of the Czech Republic in the middle of Europe has a significant impact on the quantity and composition of RES which we are able to use efficiently on the basis of current technological state. For example, RES such as geothermal energy is virtually unusable on any larger scale in our location and it is limited to small-sized heat pumps. Situation is not better even in the case of harnessing wind power. The so-called wind farms can be built in our country with efficient energy gain only in carefully selected elevated locations where the air flow - wind throughout the year is sufficient. In the case of hydropower, we are again limited by the size of the rivers, which only spring in our country and then flow to other countries, and the volume of precipitation and suitable locations for their construction. Solar energy, however, can be used to some extent practically everywhere in the whole country.

But, even though the Sun shines evenly on the whole planet, the northern location of our country and a small number of actual sunny days in the year place great demands on the efficiency of solar technologies. In late years large areas of photovoltaic panels have been put into operation in the Central Europe, however, without generous state subsidies and guaranteed tariffs their operation would not be economically feasible. Therefore, we are forced to supplement their operation with other economic activities. The situation is slightly different in the case of modern thermal solar systems, when even in our conditions we can achieve energy outputs and results that are able to ensure the economic profitability of these systems. Nevertheless, this technology does not allow universal use in all locations and cases in our region and it is always necessary to assess the individual intended application. To expand this technology to environments where it has not yet been economically viable, further research is needed to improve its efficiency and usability and to increase its attractiveness as a modern renewable energy resource which will be able to compete with conventional energy sources. This work is focused on the heat transfer fluid which is responsible for transferring the thermal energy (heat) collected by the solar collectors to the place of consumption or accumulation. The main problem which will be discussed is the chemical stability of this fluid and possible alternative to the commonly used media.

2 WORK OBJECTIVES

(1) Monitoring of experimental thermal solar system over long-period of time and its analysis.

(2) Identifying principles for aging of heat transfer fluids based on glycols in solar thermal systems and the determination and description of degradation products.

(3) Analysis of physical properties of propane-1,3-diol binary mixture with water.

(4) Assessment of propane-1,3-diol in the context of modern antifreeze heat transfer fluid.

3 STATE OF ART

3.1 THERMAL SOLAR SYSTEMS

Electricity as the highest form of energy that can be easily transformed into other forms of energy, which is effectively the basis of the modern way of life and its availability is one of the factors for assessing the quality of life. It is no wonder then, that the consumption of electricity is a significant item in family budgets. On the Fig. 3-1 we can see in detail the share of different energy consumption areas in European households and the comparison between the European countries. The figure Fig. 3-1 show the total energy demand of the household regardless of the type of energy (thermal, electrical). From the charts we can see that the energy used for hot water heating averages around 10-15 % of all household energy consumed in EU countries. This value roughly corresponds to the amount of energy consumed by lighting and home electronics. And since most of the households are using for DHW preparation electricity, outside the heating season, the living costs are rising with rising electric energy prices.

Recent trends are moving towards technologies that reduce energy consumption, due to high energy demands. These include, for example, LED lighting, modern high effective insulation, new building materials in construction, alternative energy technologies etc.

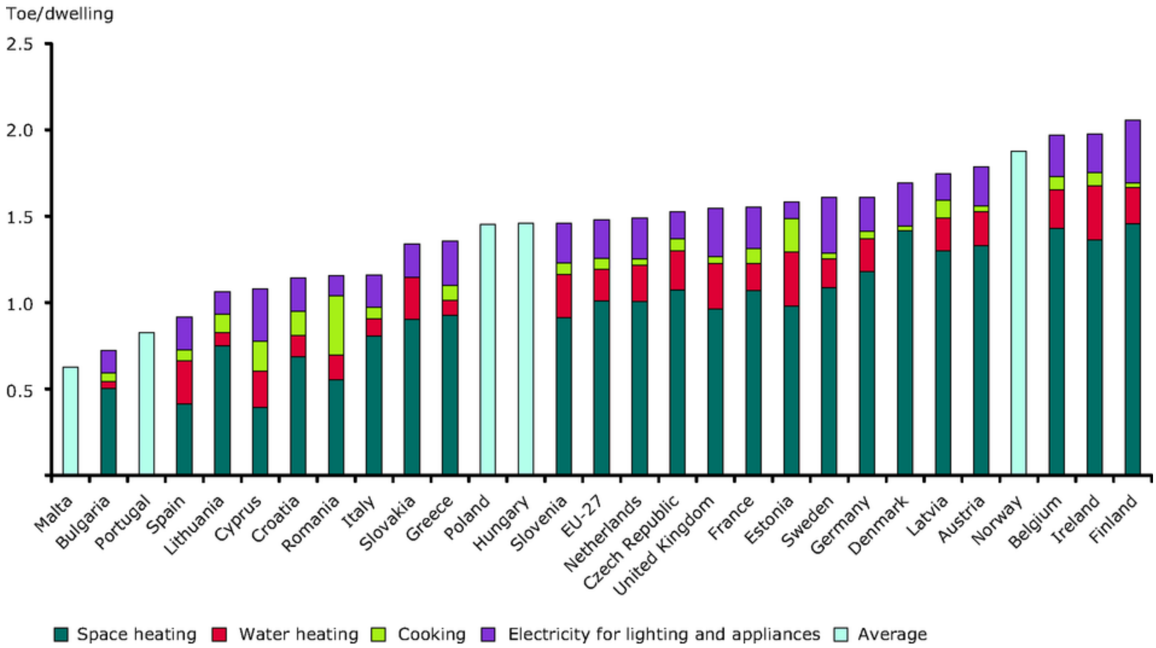

Fig. 3-1 Structure of energy consumption in the European households by country[1]

One of these alternative sources are thermal solar systems[2]. This technology is already advanced with many variations[3] and can be used to save energy demands for preparing domestic hot water by around 60-70 % in average in the geographical conditions of Czech Republic[4]. At present, this technology is especially useful for family houses where solar systems are installed for spatial reasons on an unused roof area. According to statistics, more than 50 %[5] of the population in the European Union lives in family houses or terraced houses with their own roof. Although it is not technically possible to occupy a roof area by the solar collectors in many cases (wrong direction of the roof, geographic conditions, technical design of the house or roof etc.), this area represents a significant potential for capturing solar energy.

The statistics show, that the installed area of solar collectors is growing rapidly. In Germany alone is annually installed over 1 million m^2 of solar collectors and other European countries are in trail with annual values normally accounted in hundreds of thousands of square meters[6].

3.2 TYPES OF THERMAL SOLAR SYSTEMS

Thermal solar systems can be logically divided by several criteria. Here, the division is based on the involvement of one-circuit systems and two-circuit systems that differ greatly from each another.

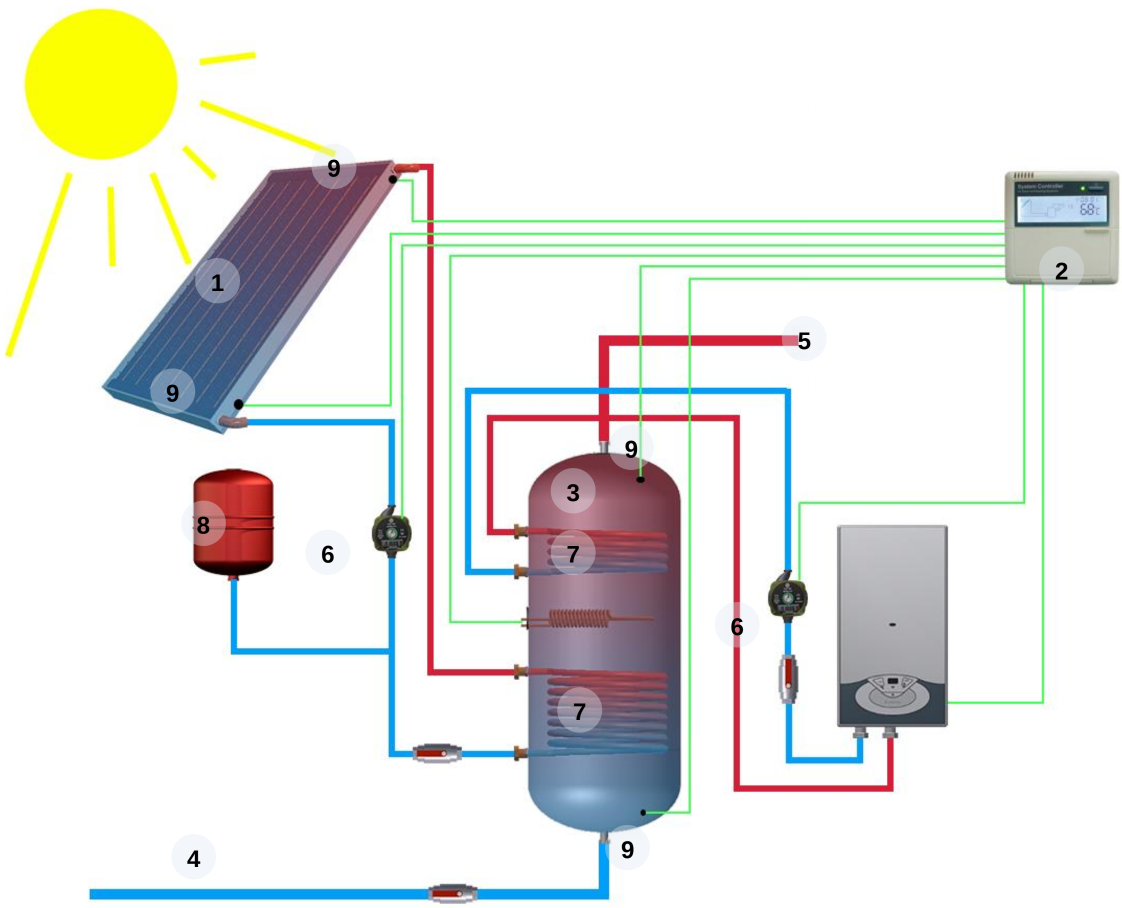

Fig. 3-2 Schema of a basic two-circuit thermal solar system; 1-Solar collector, 2-Control unit, 3-DHW boiler, 4-Cold water inlet, 5-Hot water outlet, 6-Circulating pump, 7-Spiral heat exchanger, 8-Expander, 9-Sensors.

Heat transfer medium in the one-circuit system is a substance that is also intended for direct use. As a typical example can serve pool thermal solar systems or outdoor thermal solar showers. Usage is usually only seasonal and heat transfer medium is usually plain water. The efficiency of these systems is small as the thermal insulation is basically non-existent and the collectors also usually missing a selective layer. However, their low cost and very simple connectivity have made them widely available from home-based applications to public outdoor swimming pools.

Nowadays, the most advanced thermal solar systems have the solar circuit separated from the rest of the thermal system of the house, and thus creating at least two or more circuit system with a thermal centre in a boiler or an accumulator tank. The second circuit in the solar system usually consist from the DHW itself. Other circuits may be represented by other heat energy sources such as boilers or heat pumps or consumption circuits in the form of central heating and underfloor heating. On Fig. 3-2 is a diagram of the concept of a simple two-circuit thermal solar system, which in practice represents the most common solution, while also showing the basic principles of the systems.

The base consists of a solar collector that absorbs solar radiation, thereby heating the absorbent surface. From the surface, thermal energy is drained into a heat-carrying liquid, heat transfer fluid (HTF), which is pumped by the circulating pump into the boiler or storage tank. Through the heat exchanger the HTF transfers part of its thermal energy to the boiler or storage tank and returns to the collector in the circuit.

To evaluate all processes in the thermal solar system, a good knowledge of the design of these systems is necessary.

4 THEORETICAL BACKROUND

4.1 OVERVIEW OF HEAT TRANSFER FLUID IN THERMAL SOLAR SYSTEMS

The main purpose of heat transfer fluids is, as stated in the name, to transfer heat energy from one place to another. 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 0.0 °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 thermal solar 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. The most common group of chemicals which is used as an antifreeze additive for water are glycols, as a more common name for diols. Outside the antifreeze mixtures with water we can encounter with a variety of other heat transfer fluids, which are successfully applied according to specific parameters and applications of the each thermal system. These are silicon oils, hydrocarbon oils, various alcohols, but also air and newly ionic fluids.

4.2 HEAT TRANSFER FLUIDS BASED ON DIOLS

From Ancient Greek “γλυκύς” (glukús, “sweet”) glycols are defined as any aliphatic di-alcohol with hydroxy groups on different carbon atoms[7]. Because of the two hydroxy groups, glycols are often called simply diols, though having some specific differences unique to the group[8]. Glycols are at the standard temperature and pressure usually odourless, colourless and sweet tasting liquids. The presence of two hydroxy groups is a reason for many typical properties of this group such high viscosity, hygroscopicity and full miscibility with water[8–10]. Glycol mixtures used in thermal solar systems are derived from the automotive industry and are available from 1920s[11], when the first mixtures became available on the market.

The first glycol antifreeze mixture was based on ethane-1,2-diol, commercially known under the names ethylene glycol (EG) and monoethylene glycol (MEG). At that time the mixture was also referred to as "permanent antifreeze ". MEG/water mixture was then used in the first water-cooled automobiles and gradually replaced ethanol and methanol-based water mixtures. With the advent of thermal solar systems MEG mixtures also began to be used in them. Later on, with the simplification of the production process of so far complicated propane-1,2-diol (commercial names: propylene glycol, monopropylene glycol, MPG), the mixture MPG/water also began to take the share of the market as a less toxic alternative to the MEG/water. Nowadays, the most used glycol mixtures used in automotive and thermal solar system are currently binary mixtures consisting of MEG/water and MPG/water[12]. The propane-1,2-diol and ethane-1,2-diol are taking together over 90 % of the global market with antifreeze heat transfer fluids. A very small share is also taken by propane-1,2,3-triol (glycerol)[13,14], sometimes being incorrectly put into the glycol group as well. The structural formulas of ethane-1,2-diol, propane-1,2-diol and propane-1,2,3-triol are shown on Fig. 4-1.

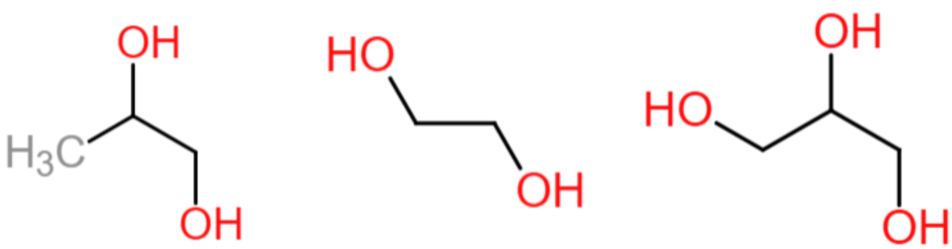

Fig. 4-1 Structural formula of selected glycols; Left: Propane-1,2-diol, middle: ethane-1,2-diol, right: Propane-1,2,3-triol.

The TSS technology development saw a great progress in the efficiency of solar systems from its beginnings especially in the 70s of the last century. However, this development also marked the biggest deviation from the parameters of thermal systems in the automotive industry, especially in the rise of temperatures and pressures in the system[15]. Mixtures in combustion engines operate at temperatures around 80 °C, whereas the conventional solar systems often work with temperatures around 100 °C and vacuum insulated systems far over 100 °C, at pressures around 150-300 kPa[16].

4.3 PROPERTIES OF HEAT TRANSFER FLUIDS IN THE THERMAL SOLAR SYSTEMS

4.3.1 Desired properties

Quality and stable heat transfer fluids for the thermal solar systems must meet certain criteria, which are essential for its long-term and all-year use. Any proposed heat transfer fluid must pass a series of tests that demonstrate a suitability for its use as a heat transfer fluid. The fundamental properties that are observed in the design and evaluation of heat transfer fluids in the all-year thermal solar systems are[12,17,18]:

- Low fusion point
- Good thermal and physical properties (similar to water)
- Low viscosity
- Low or none corrosivity
- Compatibility with sealing materials
- Non-flammability
- Environmental aspects (non-toxic, biodegradable)
- Long-term stability and heat resistance
- Price

Table 4-1. Physical properties of antifreeze additives in their pure state

Substance	Density[a,b] ρ [g·cm^{-3}]	Heat capacity[a,b] C_p [kJ·g^{-1}·K^{-1}]	Boiling point[a] T_{boil} [°C]	Melting point[a] T_{fus} [°C]	Viscosity[a,b] η [Pa·s]
Ethane-1,2-diol	1.113	2.41	197.3	−12.9	0.016
Propane-1,2-diol	1.036	2.48	188.2	−59.0	0.0581
Propane-1,2,3-triol	1.261	2.43	290.0	17.8	1.412
Propane-1,3-diol	1.053	2.29	217.0	−27.0	0.052
Water	0.998	4.18	100.0	0.0	0.001

*References[19–22]. [a]At pressure p = 101.325 kPa. [b]At temperature T = 20 °C.

For use of heat transfer fluid in the thermal solar systems in our latitudes, it is important to fill the system with liquid medium that is capable of sustaining temperatures around -20 °C to -30 °C[12]. Although water is an ideal heat transfer fluid, its use in systems for all-year operation is not possible. That is caused by the natural property of water for volumetric expansion during its freezing caused by process similar to crystallisation[23] and during the process water increases its volume approximately by 9 %. The unique interaction of water with glycols based on hydrogen bonds[24] grants the mixtures specific qualities which are apparent in many ways such as eutectic depression of fusion point. The comparison of the freezing temperature for most common antifreeze additives and their mixtures with water is shown on Fig. 4-2.

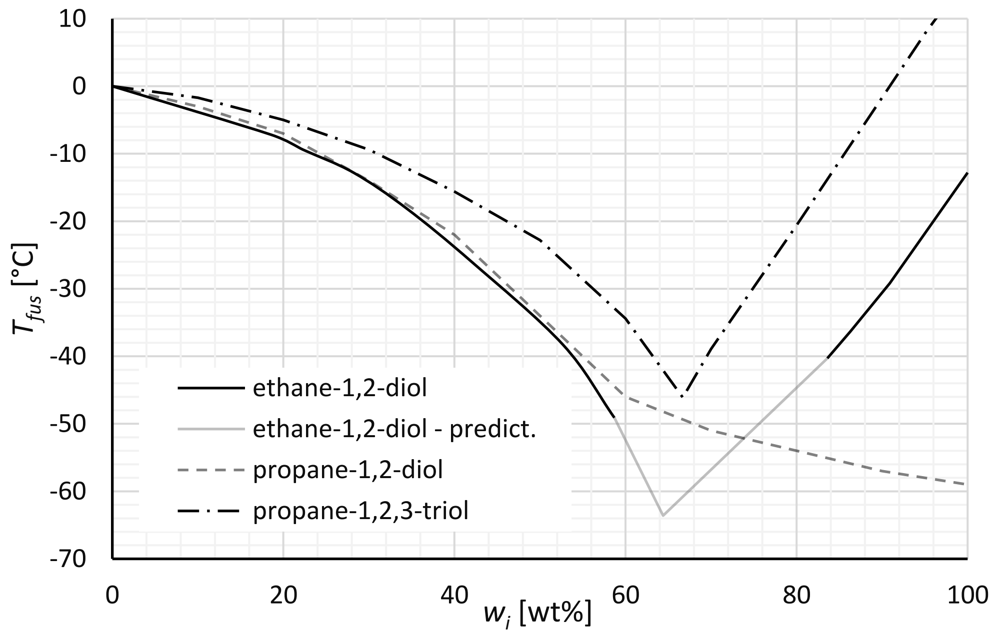

Fig. 4-2 Comparison of fusion point of some antifreeze additives in water.

4.4 AGEING OF HEAT TRANSFER FLUIDS IN TSS

Although the aging of the heat transfer fluid based on glycol is one of the decisive factors affecting the life of the system, the amount of available scientific data is relatively modest and larger studies come from the 80s of the last century based on laboratory experimenting. Also in that time the TSSs used a slightly different materials and have a completely different operating conditions[25–27].

So far, carrying out laboratory tests of products of aging heat transfer fluids based on glycol are primarily addressing the questions of forming acid and the general corrosiveness as recommended by the ASTM D1384[28]. However, the forming of organic acids does not fully explain the change of physical properties which are evidently occurring.

4.4.1 Stagnation process

At present, the stagnation of solar systems is a serious problem that reduces the service life of the heat transfer medium and the system itself. The basic principle is the overheating of the heat transfer medium in the collectors and its subsequent evaporation. This is usually caused in hot-sunny days with insufficient circulation of heat transfer media, bad dimensioning, bad management of the system and bad design of solar collectors as shown on Fig. 4-3.

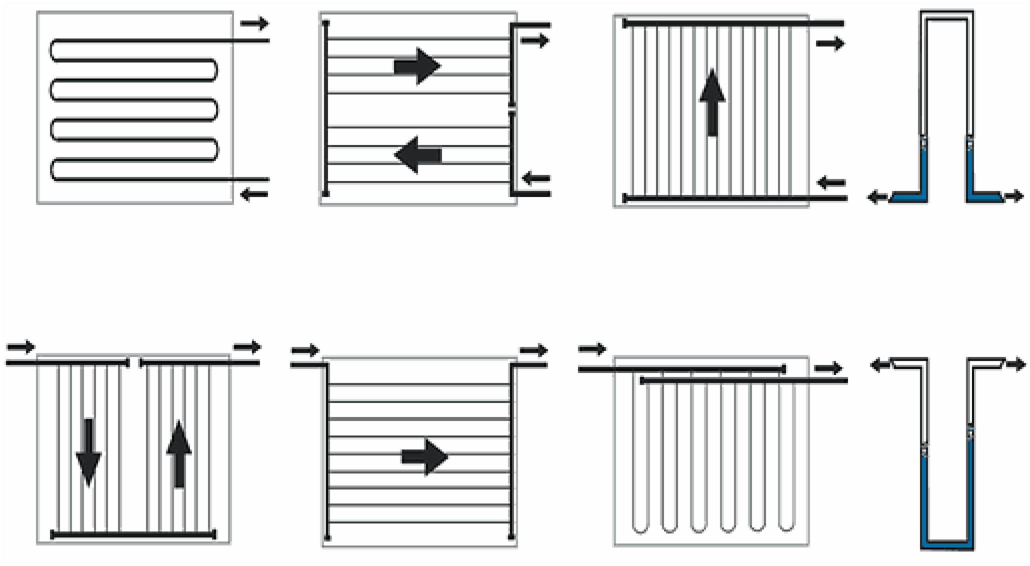

Fig. 4-3 Evacuation ability of different design solution, good (top), bad (bottom)[29]

During the stagnation the system is exposed to considerably high temperatures and pressures, though the actual values are highly dependent on the system design as has been demonstrated by several works[30–32]. Several researchers reported results from laboratory studies on the thermal degradation of the glycolic mixtures and their degradation and the effects of high temperatures is indisputable. However, the cumulative effect of continuous stagnation was not studied in such detail yet.

4.5 PROPANE-1,3-DIOL

Propane-1,3-diol, commercially known also under the designation as PDO, is a structural isomer with propane-1,2-diol, and as such, it is similar in many ways. As well as MPG it is hygroscopic and completely miscible with water. It is slightly soluble in aromatic hydrocarbons and practically immiscible with aliphatic organic solvents[33]. All of the production is used almost solely on the manufacturing of Polytrimethylene terephthalate polymer (PTT) used in carpet industry[34,35]. But, thanks to its anti-freezing properties as the others diols, the possibilities of using it as a "green" substitute for almost exclusively oil produced ethane-1,2-diol and propane-1,2-diol are currently studied[36,37]. Due to the insufficient data on its long-term toxicity, it has been not yet permitted for use in the food industry and the production of medicines and cosmetics, though is it generally considered as safe according to several claims[38,39] and short term studies[40]. From the available data and existing measurement results[17], the propane-1,3-diol is a promising substance as a new antifreeze additive[16]. However, for widespread of this substance there are still necessary some steps concerning the research on the physical and chemical properties.

4.5.1 Basic physical and chemical properties

The basic chemical and physical properties of pure propane-1,3-diol are very similar to of propane-1,2-diol. The structural differences are apparent from the Fig. 4-4. The most important data on pure propane-1,3-diol are summarized in

Table 4-2. Although most of the important data on pure propane-1,3-diol are already available in good quantity and sufficient quality, the most important data on its aqueous form are rare.

Table 4-2. Basic physical and chemical data on propane-1,3-diol

CAS Number	504-63-2
Names	Propane-1,3-diol (IUPAC); 1,3-Propanediol; 1,3-Dihydroxypropane; Trimethylene glycol;
Chemical formula	$C_3H_8O_2$
Molar mass (Mr)	76.095 $g{\cdot}mol^{-1}$
Density (at 25 °C) (ρ)	1.0597 $g{\cdot}cm^{-3}$
Melting/Fusion point (T_F)	-27 °C
Boiling point (T_B)	210-212 °C
Viscosity (at 20 °C) (η)	52.007 mPa·s
Vapour pressure	4.5 Pa
Refractive index (n_D)	1.440
pH (50 % aqueous solution at 25 °C)	6.544

References[19,41,42,exptl.]

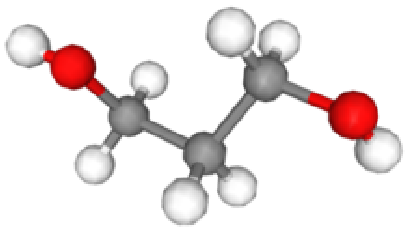

Fig. 4-4 Propane-1,3-diol 3D structural model

4.5.2 Production

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 production of propane-1,3-diol through bacterial of glycerol was thoroughly investigated by several researchers[43,44] and is still under investigation. Though, this simple bio-transformation route employs common glycerol available from bio-fuel production[45], other more direct approaches of bio-production of propane-1,3-diol are also investigated. Some of the processes are patented and were already commercialized[36], like the DuPont's Bio-PDO™ for Sorona® poly(trimethylene terephthalate) (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™.

5 EXPERIMENT

5.1 SAMPLES AND THEIR PREPARATION

5.1.1 Samples for estimation of ageing processes

System Vracov

The experimental system Vracov is located in South Moravia region in Czech Republic, Fig. 5-1. The system started its operation on 4. 4. 2007. During the whole time only one heat transfer fluid *Solaren* was used. The manufacturer of the heat transfer fluid is VELVANA a.s., Velvary, Czech Republic. The main characteristics of the system are summarized in Table 5-1.

After sampling from the system, the samples were kept in 250 mL big transparent polypropylene flasks in a refrigerator. That applies also for the sample of the original unused fluid from 2007. The sample VO2014 of the newer fluid used to toping-up the system in 2014 was kept in its original container made of opaque blue polyethylene, also in refrigerator. The pictures of the samples are shown on Fig. 5-2.

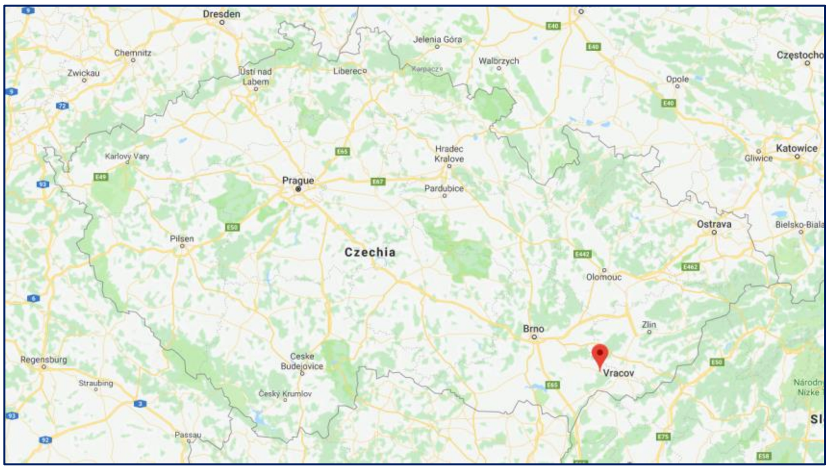

Fig. 5-1 The position of Vracov, Czech Republic

Table 5-1. Characteristics of the experimental system Vracov

Number of thermal collectors	6
Type of thermal collectors	Heliostar H400
Absorption area (sum)	10.6 m^2
DHW cylinder volume	0.3 m^3
Accumulator volume	1.3 m^3
Total length of piping	~80 m
Usage	DHW preparation + partial space heating

Table 5-2. Samples from experimental thermal solar system in Vracov

Sample designation	Sampling date	Description
VO2007	2006 (manufactured)	Original heat transfer fluid used or the first filling of the system in 2007. The fluid is a mixture of propane-1,2-diol at 48 wt% and water plus stabilizing and anticorrosion additives.
VO2014	10. 11. 2009 (manufactured)	HTF which was used to fill-up loses caused by continuous sampling. The filling up of the system was conducted only once in year 2014. Identical to VO2007 with minor changes in the inhibitor system.
V2007-V2014	2007-2014	Chronologically sampled fluids from the working experimental system in Vracov (V2007, V2008, V2009, V2011, V2012, V2013, V2014).
V2014N	13. 4. 2014	Another sample was taken after filling of 1 litre of new HTF to compensate for the losses due to sampling.

Highly degraded sample selection

Table 5-3. Selected samples of highly degraded HTF

Sample designation	Sampling date	Description
SP	12. 4. 2014	Sample of a spent HTF *Solaren* from system in Petrov, Czech Republic. The filling of the system was conducted in 2010 and from that time, the system went through several cycles of stagnation.
SJ	11. 3. 2014	Sample of a spent HTF *Solaren* from a home-sized system localized in South Moravia. System went through a several cycles of stagnation.
SD	2014	Sample of a spent HTF *Solaren* from a middle-sized system from city Ostrava, Czech Republic. Due to the faulty pump, the system was undergoing a cyclic stagnation for several days, until discovered by a technician.
TS	14. 3. 2014	Sample of spent HTF *FSV* from original filling by constructer of the system (Sonnekraft). Similarly to Solaren, this HTF is based on propane-1,2-diol.

5.1.2 Samples of propane-1,3-diol

Table 5-4. Samples of propane-1,3-diol

Sample designation	Sampling date	Description
PDOC	2010	Pure (≥ 99 %) propane-1,3-diol from a Chinese manufacturer
PDOD	2015	Pure (≥ 99.8 %) propane-1,3-diol from DuPont Tate&Lyle BioProducts™

5.2 METHODS

Systematically, the methods used in this work can be divided into two categories according to the target application and sample group.

To monitor the degradation process and analyse the degradation products sever different method was chosen. For indirect observation the basic chemical and physical properties were measured. For the samples from experimental system in Vracov their pH, conductivity, density, viscosity and freezing points were measured. The pH and conductivity were measured by standard laboratory equipment pH meter and conductivity meter. The density was measured by pycnometer and the viscosity by Ubbelohde viscometer. Furthermore, the samples from Vracov system were also measured on the water content by Karl Fisher titration. The analysis and measurement of the content of organic acids in the highly degraded samples was done by isotachophoresis. The structural changes of the mixture and the depletion of the inhibitor system was further examined by ion trap mass spectrometer for both samples from Vracov system and highly degraded samples.

The basic physical properties of aqueous propane-1,3-diol were measured and mathematically modelled. Density was measured by oscillating U-tube method and viscosity by rotational viscometer. The values on refractive index were measured at wavelength of $\lambda = 589.3$ nm and similarly the freezing points for were measured for range of mass fractions of w_i = 0.0 – 0.6.

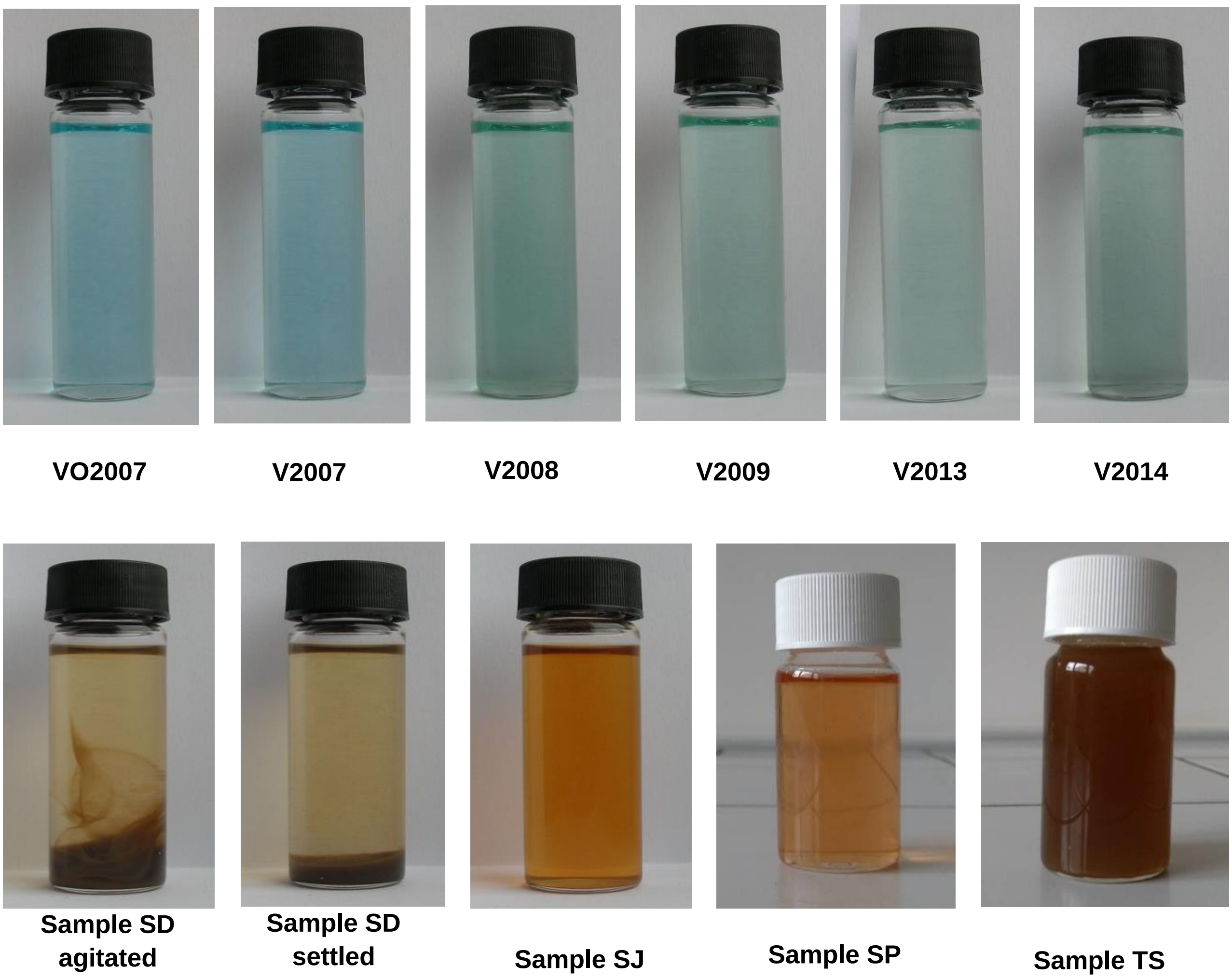

Fig. 5-2 Sample preview

6 RESULTS AND DISCUSSION

6.1 AGEING OF ANTIFREEZE MIXTURES BASED ON PROPANE-1,2-DIOL

6.1.1 Long-term observation of experimental system in Vracov

Brown and Galuk on propane-1,2-glycol and ethane-1,2-diol mixtures[25–27,46,47].

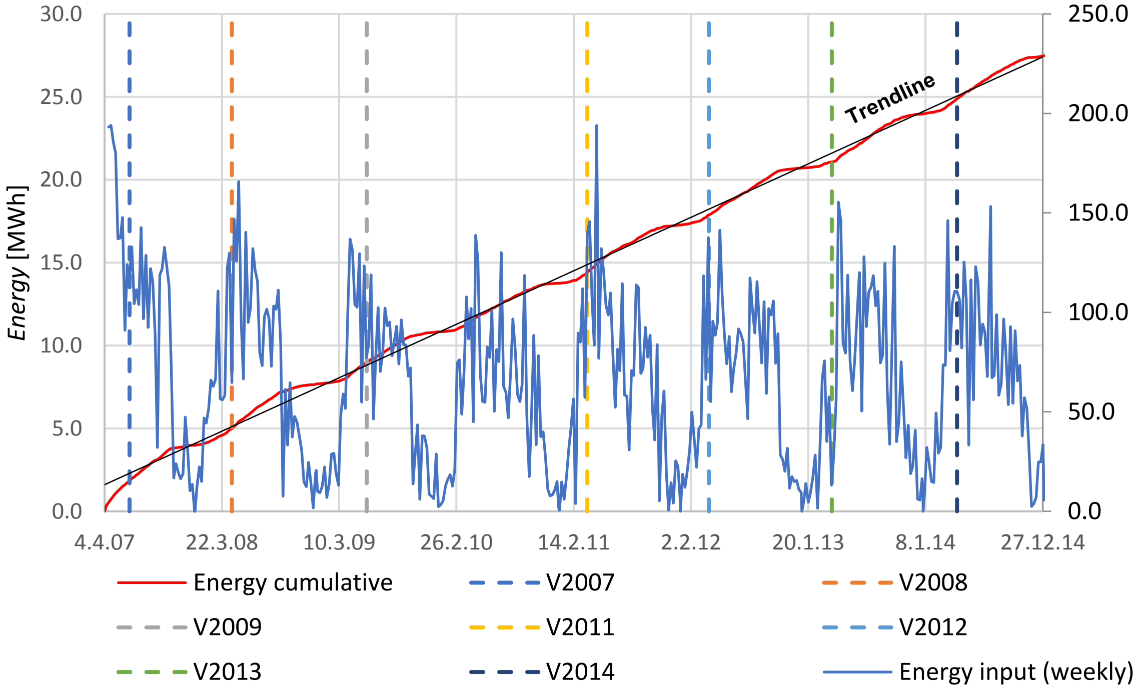

Fig. 6-1 Cumulative energy production (transported) in Vracov system

It can be seen on the Fig. 6-1 that the amount of transported energy in the Vracov system is nearly linear during the whole monitored time with only small seasonal differences. The cumulative data shows that the system was very stable during the whole time without any significant thermal load. This is an important premise for the samples from Vracov system, which can be therefore considered as an ideal chronological sequence of samples. No stagnation or serious thermal load was detected during the whole observed period of time. The comparison of the pH values between the spent and original HTFs are visualized on Fig. 6-2. The data show gradual drop of the pH over the time, though, the change is only minimal. The original fluid had pH(VO2007) = 8.144 which dropped to pH(V2014) = 8.000 during the seven years in work. It can be seen, that the most rapid change was recorded during the first years of service and during the last two years the change was practically zero. The drop in pH is connected to organic acid degradation products, which have been extensively studied in the 80s of the last century, some 30 years ago, by Rossiter,

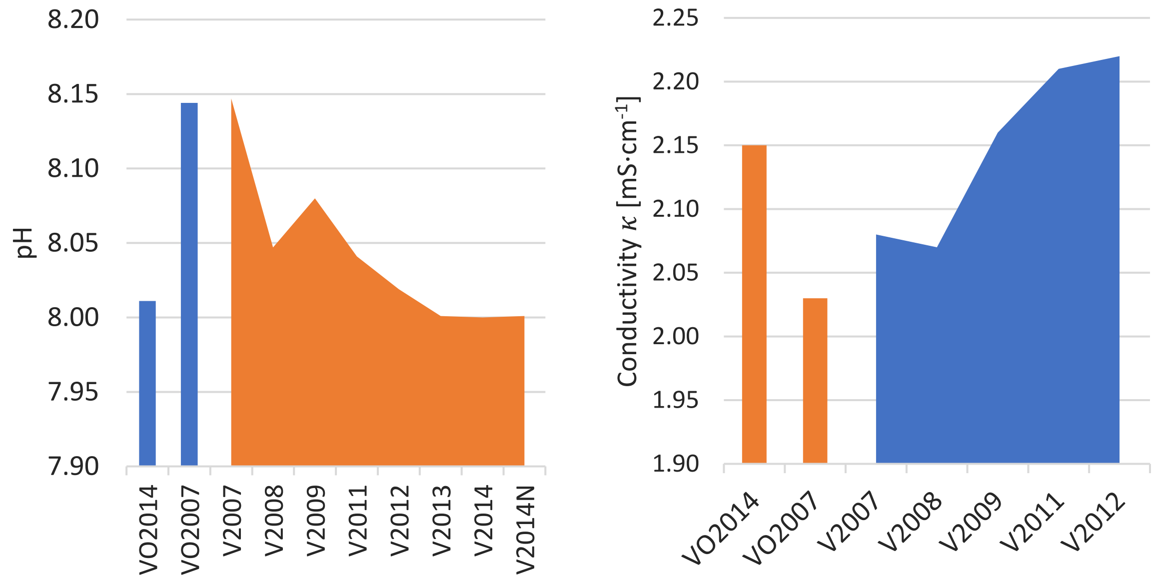

Fig. 6-2 pH and conductivity comparison of unused and used HTFs from experimental system

With the decreasing pH the conductivity of the fluid was rising following very similar trend as the pH. The rise in conductivity is directly connected to the acidity of the fluid and it is affected by the dissociation constants of the present chemicals. By lowering the pH some of the substances are dissociating into individual ions which leads to rise of the conductivity. From the definition, the conductivity describes the capability of the solution to carry charge from one place to another. In the system where different materials with different electrochemical potential are present, this property can be critical to propagate the galvanic corrosion[48,49]. However, thanks to switching to fully stainless-steel systems in the late decade, the importance of this property is now slightly less important than it was before.

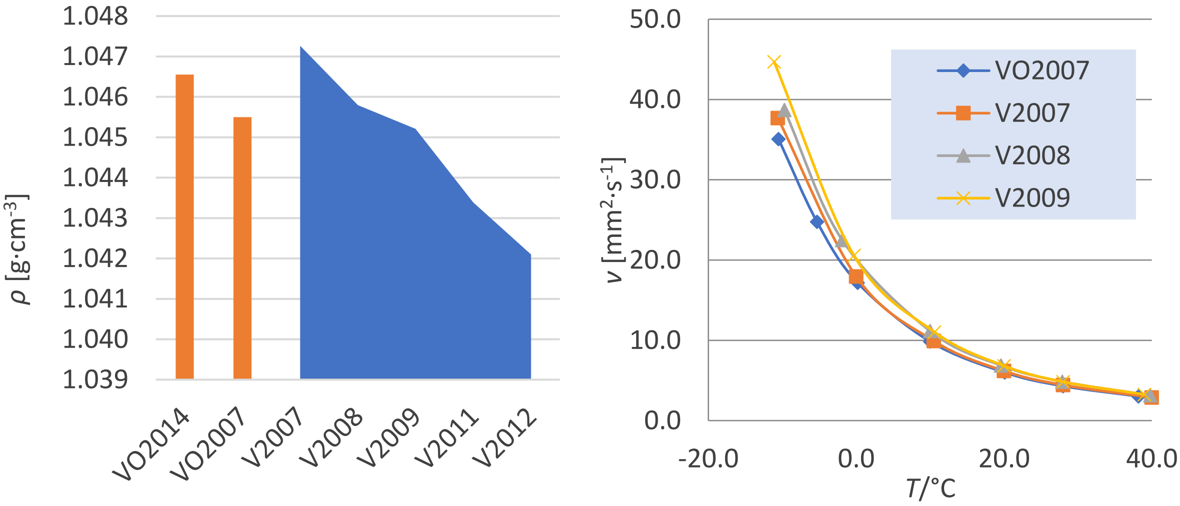

Fig. 6-3 Density and viscosity comparison of unused and used HTFs from the experimental system

Another observed property indicating the changes inside the heat transfer fluid is the density and viscosity. The results of measured density and viscosity for the samples from the Vracov system are summarised and shown Fig. 6-3. The data shows that the dependency on time is almost linear. That could mean, in comparison with other indicators such as pH and conductivity, that the decrease of density could be connected to some other processes in the system. From the density tables of the aqueous propane-1,2-diol[9,50,51] is apparent, that the drop of density could mean increase of the water content. However, that does not comply with the rise of viscosity.

In the beginning, we can root out the possibility of sample manipulation error as all of the samples were treated in the same way and it would not explain the gradual decrease of the density like the data displays. One of the possible explanation could be gradual condensation of the glycol to its etheric form. The three isomeric products of the alcoholic condensation process of propane-1,2-diol, often called by a collective name dipropylene glycol[33], are shown on Fig. 6-4.

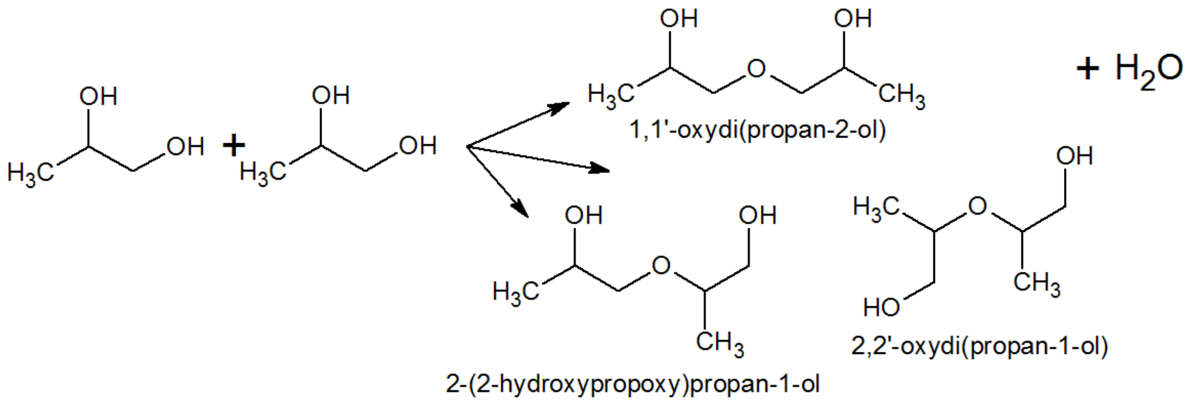

Fig. 6-4 Dipropylene glycol isomers - products of condensation reaction of MPG

Density of these products is also lower than the density of propane-1,2-diol, although, still higher than water (ρ_{dg} = 1.0206 g·cm^{-3})[41]. The formation of the etheric form was also supported by mass spectrometry (MS) analysis, where the dipropylene glycols (*Mr* = 134.0943 g·mol^{-1}) were found mostly as protonated or sodium adducts.

The intensity of the peaks of dipropylene glycol on Fig. 6-5 is rising through the samples according to operation time inside the system, suggesting rise in concentration, with anomaly high intensity of sample V2007. Interesting is also comparison between the VO2007 and VO2014 where the intensity of the dipropylene glycol peak is in case of VO2014 ten times lower, although it must be noted, that a simple comparison of MS spectra in not a sufficient method for sound concentration estimation. That could mean different source or better refined propane-1,2-diol in the newer fluid. The very low concentration would also explain the drop in the concentration between V2014 and V2014N when the fluid in the Vracov system was topped (in 2014) with the VO2014 and therefore diluting the dipropylene glycol in the whole system. Furthermore, the higher content of dipropylene glycol would also explained the lower density of VO2007 compared to VO2014 and because the aqueous dipropylene glycol has higher viscosity[51] it also explains the rise in its value.

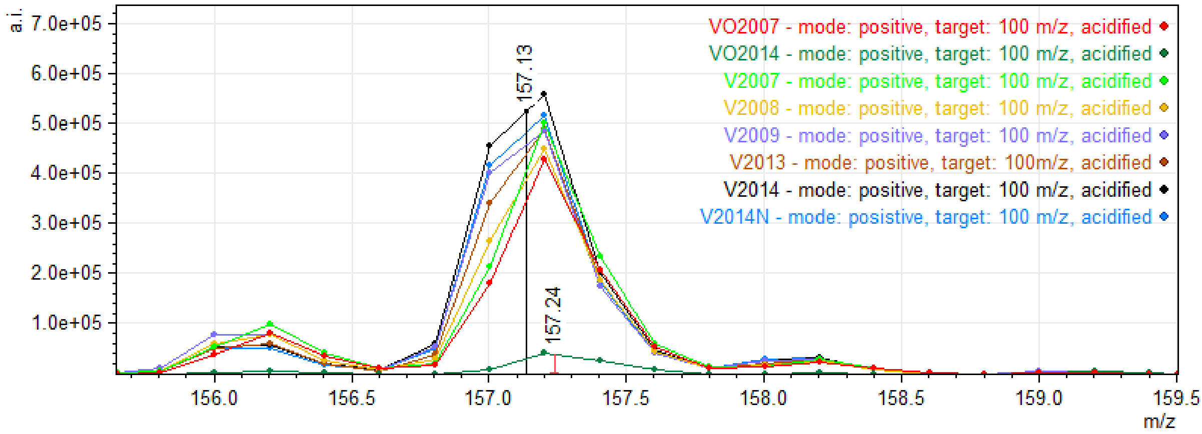

Fig. 6-5 MS peaks of dipropylene glycol through time

6.1.1 Acidification of hydroxy groups in propane-1,2-diol based mixtures

It has been reported by extensive research of Rossiter and his colleagues[25–27,46,47] on the topic of propane-1,2-diol and ethane-1,2-diol degradation, that an important factor, especially for formation of acidic degradation products, is the presence of oxygen. The modern systems are usually completely sealed, and therefore, it is to be expected that the composition of the acidic degradation will lead to different production rates of the organic acids if ever. For that reason, several visibly degraded heat transfer fluids from various systems were selected and the content of acidic products was measured by isotachophoresis (ITP). To establish the basic dataset for qualitative analysis, several different organic acids were measured separately and the RSH (Relative step height) was then calculated according to their isotachophoregrams

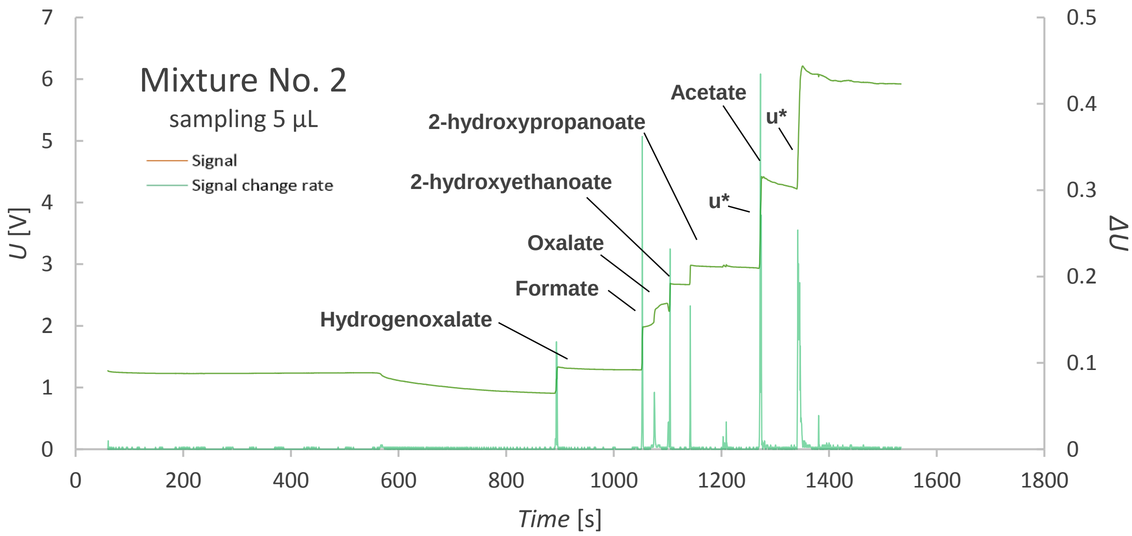

Fig. 6-6 Isotachophoregram of mixed standard, u - unknown/impurities*

On Fig. 6-6 is shown a testing run with standard mixture to establish the RSH and to identify the present organic acids in the samples. The quantitative analysis is based on the time of elution of the individual steps that represent the individual analytes. The example of data analysis is shown on Fig. 6-9. All the analytes were recognized positively in the samples with standard deviation being between 0.6 % – 2.7 % with 1.9 % on average. On the Fig. 6-7 and Fig. 6-8 are depicted possible routes of organic acid formation from propane-1,2-diol.

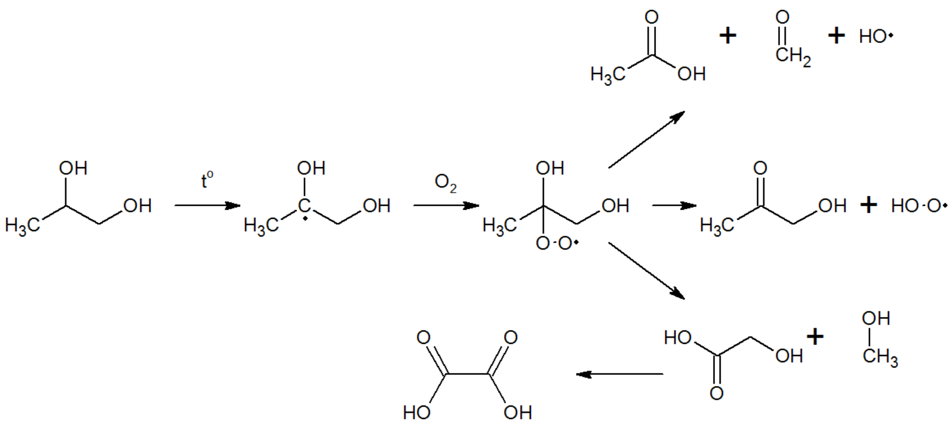

Fig. 6-7 Degradation process of propane-1,2-diol through C_2 thermal oxidation

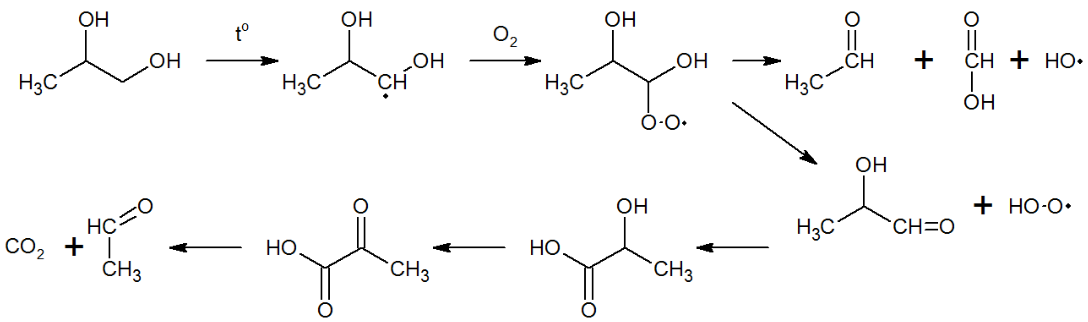

Fig. 6-8 Degradation process of propane-1,2-diol through C_1 thermal oxidation

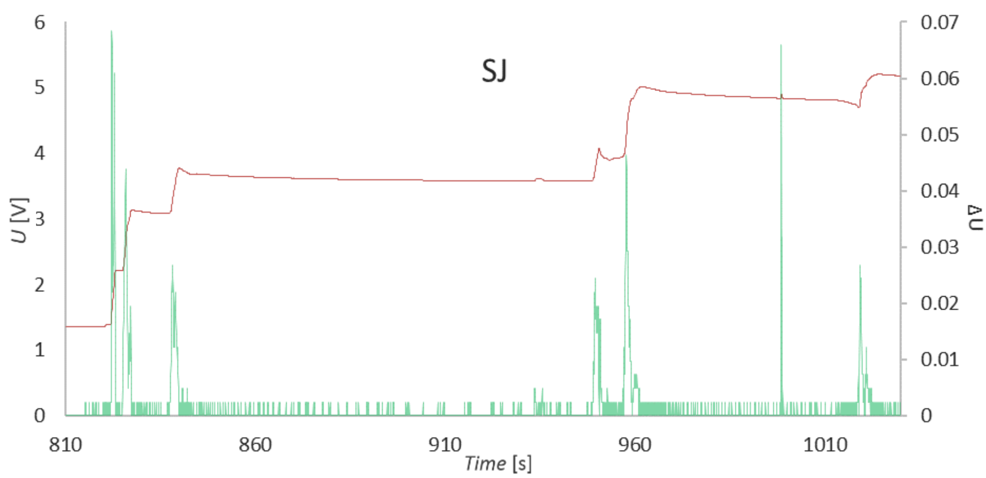

Fig. 6-9 Examples of data samples analysis from real samples

In the samples SD and SJ was positively confirmed sebacic acid in form of sebacate. In the more degraded SJ the amount of sebacate is dramatically reduced as a definite proof of the inhibitor depletion process.

When comparing these data to the literature, it is apparent that the amounts of acidic degradation product formation is much smaller than stated in literature. According to literature (Rossiter et al.[27] and DOW[52]) sources the dominant product for aqueous propane-1,2-diol degradation should be 2-hydroxypropanoic acid (lactic acid). That is, in case of oxidative environment and presence of copper.

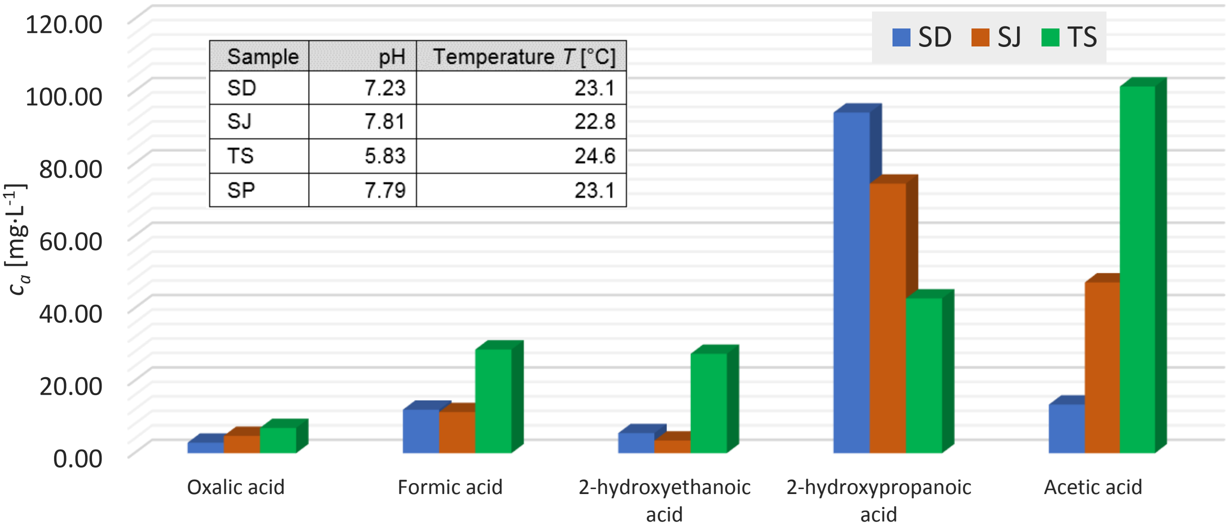

Fig. 6-10 pH and organic acid content - comparison of analysed samples

For comparison the samples V2007, V2008, V2009, V2013 and V2014 were also tested on the presence of acidic degradation products. From the pH change would seem that some acidification occurs even in stable systems, however, the results for the presence of organic acid were negative in all cases. The only positively identified acid inside the samples was sebacic acid from the corrosion inhibitor system.

6.1.1 Inhibitor additives depletion and other degradation products

The analysis of available samples by mass spectroscopy uncovered several aspects, which are not discussed in the literature. The mass spectra were analysed by an open source program mMass[53–55]. The data were acquired in both positive and negative modes for three different target m/z: 100 m/z, 500 m/z and 1000 m/z. Because the used ionizing technique was ESI (electrospray), which is soft ionizing method, most of the analytes were found in their full molecular state and the problem was achieving sufficient intensity and variability of ionized adducts to positively and fully identify selected components.

The complete overview of the main components is shown on Fig. 6-11. From the overview is apparent how much the sebacic acid is dominating the spectra. The relative intensity of the sebacic acid can serve as a good indicator of other substances, because the concentration of it seems to be stable, or not dropping. The comparison of individual peak intensity is provided on Fig. 6-12. As can be seen, the intensity of the peaks does not follow any distinguishable trend and it is assumed that the amount of the corrosion inhibitors does not rapidly changes in the samples from experimental system in Vracov. Quite different situation can be seen on the example from the highly degraded samples SJ and SP which are also originally HTF *Solaren* (VO2007) on Fig. 6-13. In these samples the intensity of the main components significantly differs despite the same original concentration.

The difference in the case of sample SP is probably caused by partial water depletion during the stagnation process and subsequent concentration. Water has lower boiling point and it is usually water which turns to steam, and it is released through the safety pressure valve outside the system. This situation is frequently encountered in new systems which are fully filled and the expansion tank is not capable to compensate for the big volumetric change of the fluid.

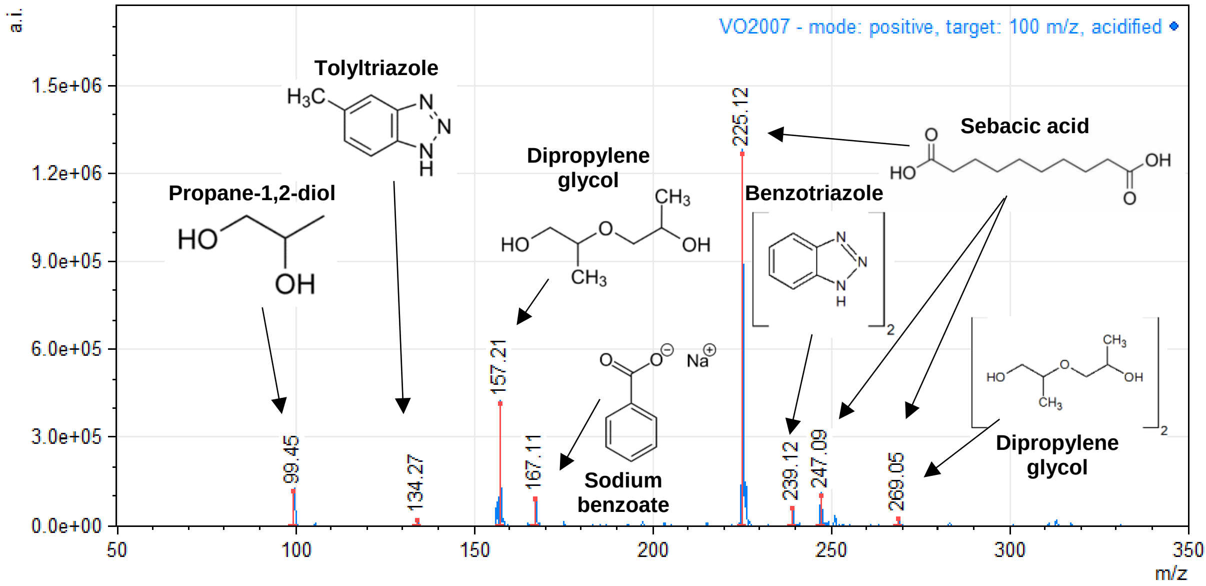

Fig. 6-11 Overview of main components in Solaren HTF

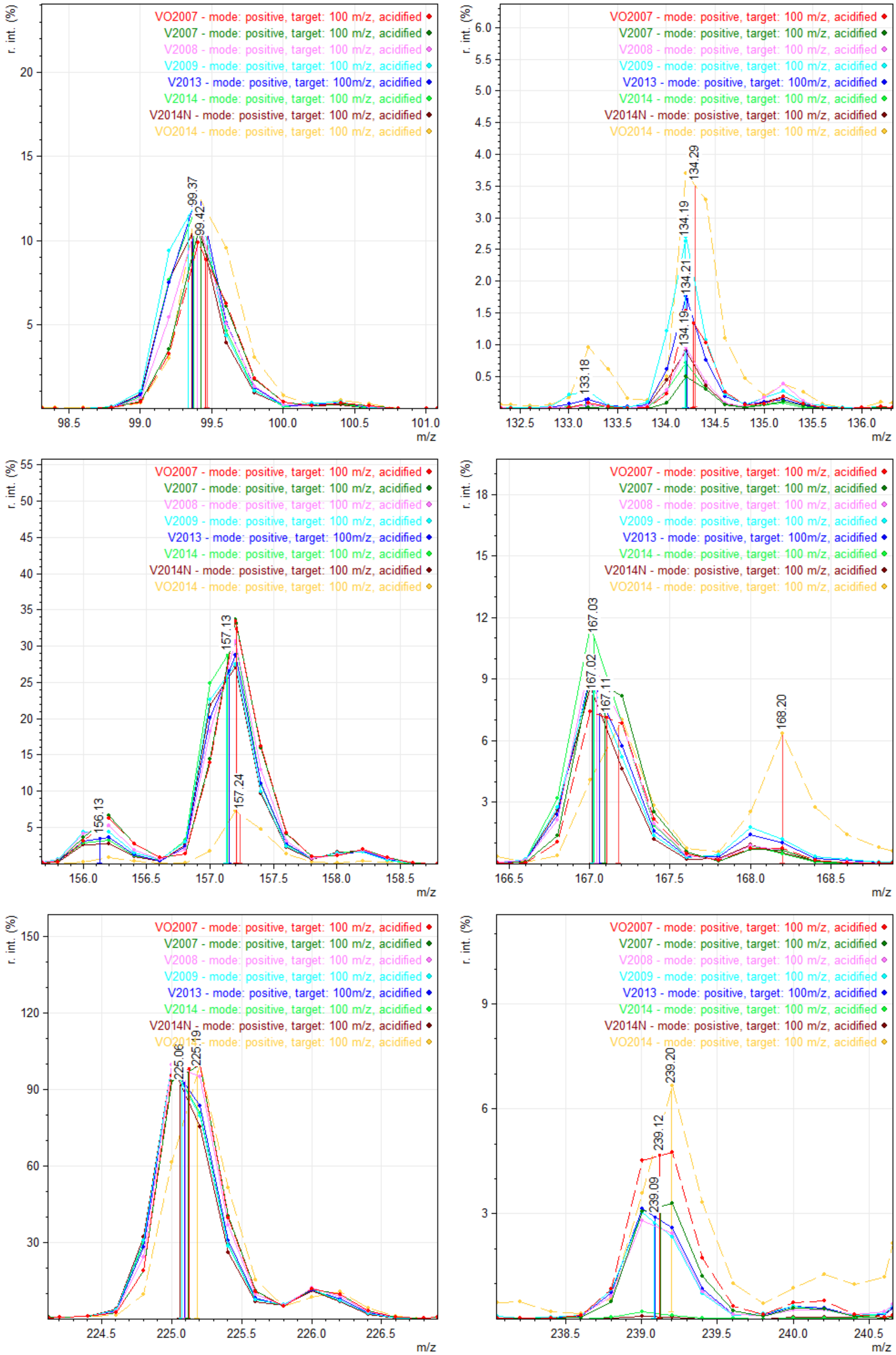

Fig. 6-12 Change of relative peak intensity on traced substances

Completely different situation is observed in case of sample SJ. The reasons for such dramatic changes can be several. The notable factor is high intensity of peak at 157 m/z (dipropylene glycol). The possible causes for such difference is addition of different mixture to the system, however the original inhibitor selection seems to be the same. The important factor stays at the dramatic depletion of sebacic acid and complete depletion of some other inhibitors.

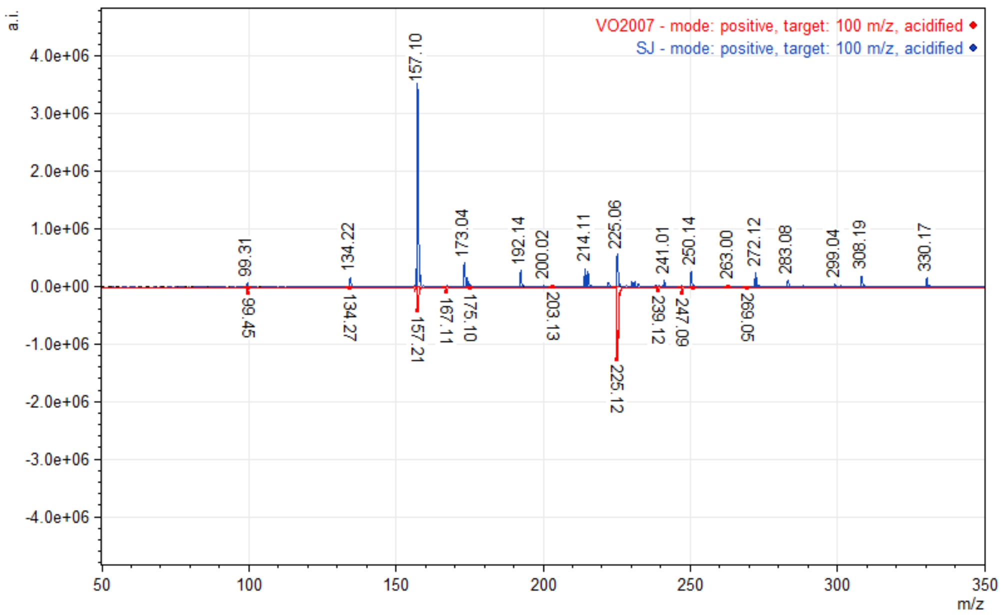

Fig. 6-13 Comparison of highly degraded fluids sample SJ with original

6.1.1 Polymerization of propane-1,2-diol based mixtures?

During the measurement with the target of 500 m/z a curious pattern was observed in the middle region of the active range. As can be seen on the Fig. 6-14, the number of peaks of the fluid sampled from the system is incomparable richer than of the original filling. Upon further analysis of the “forest” of peaks was discovered a certain pattern which corresponds to a weight shift of 44 m/z which could indicate a polyethylene glycol ($C_{2n}H_{4n+2}O_{n+1}$) row. However, the formation of polyethylene glycol from propane-1,2-diol is not likely to occur even under stagnation conditions. Furthermore, in case a progressing polymerisation a change of the pattern should be visible, however the change between the samples of chronological order from V2007 to V2014 was near to none.

The contamination of samples from the plastic containers was ruled out in the previous section, however, the option of contamination[56] from the system is fully possible. What also support the contamination theory is different outcome for samples SJ and SP which were also tested on the presence of this pattern. Similar situation was observed for another glycol-based fluid of sample TS, where no distinguishable polymeric pattern was observed despite high degradation and high content of organic acids.

In case of peak-rich spectra of the samples from experimental system in Vracov is actually available another theory explaining such outcome and it is copper complexes with the organic compounds, such as dipropylene glycol or sebacic acid. This theory is partially supported by the shape of some of the isotopic peaks. To positively identify any copper complexes additional research will be necessary, although, it is reasonable to expect them in some amount, even though that the visible peaks in the MS spectra are not made by them. Unfortunately, this option was not available during the creation of this work and it will be a subject of a continuing research.

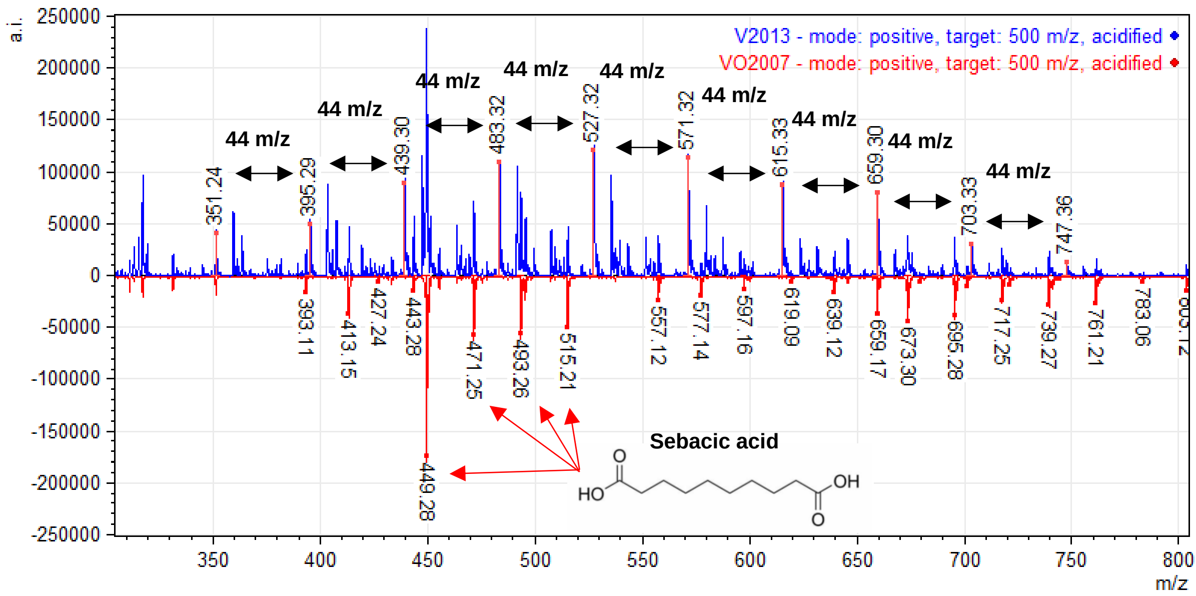

Fig. 6-14 Comparison of original fluid and after 6 years of operation

To further support the theory about the condensation type of polymerisation the Karl Fisher titration was attempted. The data and measurement conditions from the measurement together with the results are shown on Fig. 6-15.

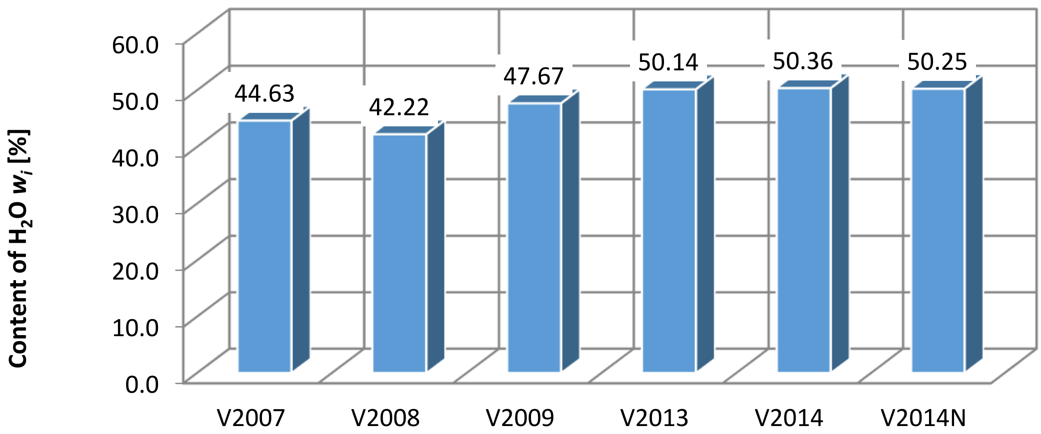

Fig. 6-15 Water content according to Karl Fisher titration

During the process of condensation type of polymerisation (or the creation of dipropylene glycol), the water is released and theoretically the water content should be higher for more degraded/polymerised samples. However, as can be seen from the measured data, the results are exact opposite. The older samples V2007, V2008 and V2009 are showing the smallest amount of water, much smaller than the original mixture, where water should be less than 50 % (48 % of propane-1,2-diol and 3-4 % inhibitors and stabilizing chemicals). Because some higher numbers for newer samples were achieved in the same way, the method itself is presumably correct. The possible cause for this difference would be, with high probability, the manipulation with the samples over the years. The samples were extensively used by several graduate students as well as the writer of this thesis for different types of research. During that time, part of the water was evaporated which caused this discrepancy.

6.2 AQUEOUS PROPANE-1,3-DIOL CHARACTERISTICS

Several researchers have already reported some of the physical and chemical data on the pure propane-1,3-diol, but the data on aqueous propane-1,3-diol are incredibly scarce. The first very basic limited set of data on the propane-1,3-diol/water mixture were prepared by Lee et al.[57] in 2000. Density, speed of sound, relative permittivity and viscosity, were reported by George and Sastry[58] together with other water/alkanediols systems. The most up to date study of the propane-1,3-diol/water mixture was published by Moosavi and Rostami[59] in 2017 focusing on density, viscosity, refractive index. These are actually most of the papers dealing with aqueous propane-1,3-diol. Furthermore, they are often lacking necessary temperature range or precision for using as an antifreeze additive[60]. For that reason, the following basic data on propane-1,3-diol were prepared in collaboration with an antifreeze manufacturer company Classic Oil s.r.o. from Kladno in the Czech Republic.

6.2.1 Density

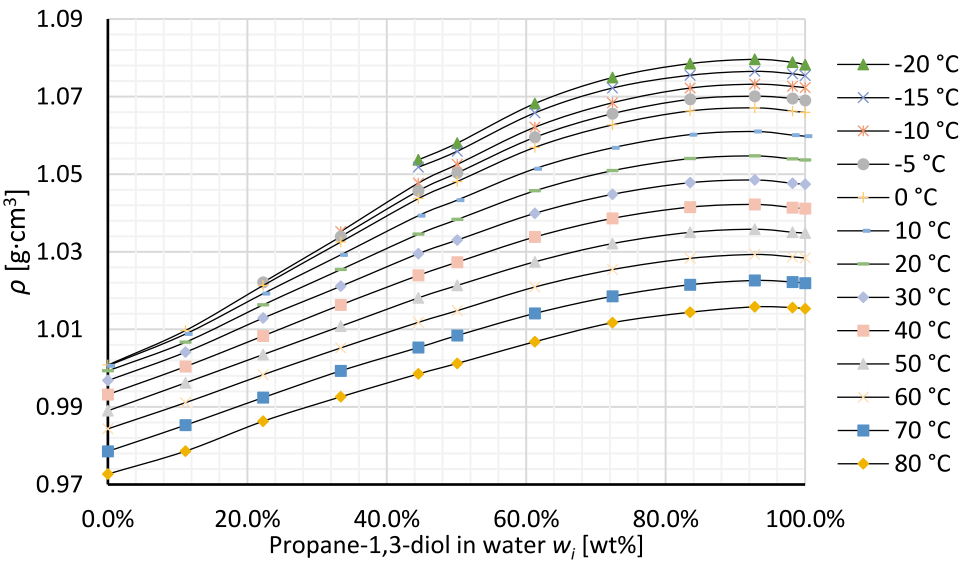

Fig. 6-16 Density of propane-1,3-diol on mass fraction (top) and temperature (bottom)

The measured data on density of propane-1,3-diol are presented on Fig. 6-16. The acquired data of pure propane-1,3-diol are in good agreement with available literature sources[57–59] and the standard deviation does not exceed $\sigma = 0.002$ for the compared range of 20 °C to 65 °C.

To describe the influence of the water dilution on the density of PDO it was used the method of excess molar volume $V^E/(\mathrm{cm^3 \cdot mol^{-1}})$. For that purpose, it was necessary to recalculate the mass fractions from the original data set to molar fractions. The calculated excess molar volumes were then fitted to Redlich-Kister[61,62] (R-K) equation (expansion) described as:

$$Y^E = x_i x_j \sum_{n=0}^{k} A_k \left(x_i - x_j\right)^k, \tag{6.2.1}$$

where the Y^E states for the specific excess property, x_i and x_j are representing the respective mole fractions of the components of the binary fluid and the A_k is used for expansion fitted parameters. The results are shown on Fig. 6-17.

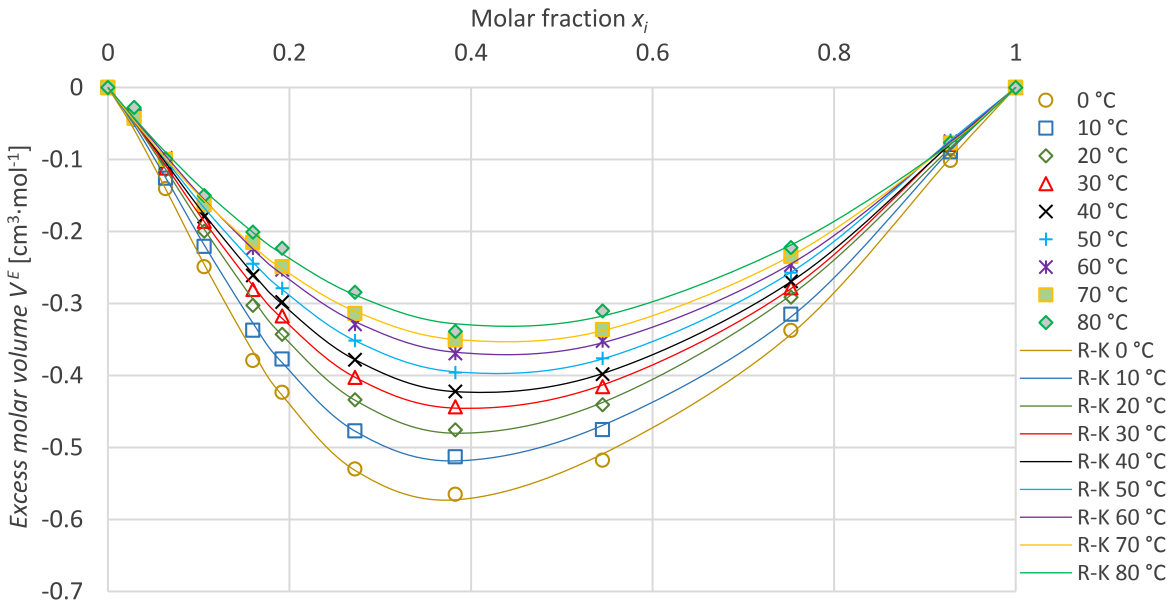

Fig. 6-17 Excess molar volume and Redlich-Kister equation fitting

The aqueous propane-1,3-diol shows the highest excess molar volumes naturally at lower temperatures. The actual minimum is changing with temperature around $x_i \sim 0.4$ ($w_i = 0.7 \sim 0.8$) uncovering the propane-1,3-diol as the main driving force for the change. The shift in the excess molar volume is mainly caused by the fact that the density is in practice higher than of the pure substances, reaching its minimum around equimolar quantity, as can be seen on Fig. 6-16. This behaviour is caused by the hydroxyl-water interaction and it is typical for some α,ω-alkanediols such as propane-1,3-diol and butane-1,4-diol. This unique property has been demonstrated and explained in the works of Nagamachi and Francesconi[63] and Takahashi and Nishi[64].

6.2.2 Viscosity

To easily compare the viscosity deviation of a real mixture against an ideal mixture and establish the dependence of the viscosity deviation is defined as follows:

$$\Delta\eta = \eta_{12} - (x_1\eta_1 + x_2\eta_2). \tag{6.2.2}$$

In the Eq. (6.2.2) the viscosity deviation $\Delta\eta$ is defined as a difference between the experimental value of dynamic viscosity η_{12} and the linear behaviour of the ideal mixture, where η_1 and η_2 are the viscosities of the pure substances and x_1 and x_2 are their respective mole fractions. The deviation was similarly to density fitted to Redlich-Kister equation (6.2.1) to establish a mathematical dependency shown on Fig. 6-18.

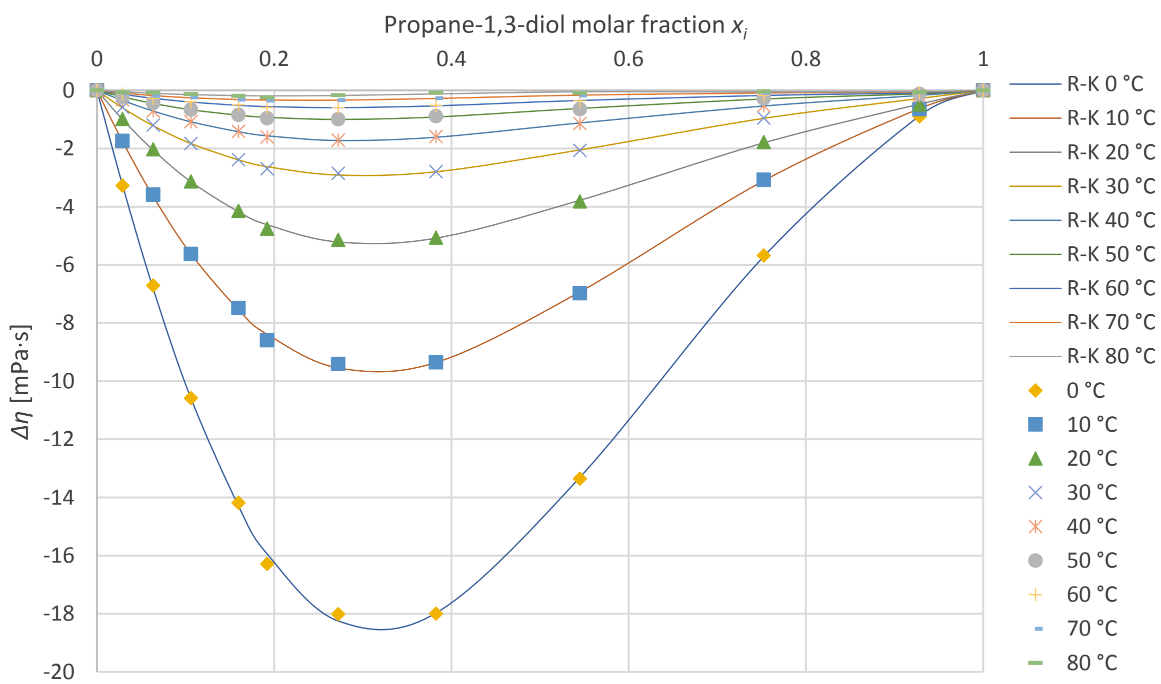

Fig. 6-18 Excess viscosities and Redlich-Kister approximation of aqueous propane-1,3-diol

The dependency of aqueous propane-1,3-diol on temperature, molar and mass fraction is not linear, which is a typical property of aqueous alcohols and diols[65]. To describe these dependencies several models are mentioned in literature by various authors. These models are based on theoretical background or empirical findings. Many of these models are based on the ideal mixture calculation originating from Arrhenius equation:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2, \tag{6.2.3}$$

where η_{12} is the overall dynamic viscosity and x_1, x_2 and, η_1, η_2 are the mole fractions and dynamic viscosities of the pure substances respectively. To get a good agreement with the experimental data several different modifications were tested.

Basic and simple modification of the linear Arrhenius model, with significant improvement of the precision, brings Grunberg-Nissan[66,67] model. The Grunberg-Nissan model introduces the fitting interaction parameter g_i to the original Eq. (6.2.3). The interaction fitting parameter g_i of the binary mixture is proportional to the interchange energy, therefore, it is proportional to the temperature. The basic form of Grunberg-Nissan (G-N1) equation is written as

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + \sum_{i=0}^{n} x_1 x_2 g_i (x_1 - x_2)^i. \tag{6.2.4}$$

Another form of the equation (6.2.3) was proposed by Lederer[68,69]:

$$\ln \eta_{12} = \left(\frac{x_1}{x_1 + x_2 s}\right) \ln \eta_1 + \left(\frac{x_2 s}{x_1 + x_2 s}\right) \ln \eta_2. \tag{6.2.5}$$

Lederer's equation emphasizes the significance of mixing two components with substantially different viscosities[70]. The more viscous propane-1,3-diol is represented in the Eq. (6.2.5) by its molar (or mass) fraction x_2. The interaction adjusted by a single empirical constant s, which can be correlated to temperature.

The Heric model expands the original Arrhenius equation by following the Eyring theory[71,72] of ideal mixture with zero excess of activation Gibbs free energy ($\Delta G^{*E} = 0$). The model works with molar weights of the mixed liquids M_1 and M_2 and the resulting equation is devised for kinematic viscosity ν_{12} written as a logarithm:

$$\begin{aligned} \ln \nu_{12} = {} & x_1 \ln(\nu_1 M_1) + x_2 \ln(\nu_2 M_2) - \ln(x_1 M_1 + x_2 M_2) \\ & + \left(\sum_{i=0}^{n} \alpha_i x_1 x_2 (x_1 - x_2)^i\right), \end{aligned} \tag{6.2.6}$$

where x_i, ν_i and M_i represent the mole fraction, kinematic viscosity and molar weight of the individual component. Furthermore, McAllister's model was also established.

Basic shortcoming of the viscosity models is the necessity for large amount of experimental data as the purely theoretical concepts for polar fluids usually lacks some accuracy and are also limited by the measurable temperature range of the pure substances. However, by acquiring sufficiently large set of data sample some of these models can be extended over the whole mole or mass fraction region. That is mainly thanks to the direct dependency of the fitting parameters on temperature. To produce such dependency, above stated models were all used for that purpose with substantial success by creating a mathematical dependency on the fitting parameters based on temperature. A simple polynomial regression was used for that purpose.

With prepared dependencies of the fitting parameters itself it has been attempted to combine these models with models for pure substances. The reason for that was to create a universal model which would be able to fully predict the viscosity in the selected region of dilutions and temperatures. The base model for the pure substances was used Arrhenius model in the following form:

$$\eta = \eta_0 e^{E_a/RT}, \qquad (6.2.7)$$

where η is the viscosity, η_0 is the preexponential (entropic) factor and E_a, R and T are the Arrhenius activation energy, universal gas constant and absolute temperature, respectively. However, the basic form of the Arrhenius equation does not provide necessary accuracy for polar liquids[73] and therefore an empirical enhancement was added:

$$\eta = \eta_0 e^{\left[\frac{A}{t_0 + t_1 T + t_2 T^2}\right]}. \qquad (6.2.8)$$

All the previous models were tried with the adjusted Arrhenius model for pure substances to create a universal combined model with only one set of constants and two variables in form of temperature and molar or mass fraction. For example Lederer's equation in combination with Arrhenius equation (6.2.8) will be written as:

$$\begin{aligned} \ln \eta_{12} = {} & \left(\frac{x_1}{x_1 + x_2(s_0 + s_1 T + s_2 T^2)}\right)\left(\ln \eta_{10} + \frac{A_1}{t_{10} + t_{11} T + t_{12} T^2}\right) \\ & + \left(\frac{x_2(s_0 + s_1 T + s_2 T^2)}{x_1 + x_2(s_0 + s_1 T + s_2 T^2)}\right)\left(\ln \eta_{20}\right. \\ & \left. + \frac{A_2}{t_{20} + t_{21} T + t_{22} T^2}\right) \end{aligned} \qquad (6.2.9)$$

The results of the combination for Lederer's model are shown on Fig. 6-19. On average, the combined models are providing very good fit with the experimental data and they are not exceeding 5 % of absolute average deviation – AAD [%]. Especially good results are showing the Grunberg – Nissan's and Lederer's model, when they are reaching around AAD = 1 % on average. However, it is necessary to point out that the complexity of this modelling does not lie in the average fit but rather in local deviations. Near the boundary conditions (freezing point) maxima can easily reach 10 % or more. Such models than have limited application as the deviation is exceeding safety margins. To compensate for this effect, we have two options. The more usual is to state for each model the application range (temperature, dilution) or broaden the safety margins for the application itself.

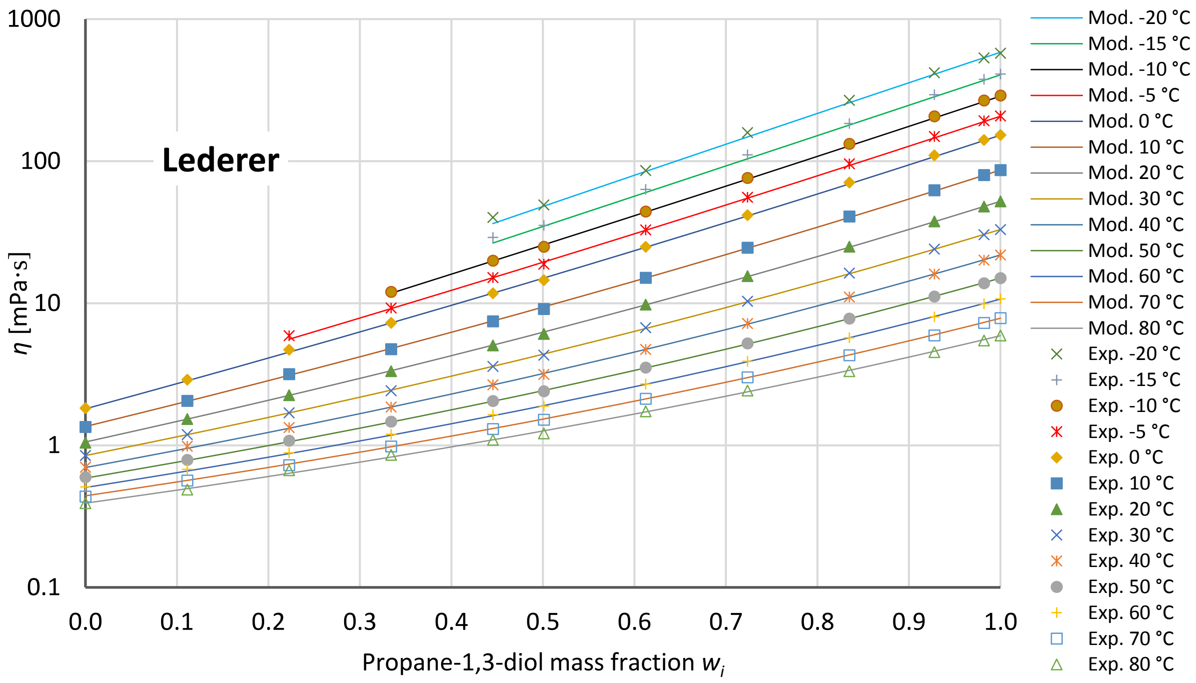

Fig. 6-19 Combined viscosity models in comparison with experimental data

6.2.1 Refractive index

Data on refractive indices are shown on Fig. 6-20. As a basis to create a connection between optical and volumetric properties the Clausius-Mossotti equation was used. This equation describes the relative permittivity ε_r (dielectric constant) of a material, or a mixture this way:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha'}{3\varepsilon_0}. \tag{6.2.10}$$

In the above equation N represents the number of particles per volume, ε_0 is vacuum permittivity and α' is polarizability volume. The polarizability volume α' expressed in SI units will give polarizability as $\alpha = 4\pi\varepsilon_0\alpha'$. In case of a mixture, the right side of the previous equation becomes a sum of calculated individual bodies dependent on the number of particles. To connect the refractive index n_D and relative permittivity was used the Lorenz-Lorenz equation by the Maxwell relation:

$$\frac{n_D^2 - 1}{n_D^2 + 2} = \frac{4\pi}{3} N\alpha, \tag{6.2.11}$$

where the refractive index n_D is expressed as $n_D^2 = \varepsilon_r$, N states the number of particles in the volume and α is the polarizability from the abovementioned relation to polarizability volume α'. From that relation we can deduce the molar refraction R_m [mol^{-1}] as:

$$R_m = \frac{n^2 - 1}{n^2 + 2}\frac{M}{\rho} = \frac{4\pi}{3} N_A \alpha, \tag{6.2.12}$$

where M is calculated average molar mass, ρ is density and N_A is the Avogadro constant. The polarizability of water at 20 °C was calculated as $\alpha = 1.47 \times 10^{-24}$ cm^3·mol^{-1}, which agrees with values from literature[74]. The polarizability of propane-1,3-diol was find out as $\alpha = 7.54 \times 10^{-24}$ cm^3·mol^{-1} and it agrees with values find out by Moosavi and Rostami[59]. Notable are also the respective trends of the polarizability and molar refraction. In case of water, the values are dropping with the rising temperature, however the values for propane-1,3-diol are rising. The respective differences are $\Delta\alpha = 0.1 \times 10^{-24}$ cm^3·mol^{-1} for propane-1,3-diol and $\Delta\alpha = 0.02 \times 10^{-24}$ cm^3·mol^{-1} for water in the range of 10 °C to 40 °C. That shows higher dependency of activity on temperature for propane-1,3-diol.

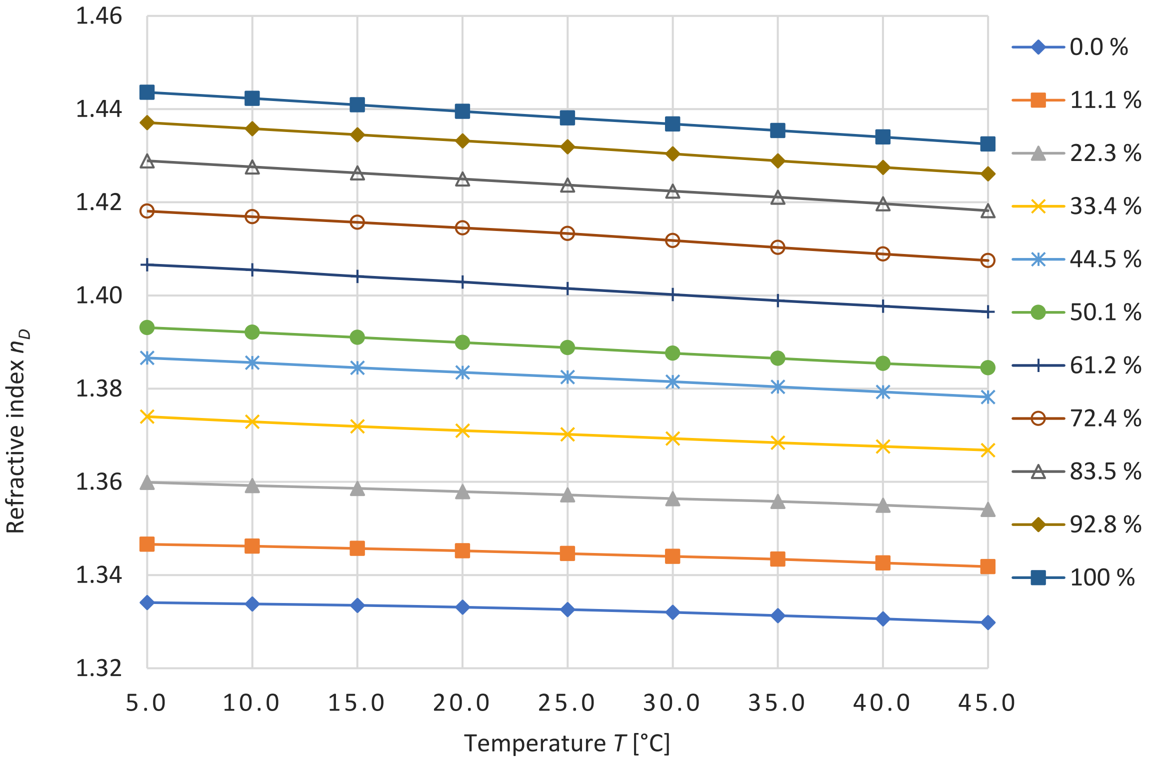

Fig. 6-20 Refractive index of aqueous propane-1,3-diol on temperature

6.2.1 Freezing point

One of the key properties for using propane-1,3-diol as an antifreeze additive is its capability of depressing freezing point (fusion point) of water. The results of the freezing point depression of the aqueous propane-1,3-diol are shown on Fig. 6-21.

Comparison of the freezing point is provided on the available data of Sunterra bio-propane-1,3-diol of high purity. The literature reference from the Fig. 6-21 (Ref.[75]) is using for measurement the same bio-produces propane-1,3-diol as was used in this work as sample PDOD. For comparison was also measured a sample PDOC from Chinese manufacturer with stated purity of 99 %. All the results are in good agreement with literature and between each other, proving good quality of the examined chemicals and possibly good repeatability of the method.

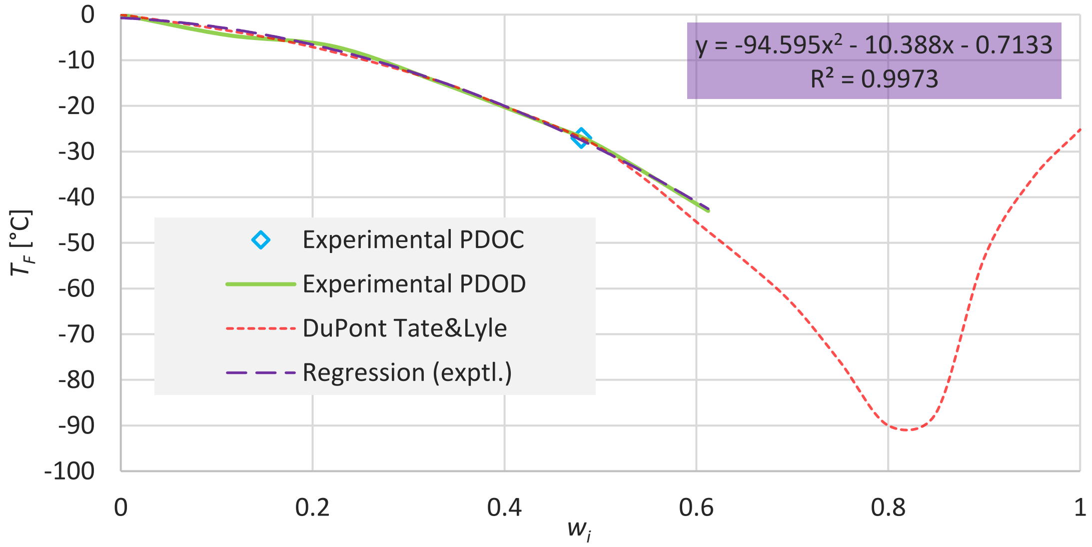

Fig. 6-21 Freezing point of aqueous propane-1,3-diol in comparison with literature[75]

When comparing the data on freezing depression of propane-1,3-diol with other glycols from Fig. 4-2 it is apparent that propane-1,3-diol does not have such strong freezing point depression for water as propane-1,2-diol and ethane-1,2-diol and for the same freezing protection of water is necessary higher concentration of propane-1,3-diol. That gives another blow to the feasibility of already over-expensive use of propane-1,3-diol. To achieve the same freezing protection, it is necessary additional 5-10 % of propane-1,3-diol.

6.3 HEAT TRANSFER FLUID BASED ON PROPANE-1,3-DIOL

6.3.1 Thermal degradation processes

The thermal degradation process of propane-1,3-diol is yet to be properly studied, but some of the basic information are already available. The stability of the aqueous propane-1,3-diol was for the first time studied by Eaton and co-workers[37] when comparing it to the ethane-1,2-diol for usage in exhaust gas recirculation devices use. The results of their research were seemingly higher thermal stability of propane-1,3-diol compared to the common systems using propane-1,2-diol and ethane-1,2-diol. The main setting for the experiment was oxidative degradation of the aqueous propane-1,3-diol, when most of the modern systems are not exposed to direct oxidative stress through dissolved oxygen.

Another study was provided by one the biggest manufacturer of bio propane-1,3-diol DuPont Tate&Lyle[75,76]. The aqueous propane-1,3-diol was again compared to the common systems of propane-1,2-diol and ethane-1,2-diol. The three samples of 50 wt% solutions were inhibited by addition of 2.2 wt% of standard heavy-duty inhibitor system Penray 2792[77] and the formation of glycolate, formate and inhibitor depletion was studied. The temperature of the test was chosen to be 192 ± 10 °C and the test was conducted for 16 hours (instead of 150 °C and 336 hours in case of Eaton[37]). However, several things in this study is questionable. The experiment was conducted in glassware only without adding any standard metals that can be encountered in standard systems. Only glycolate and formate degradation products were studied and no information on change of pH or conductivity was given. Therefore, even thought that the results are very intriguing, the validity of this study is somehow questionable, adding to it the very short time of the actual experiment.

6.3.2 Corrosivity properties

To test the actual corrosion properties a standard ASTM D1384[28] corrosivity test for antifreeze glycol-based mixtures was conducted. Test was conducted in the laboratory of Classic Oil s.r.o. and the data were kindly provided by Dr. Jan Skolil. The used inhibitor was a hybrid inhibitor system Cemkor C33[78] based on silicates from Slochem Trade s.r.o.

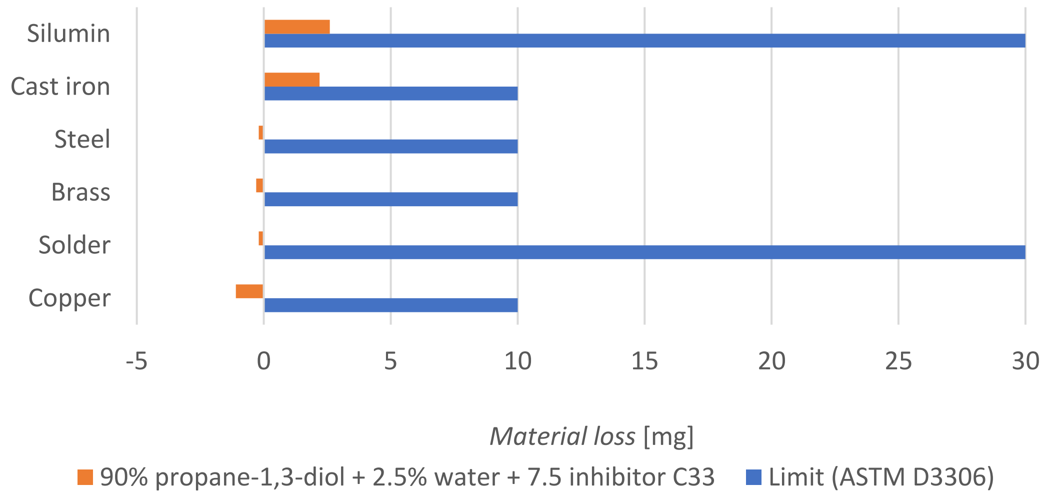

Fig. 6-22 Corrosion test of aqueous propane-1,3-diol according to ASTM D1384

As it was expected, the propane-1,3-diol is stable and shows only a limited amount of corrosion basically on the verge of measurement and method error. However, it is necessary to note, that this method is intended only as a basic information source about its corrosivity and the actual situation in the real system can significantly vary from these results as it is directly described in the standard itself. Unfortunately, any comparative study has yet been published to confirm this assumptions.

6.3.3 Perspectives of utilisation of propane-1,3-diol as a novel antifreeze additive

Despite all the positive properties of propane-1,3-diol, its simple utilisation as novel antifreeze additive is a different problem. The main setbacks so far is its high price around 1500-2000 $ per ton (based on survey on Alibaba.com) when propane-1,2-diol is in the range of 800-1400 $[79] per ton and ethane-1,2-diol in the range of 500-1000 $[80] per ton, depending on quality and season. The market is strongly influenced by Chinese manufacturers as China is becoming the largest single consumer and producer of glycols in the world[81]. Furthermore, the price for propane-1,3-diol is only an estimation for limited quantity. That is because the global market of propane-1,3-diol is yet to be established, the number of actual producers is highly limited, and therefore, the price varies significantly according to manufacturer and ordered amount. The biggest producer so far, DuPont Tate&Lyle[82], is producing propane-1,3-diol mainly for its own manufacturing purposes (see chapter 4.5.2 for more information) and in general, acquiring any stable supply of propane-1,3-diol for a continuous production is a difficult task.

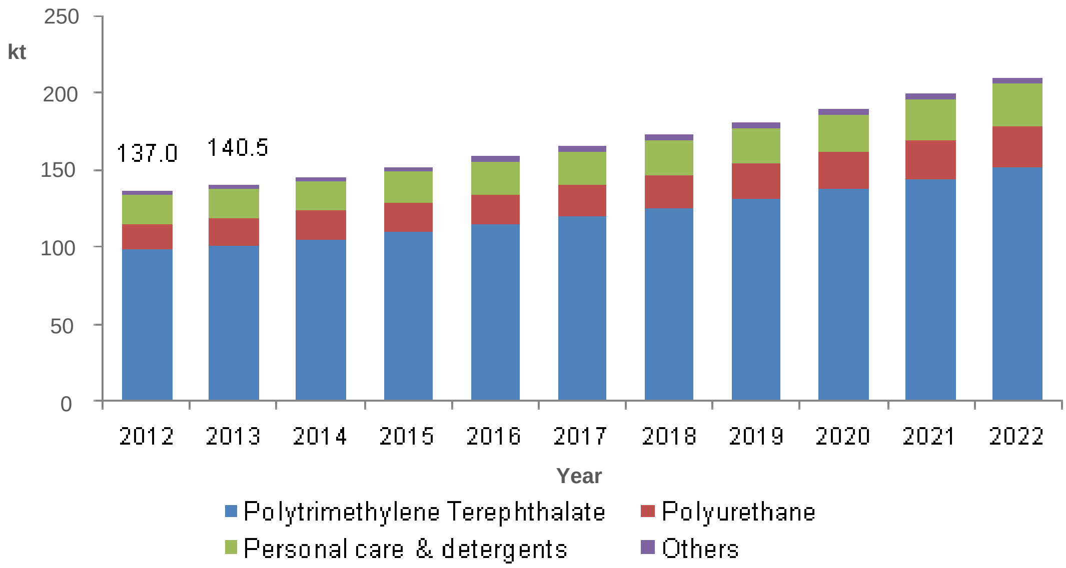

Fig. 6-23 Market volume of propane-1,3-diol by application (prediction 2015+)[83]

The situation in favour for propane-1,3-diol as a novel antifreeze was changing only very slowly during the last decade[16]. It was mainly caused by the limited production capacities, and therefore high price, and very limited amount of available information on the physical and chemical properties of propane-1,3-diol. The main producer DuPont Tate&Lyle is advertising propane-1,3-diol as novel antifreeze additive for couple of years now[75,84], however, on the actual market is nearly impossible to find any developed product.

However, the prognosis for other applications except polymer industry is somehow dim as can be seen from the prediction from Fig. 6-23. That prediction is made on the basis of the market development so far and the demand for green technologies is not fully accounted or understood.

7 CONCLUSION

An experimental thermal solar system in Vracov, Czech Republic was observed over a time span of 7 years with periodically sampling of the heat transfer fluid based on propane-1,2-diol for chemical and physical analysis. The results of the analysis show that even after seven years of continuous operation, the fluid is in relatively good condition and can be used unaltered further on. Such a good state of the fluid can be seen as little bit surprising, because the manufacturers of the heat transfer fluids recommend to change the fluid every five years on a general basis. The main factor of the fluid, freezing point was not affected, and if, it was in an amount which is negligible and will not affect the performance of the fluid. The data of pH and conductivity are showing reaching a pseudo-equilibrium and possible slowing down of the fatal degradation process. The prefix “pseudo” is used in this context rightfully as it is not reasonable to expect this state to hold out forever, even though all the measurements indicate a significantly prolonged time of operation of the fluid in the Vracov system without the necessity of replacement.

This state is further on supported by the mass spectrometry analysis on the presence of the corrosion inhibitors in the mixture. During the whole monitored time, the amount seems to be constant without significant drop of their concentration and sustained effective protection of the system. The samples from Vracov were also tested on presence of organic acids as one the typical products of degradation. During the whole period of observation from 2007 to 2014 the amount of monitored organic acids, known to be formed in the propane-1,2-diol-based antifreeze systems, were not detected in amount more than 1 $mg \cdot l^{-1}$. This also proves very good condition of the fluid and expected prolonged life-span of the fluid.

But some change was detected after all. If we look at the results for density a clear trend of continuous density drop can be observed. There may be two reasons for this change. First is connected to change of the concentration of propane-1,2-diol and water. During the operation the temperatures exceed 120°C from time to time (boiling point of water at 2 bars) and part of the water is evaporated and if the pressure exceeds 6 bar the steam is vented to the atmosphere through the safety pressure relief valve. However, this situation was not detected during the operation of the Vracov system and what more, this would cause a density rise not a decrease like in this case. Therefore, a different explanation is necessary. A possible cause of this change could be actual change in the chemical makeup of the mixture. By additional mass spectrometry analysis, a seemingly increasing concentration of dipropylene glycol isomers was observed. This would completely explain the drop of the density, rise of the viscosity and at the same time preservation of some of the key properties of the fluid such as freezing point. What more, this change seems to be gradual and no serious harm to the system is expected by the means of this change. However, this discovery is very important for further manipulation with the spent fluid, especially in case of intended recycling. If the concentration of the dipropylene glycol become too high, the change of viscosity could cause some technological problems and would be better to be avoided. To fully support this thesis and establish a reaction kinetics for this change further research is necessary.

Not completely different situation was observed during the analysis of samples from several other systems which were using the same original fluid for their operation or, in case of sample TS, the same organic base propane-1,2-diol. The samples were collected form several thermal solar systems from the region of South Moravia and North Moravia. The samples were selected on the basis of their highly progressed degradation and that none of them was in operation longer than the experimental system in Vracov. The biggest difference of these samples was therefore not the fluid composition but their operating conditions. All of the samples were taken from systems that went through a series of system stagnation resulting in high thermal stress on the fluid and consequent system damage. The main purpose of this measurement of observation of the acidic degradation product formation in anoxic conditions. According to current knowledge, the degradation of propane-1,2-diol is complicated process consisting mainly from formation of organic acid products which are reducing the pH of the fluid and supporting corrosive properties of the fluid. However, this process was mainly studied in environments rich on dissolved oxygen and any comparative studies for modern systems are not available. This work shows, that these products are formed even in environment depleted of oxygen and are directly connected to the temperature. The highest concentrations of the organic acids were found in the sample TS equipped with evacuated tube collectors and with the highest stagnation temperatures. An interesting finding was the high concentration of acetate in case of the TS sample which goes against the current knowledge stating the main degradation product of propane-1,2-diol to be 2-hydroxypropionate (lactate). However, the possibility of some catalytic influence cannot be ruled out, thanks to different inhibitor system, because the samples SD and SJ, of the same origin, developed according to known preferences. Another finding was relatively low concentration of the monitored organic acids. In the available studies conducted usually over a short period of time, the concentrations of the main products (2-hydroxypropionate in case of propane-1,2-diol and 2-hydroxyethanoate in case of ethane-1,2-diol) is in range of grams per litre but this work shows milligram concentrations. The cause for such discrepancy may lie exactly in the time difference. In the case of the laboratory test, the samples are tested almost immediately for the monitored organic acids, however, in the real systems the acids are continuously interacting with the environment and causing corrosion. The result is, as shown in the work of Brown et al.[47], formation of several copper complexes with the organic acids and their precipitation from the mixture. The precipitate in the continuously circulating system sediments in hydrodynamically suitable places or it is filtered out by the system's filter. That is also a reason why in the working systems the precipitate is hard to find in the fluid itself and why it could have been found in a great quantity in the sample SD. Because the stagnation of the system of sample SD was caused by pump malfunction, the fluid was not circulating, the sedimentation occurred only freely, and the precipitate was also not filtered out by the system filter. Therefore, during the sampling when the fluid was moved for the first time after several days of stagnation, the lightly sedimented precipitate was easily agitated and could be sampled with the rest of the fluid. This means that only the measurement of pH does not have to be sufficient to assess the system state as it does not describe the actual damage but only its current rate, especially in systems, which underwent stagnation conditions.

Comparing the experimental system in Vracov with the results of the highly degraded samples an obvious conclusion offers itself. The degradation process is more connected to the system design and control than the chemical makeup of the fluid itself. Poorly designed systems are prone to overheating and stagnation, which according to this work is the main cause for the heat transfer fluid collapse. This results in shortened life-span of the system and economical losses. With proper design and robust control, the lifespan of the fluid can be significantly extended together with the lifespan of the system.

In the second half of this thesis a full investigation of selected physical properties on the aqueous propane-1,3-diol was conducted. The goal of this investigation was to establish a basic model tool, which can be used as an engineering base for further testing and progress of development of a novel antifreeze fluid based on propane-1,3-diol. The mathematical analysis included a creation of a new combined viscosity model combining three mathematical expression of water, propane-1,3-diol and standard viscosity model. Several different models were established with various level of agreement with the experimental data. The simplest model, and also one of the best fits, was produced by combined Lederer's model with adjusted Arrhenius viscosity expression for pure liquids. For better agreement, the Arrhenius model was refined by second polynomial sequence. Thanks to this adjustment, the resulting absolute average deviation (AAD [%]) for the whole data set was equal to ~1 % in case of Lederer model. Other models' deviations were higher, however, they did not exceed 5 %. But the problem of these models was not in the overall average deviations but in the local deviations which could reach up to 10-15 %. This situation was observed in case of all models. Though, it was strictly localised near the freezing point of the mixtures which means, that these models can be comfortably used in most of the range and the caution should be taken near the boundary conditions.

As the data shows, the viscosity and density are not that different compared to the common propane-1,2-diol and ethane-1,2-diol. Though, the viscosity is lower in case of aqueous propane-1,3-diol, the substance is little bit losing in terms of freezing protection. To achieve the same level of protection 5-10 % more of the propane-1,3-diol must be added to the mixture, which consequently rises the viscosity of the mixture as well. Connecting this with the higher price of the propane-1,3-diol, the competitiveness of this chemical is still limited. However, the results on the thermal stability and corrosivity show far better qualities than these of propane-1,2-diol and ethane-1,2-diol which possibly could overrule the higher costs connect with the use of antifreeze mixtures based on propane-1,3-diol.

8 LITERATURE

1. EUROPEAN ENVIRONMENT AGENCY. Energy efficiency and energy consumption in the household sector. *Assessment published* [online]. 2012. Available from: http://www.eea.europa.eu/data-and-maps/indicators/energy-efficiency-and-energy-consumption-5/assessment
2. TIAN, Y. and ZHAO, C.Y. A review of solar collectors and thermal energy storage in solar thermal applications. *Applied Energy* [online]. April 2013. Vol. 104, p. 538–553. DOI 10.1016/j.apenergy.2012.11.051. Available from: http://dx.doi.org/10.1016/j.apenergy.2012.11.051
3. KALOGIROU, Soteris A. *Solar thermal collectors and applications*. 2004. ISBN 3572240646.
4. VOHNICKÝ, Aleš. Racionální využití sluneční energie. *TZB-info* [online]. 2004. Available from: http://oze.tzb-info.cz/solarni-kolektory/2072-racionalni-vyuziti-slunecni-energie
5. EUROSTAT. Housing statistics. [online]. 2015. Available from: http://www.homesandcommunities.co.uk/housing-statistics
6. ESTIF. Solar Thermal Markets in Europe. . 2012. No. June, p. 1–20.
7. MOSS, G. P., SMITH, P. A. S. and TAVERNIER, D. *Glossary of class names of organic compounds and reactivity intermediates based on structure (IUPAC Recommendations 1995)* [online]. 1995. ISBN 0-521-51150-X. Available from: https://www.degruyter.com/view/j/pac.1995.67.issue-8-9/pac199567081307/pac199567081307.xml
8. WERLE, Peter and MORAWIETZ, Marcus. Alcohols, Polyhydric. In : *Ullmann's Encyclopedia of Industrial Chemistry* [online]. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2000. Available from: http://doi.wiley.com/10.1002/14356007.a01_305
9. THE DOW CHEMICAL COMPANY. *A Guide to Glycols*. 2003.
10. IWAMOTO, Reikichi, MATSUDA, Toshihiko and KUSANAGI, Hiroshi. Contrast effect of hydrogen bonding on the acceptor and donor OH groups of intramolecularly hydrogen-bonded OH pairs in diols. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*. 2005. Vol. 62, no. 1–3, p. 97–104. DOI 10.1016/j.saa.2004.12.007.
11. PATRICK, Bethanne Kelly. and THOMPSON, John M. (John Milliken). *An uncommon history of common things*. 2009. ISBN 1426204205.
12. MATUŠKA, Tomáš. Prvky solárních soustav (I). *TZB-info* [online]. 2006. Available from: http://www.tzb-info.cz/
13. BOSEN, Sidney F., BOWLES, William A., FORD, Emory A. and PERLSON, Bruce D. Antifreezes. In : *Ullmann's Encyclopedia of Industrial Chemistry* [online]. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2000. Available from: http://doi.wiley.com/10.1002/14356007.a03_023
14. HUDGENS, R. Douglas, HERCAMP, Richard D., FRANCIS, Jaime,

NYMAN, Dan A. and BARTOLI, Yolanda. An evaluation of glycerin (glycerol) as a heavy duty engine antifreeze/coolant base. *SAE Technical Paper 2007-01-4000* [online]. 2007. No. 724, p. 776–790. DOI 10.4271/2007-01-4000. Available from: http://www.sae.org/technical/papers/2007-01-4000

15. THIRUGNANASAMBANDAM, M, INIYAN, S and GOIC, R. A review of solar thermal technologies. *Renewable & Sustainable Energy Reviews*. 2010. Vol. 14, no. 1, p. 312–322. DOI 10.1016/j.rser.2009.07.014.
16. MIKŠÍK, František. *Nemrznoucí teplonosné kapaliny pro solární systémy*. Brno University of Technology, 2010.
17. SKOLIL, Jan. *Physicochemical Aspects of Ecological Heat-Transfer Fluids*. Brno University of Technology, 2016.
18. MATUŠKA, Tomáš. Problematika stagnace u solárních tepelných soustav (I). *TZB-info* [online]. 2006. Available from: http://www.tzb-info.cz/3462-problematika-stagnace-u-solarnich-tepelnych-soustav-i
19. LINSTROM, P. J. and MALLARD, W. G. NIST chemistry Webbook. *Choice Reviews Online* [online]. 1 January 1998. Vol. 35, no. 05, p. 35–2709. [Accessed 30 July 2017]. DOI 10.5860/CHOICE.35-2709. Available from: http://choicereviews.org/review/10.5860/CHOICE.35-2709
20. GÓRALSKI, Pawel and TKACZYK, Mariola. Heat Capacities of Some Liquid a , ω -Alkanediols within the Temperature Range between (293 . 15 and 353 . 15) K. *Journal of Chemical & Engineering Data*. 2008. Vol. 111, no. 53, p. 1932–1934. DOI 10.1021/je800356x.
21. ZORĘBSKI, Edward, DZIDA, Marzena and PIOTROWSKA, Martyna. Study of the Acoustic and Thermodynamic Properties of 1,2- and 1,3-Propanediol by Means of High-Pressure Speed of Sound Measurements at Temperatures from (293 to 318) K and Pressures up to 101 MPa. *Journal of Chemical & Engineering Data* [online]. 12 January 2008. Vol. 53, no. 1, p. 136–144. DOI 10.1021/je7004374. Available from: http://pubs.acs.org/doi/abs/10.1021/je7004374
22. ZÁBRANSKÝ, Milan, KOLSKÁ, Zdenka, RŮŽIČKA, Vlastimil and DOMALSKI, Eugene S. Heat capacity of liquids: Critical review and recommended values. Supplement ii. *Journal of Physical and Chemical Reference Data*. 2010. Vol. 39, no. 1, p. 3–404. DOI 10.1063/1.3182831.
23. WEINGÄRTNER, Hermann, FRANCK, Ernst Ulrich, WIEGAND, Gabriele, DAHMEN, Nicolaus, SCHWEDT, Georg, FRIMMEL, Fritz H., GORDALLA, Birgit C., JOHANNSEN, Klaus, SUMMERS, R. Scott, HÖLL, Wolfgang, JEKEL, Martin, GIMBEL, Rolf, RAUTENBACH, Robert and GLAZE, William H. Water. In : *Ullmann's Encyclopedia of Industrial Chemistry* [online]. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2000. Available from: http://doi.wiley.com/10.1002/14356007.a28_001
24. SOKHAN, Vlad P., JONES, Andrew P., CIPCIGAN, Flaviu S., CRAIN, Jason and MARTYNA, Glenn J. Signature properties of water: Their molecular

electronic origins. *Proceedings of the National Academy of Sciences* [online]. 2015. Vol. 112, no. 20, p. 6341–6346. DOI 10.1073/pnas.1418982112. Available from: http://www.pnas.org/lookup/doi/10.1073/pnas.1418982112

25. CLIFTON, James R, ROSSITER, Walter J. and BROWN, Paul W. Degraded aqueous glycol solutions: pH values and the effects of common ions on suppressing pH decreases. *Solar Energy Materials* [online]. March 1985. Vol. 12, no. 1, p. 77–86. DOI 10.1016/0165-1633(85)90026-7. Available from: http://linkinghub.elsevier.com/retrieve/pii/0165163385900267
26. ROSSITER, Walter J., GODETTE, McClure, BROWN, Paul W. and GALUK, Kevin G. An investigation of the degradation of aqueous ethylene glycol and propylene glycol solutions using ion chromatography. *Solar Energy Materials* [online]. January 1985. Vol. 11, no. 5–6, p. 455–467. DOI 10.1016/0165-1633(85)90016-4. Available from: http://linkinghub.elsevier.com/retrieve/pii/0165163385900164
27. ROSSITER, Walter J., BROWN, Paul W. and GODETTE, McClure. The determination of acidic degradation products in aqueous ethylene glycol and propylene glycol solutions using ion chromatography. *Solar Energy Materials* [online]. October 1983. Vol. 9, no. 3, p. 267–279. DOI 10.1016/0165-1633(83)90049-7. Available from: http://linkinghub.elsevier.com/retrieve/pii/0165163383900497
28. ASTM D1384. *Standard Test Method for Corrosion Test for Engine Coolants in Glassware* [online]. 2004. West Conshohocken, PA : ASTM International. Available from: www.astm.org
29. MATUŠKA, Tomáš. Problematika stagnace u solárních tepelných soustav (II). *TZB-info* [online]. 2006. Available from: http://www.tzb-info.cz/3474-problematika-stagnace-u-solarnich-tepelnych-soustav-ii
30. HAUSNER, Robert and FINK, Christian. Stagnation behaviour of solar thermal systems. *IEA Task 26*. 2002. No. November.
31. DRAGSTED, Janne, FURBO, Simon, CHEN, Ziqian and PERERS, Bengt. Pressure and Temperature Development in a Solar Heating System During Stagnation. In : *Proceedings of the EuroSun 2010 Conference* [online]. Freiburg, Germany : International Solar Energy Society, 2010. p. 1–8. ISBN 978-3-901425-13-4. Available from: http://proceedings.ises.org/citation?doi=eurosun.2010.07.06
32. HILLERNS, Frank. The Behaviour of Heat Transfer Media in Solar Active Thermal Systems in View of the Stagnation Conditions. In : *9. Symposium Thermal Solar Energy in Staffelstein*. 1999. p. 1–3.
33. SULLIVAN, Carl J. Propanediols. In : *Ullmann's Encyclopedia of Industrial Chemistry* [online]. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2000. Available from: http://doi.wiley.com/10.1002/14356007.a22_163
34. MUSKA, Carl F and ALLES, Carina. A New Platform Chemical For The 21st

Century. *BREW Symposium* [online]. 2005. P. 1–38. Available from: http://brew.geo.uu.nl/BREWsymposiumWiesbaden11mei2005/WEBSITEBrewPresentations51105.PDF

35. KRAUS, George A. Synthetic methods for the preparation of 1,3-propanediol. *Clean - Soil, Air, Water*. 2008. Vol. 36, no. 8, p. 648–651. DOI 10.1002/clen.200800084.
36. KURIAN, Joseph V. A New Polymer Platform for the Future — Sorona® from Corn Derived 1,3-Propanediol. *Journal of Polymers and the Environment* [online]. April 2005. Vol. 13, no. 2, p. 159–167. DOI 10.1007/s10924-005-2947-7. Available from: http://link.springer.com/10.1007/s10924-005-2947-7
37. EATON, Edward R., BOON, W. H. and SMITH, Chris J. A Chemical Base for Engine Coolant / Antifreeze with Improved Thermal Stability Properties. In : *Journal of Catalysis* [online]. 5 March 2001. p. 170–177. Available from: http://papers.sae.org/2001-01-1182/
38. WOOD, David. GRAS exepmtion claim: 1,3-propanediol. [online]. 2009. P. 1–7. Available from: https://www.fda.gov/downloads/Food/IngredientsPackagingLabeling/GRAS/NoticeInventory/ucm269352.pdf
39. US-EPA. *1,3-Propanediol; Exemptions From the Requirement of a Tolerance* [online]. 2013. Available from: https://www.federalregister.gov/articles/2013/06/12/2013-13823/13-propanediol-exemptions-from-the-requirement-of-a-tolerance
40. GARG, Uttam, FRAZEE, C Clinton, KISCOAN, Mike, SCOTT, David, PETERSON, Bonita and CATHCART, David. A Fatality Involving 1,3-Propanediol and its Implications in Measurement of other Glycols. *Journal of Analytical Toxicology*. 2008. Vol. 32, no. May, p. 324–326.
41. LIDE, David R. *CRC Handbook of Chemistry and Physics 88th Edition* [online]. 2007. ISBN 0849304881. Available from: http://books.google.com/books?id=gb8OAwAACAAJ&printsec=frontcover
42. NATIONAL CENTER FOR BIOTECHNOLOGY INFORMATION. Propanediol. *PubChem Compound database; CID=10442* [online]. 2018. [Accessed 1 May 2018]. Available from: https://pubchem.ncbi.nlm.nih.gov/compound/10442
43. PAPANIKOLAOU, Seraphim, FAKAS, Stylianos, FICK, Michel, CHEVALOT, Isabelle, GALIOTOU-PANAYOTOU, Maria, KOMAITIS, Michael, MARC, Ivan and AGGELIS, George. Biotechnological valorisation of raw glycerol discharged after bio-diesel (fatty acid methyl esters) manufacturing process: Production of 1,3-propanediol, citric acid and single cell oil. *Biomass and Bioenergy*. 2008. Vol. 32, no. 1, p. 60–71. DOI 10.1016/j.biombioe.2007.06.007.
44. SZYMANOWSKA-POWAŁOWSKA, Daria, DROŻDŻYŃSKA, Agnieszka and REMSZEL, Natalia. Isolation of New Strains of Bacteria Able to

Synthesize 1,3-Propanediol from Glycerol *. *Advances in Microbiology* [online]. 2013. Vol. 3, no. June, p. 171–180. DOI 10.4236/aim.2013.32027. Available from: http://dx.doi.org/10.4236/aim.2013.32027%5Cnhttp://www.scirp.org/journal/aim
45. QUISPE, César A.G., CORONADO, Christian J.R. and CARVALHO JR., João A. Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renewable and Sustainable Energy Reviews* [online]. November 2013. Vol. 27, p. 475–493. DOI 10.1016/j.rser.2013.06.017. Available from: http://dx.doi.org/10.1016/j.rser.2013.06.017
46. BROWN, Paul W., ROSSITER, Walter J. and GALUK, Kevin G. A mass spectrometric investigation of the thermal oxidative reactivity of ethylene glycol. *Solar Energy Materials* [online]. April 1986. Vol. 13, no. 3, p. 197–202. DOI 10.1016/0165-1633(86)90018-3. Available from: http://linkinghub.elsevier.com/retrieve/pii/0165163386900183
47. BROWN, Paul Wencil, GALUK, Kevin G. and ROSSITER, Walter J. Characterization of potential thermal degradation products from the reactions of aqueous ethylene glycol and propylene glycol solutions with copper metal. *Solar Energy Materials*. 1987. Vol. 16, no. 4, p. 309–313. DOI 10.1016/0165-1633(87)90079-7.
48. GRÄFEN, Hubert, HORN, Elmar-Manfred, SCHLECKER, Hartmut and SCHINDLER, Helmut. Corrosion. In : *Ullmann's Encyclopedia of Industrial Chemistry* [online]. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2000. Available from: http://doi.wiley.com/10.1002/14356007.b01_08
49. MONTICELLI, C., BRUNORO, G., TRABANELLI, G. and FRIGNANI, A. Corrosion in solar heating systems. I. Copper behaviour in water/glycol solutions. . 1986. Vol. 37, p. 479–484.
50. MACBETH, Gordon and RALPH THOMPSON, A. Densities and Refractive Indexes for Propylene Glycol-Water Solutions. *Analytical Chemistry*. 1951. Vol. 23, no. 4, p. 618–619. DOI 10.1021/ac60052a019.
51. SUN, T and TEJA, a S. Density, viscosity and thermal conductivity of aqueous solutions of propylene glycol, dipropylene glycol, and tripropylene glycol between 290~{K} and 460~{K}. *J. Chem. Eng. Data*. 2004. Vol. 49, p. 1311–1317.
52. THE DOW CHEMICAL COMPANY. What are the thermal degradation products of glycol based fluids such as DOWCAL™, DOWTHERM™ SR-1, DOWTHERM™ 4000 and DOWFROST™? *Dow Answer Center* [online]. 2017. [Accessed 10 April 2018]. Available from: https://dowac.custhelp.com/app/answers/detail/a_id/11979/related/1
53. STROHALM, Martin, HASSMAN, Martin, KOŠATA, Bedřich and KODÍČEK, Milan. mMass data miner: an open source alternative for mass spectrometric data analysis. *Rapid Communications in Mass Spectrometry*

[online]. 30 March 2008. Vol. 22, no. 6, p. 905–908. DOI 10.1002/rcm.3444. Available from: http://doi.wiley.com/10.1002/rcm.3444

54. STROHALM, Martin, KAVAN, Daniel, NOVÁK, Petr, VOLNÝ, Michael and HAVLÍČEK, Vladimír. mMass 3: A Cross-Platform Software Environment for Precise Analysis of Mass Spectrometric Data. *Analytical Chemistry* [online]. June 2010. Vol. 82, no. 11, p. 4648–4651. DOI 10.1021/ac100818g. Available from: http://pubs.acs.org/doi/abs/10.1021/ac100818g

55. NIEDERMEYER, Timo H. J. and STROHALM, Martin. mMass as a Software Tool for the Annotation of Cyclic Peptide Tandem Mass Spectra. KOOMEN, John Matthew (ed.), *PLoS ONE* [online]. 13 September 2012. Vol. 7, no. 9, p. e44913. DOI 10.1371/journal.pone.0044913. Available from: http://dx.plos.org/10.1371/journal.pone.0044913

56. KELLER, Bernd O., SUI, Jie, YOUNG, Alex B. and WHITTAL, Randy M. Interferences and contaminants encountered in modern mass spectrometry. *Analytica Chimica Acta*. 2008. Vol. 627, no. 1, p. 71–81. DOI 10.1016/j.aca.2008.04.043.

57. LEE, J. W., PARK, S. B. and LEE, H. Densities, surface tensions, and refractive indices of the water + 1,3-propanediol system. *Journal of Chemical and Engineering Data*. 2000. Vol. 45, no. 2, p. 166–168. DOI 10.1021/je990196m.

58. GEORGE, John and SASTRY, Nandhibatla V. Densities, Dynamic Viscosities, Speeds of Sound, and Relative Permittivities for Water + Alkanediols (Propane-1,2- and -1,3-diol and Butane-1,2-, -1,3-, -1,4-, and -2,3-Diol) at Different Temperatures. *Journal of Chemical and Engineering Data*. 2003. Vol. 48, no. 6, p. 1529–1539. DOI 10.1021/je0340755.

59. MOOSAVI, Mehrdad and ROSTAMI, Abbas Ali. Densities, viscosities, refractive indices, and excess properties of aqueous 1,2-etanediol, 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol binary mixtures. *Journal of Chemical and Engineering Data*. 2017. Vol. 62, no. 1, p. 156–168. DOI 10.1021/acs.jced.6b00526.

60. MIKŠÍK, František, SKOLIL, Jan, KOTLÍK, Josef, ČÁSLAVSKÝ, Josef, MIYAZAKI, Takahiko, KOYMA, Shigeru and LEVEK, Petr. Antifreeze heat transfer fluid based on Propane-1,3-diol. In : *IEICES2017 Proceedings and Program*. Fukuoka : Kyushu University, 2017. p. 117–120.

61. REDLICH, Otto and KISTER, A. T. Thermodynamics of Nonelectrolyte Solutions - x-y-t relations in a Binary System. *Industrial & Engineering Chemistry* [online]. 1948. Vol. 40, no. 2, p. 341–345. DOI 10.1021/ie50458a035. Available from: http://pubs.acs.org/doi/abs/10.1021/ie50458a035

62. DE OLIVEIRA, Jaime D Gomes and REIS, João Carlos R. The two faces of the Redlich-Kister equation and the limiting partial molar volume of water in 1-aminopropan-2-ol. *Thermochimica Acta*. 2008. Vol. 468, no. 1–2, p. 119–

123. DOI 10.1016/j.tca.2007.12.002.

63. NAGAMACHI, M. Y. and FRANCESCONI, A. Z. Measurement and correlation of excess molar enthalpy HEm for (1,2-propanediol, or 1,3-propanediol, or 1,4-butanediol + water) at the temperatures (298.15, 323.15, and 343.15) K. *Journal of Chemical Thermodynamics*. 2006. Vol. 38, no. 4, p. 461–466. DOI 10.1016/j.jct.2005.06.018.
64. TAKAHASHI, Satoru and NISHI, Nobuyuki. Hydrate Cluster Formation of Diol Compounds in Aqueous Solution. *Bulletin of the Chemical Society of Japan*. 1995. Vol. 68, no. 2, p. 539–546. DOI https://doi.org/10.1246/bcsj.68.539.
65. BELDA MAXIMINO, R. Viscosity and density of binary mixtures of alcohols and polyols with three carbon atoms and water: Equation for the correlation of viscosities of binary mixtures. *Physics and Chemistry of Liquids*. 2009. Vol. 47, no. 5, p. 515–529. DOI 10.1080/00319100802372114.
66. GRUNBERG, L and NISSAN, A H. The energies of vaporisation, viscosity and cohesion and the structure of liquids. *Transactions of the Faraday Society* [online]. 1949. Vol. 45, p. 125–137. DOI 10.1039/tf9494500125. Available from: https://www.scopus.com/inward/record.uri?eid=2-s2.0-0001549023&partnerID=40&md5=519954731e84a47809dbf3e59bd28123
67. GRUNBERG, L and NISSAN, A. Mixture law for viscosity. *Nature*. 1949. Vol. 164, no. 4175, p. 799–800. DOI 10.1038/164799b0.
68. LEDERER, E.L. Viscosity of mixtures with and without diluents. In : *Proceedings of the First World Petroleum Congress London*. London, 1933. p. 526–528.
69. LEDERER, E. L. Viscosity of Binary Mixtures. *Nature* [online]. 2 January 1937. Vol. 139, no. 3505, p. 27–28. DOI 10.1038/139027c0. Available from: http://www.nature.com/articles/139027c0
70. ZHMUD, Boris, PH, D and PROF, Assoc. Viscosity Blending Equations. *Lube Magazine*. June 2014. No. 5, p. 2–5.
71. ONKEN, Ulfert, FISCHER, Kai and RAREY, Jürgen. Estimation of Physical Properties. In : *Ullmann's Encyclopedia of Industrial Chemistry* [online]. Weinheim, Germany : Wiley-VCH Verlag GmbH & Co. KGaA, 2000. Available from: http://doi.wiley.com/10.1002/14356007.b01_06
72. EYRING, Henry. and HIRSCHFELDER, Joseph. The Theory of the Liquid State. *The Journal of Physical Chemistry* [online]. February 1937. Vol. 41, no. 2, p. 249–257. DOI 10.1021/j150380a007. Available from: http://pubs.acs.org/doi/abs/10.1021/j150380a007
73. KACEM, R.B.H., ALZAMEL, N.O. and OUERFELLI, N. Sensitivity of viscosity Arrhenius parameters to polarity of liquids. *Russian Journal of Physical Chemistry A*. 2017. Vol. 91, no. 9, p. 1654–1659. DOI 10.1134/S0036024417090138.

74. ANSLYN, Eric V and DOUGHERTY, Dennis A. *Modern Physical Organic Chemistry* [online]. 2006. ISBN 9781891389313. Available from: http://iupac.org/publications/pac/69/2/0259/
75. DUPONT TATE&LYLE. *Susterra 1,3 Propanediol For Brewery Heat Transfer Fluids* [online]. 2016. DuPont Tate&Lyle. Available from: http://www.duponttateandlyle.com/sites/default/files/Susterra for Brewery Heat Transfer Fluids_5 30 14_Brewery.pdf
76. DUPONT TATE&LYLE. *Susterra ® Propanediol : Heat Transfer Fluid is Advantaged for High Temperature Applications*. 2016. Loudon : DuPont Tate&Lyle.
77. PENRAY. HEAVY-DUTY CONVENTIONAL INHIBITOR 2792. [online]. 2018. [Accessed 1 May 2018]. Available from: http://penray.com/products/fully-formulated-for-eg-2792/
78. SLOCHEM TRADE S.R.O. *Bezpečnostní list Cemkor C33*. 2014. Trnava.
79. ECHEMI.COM. Propylene Glycol Market in Q3, 2017: Increased Prices and Declined Supply. *Echemi Analysis* [online]. 2017. [Accessed 1 May 2018]. Available from: http://info.echemi.com/en-price/9031.html
80. ECHEMI.COM. Analysis of the Ethylene Glycol Market in Q3, 2017. *Echemi Analysis* [online]. 2017. [Accessed 1 May 2018]. Available from: http://info.echemi.com/en-price/9069.html
81. GRAND VIEW RESEARCH, Inc. Glycols Market Analysis By Product, By Application (Automotive, HVAC, Textiles, Airline, Medical, Pipeline Maintenance Polyester Fibers & Resin, And Food & Beverage Processing), By Region, And Segment Forecasts, 2018 - 2025. *Report ID: GVR-1-68038-402-4* [online]. 2017. [Accessed 1 May 2018]. Available from: https://www.grandviewresearch.com/industry-analysis/glycols-market
82. MARKETSANDMARKETS.COM. 1 , 3 - Propanediol (PDO) Market by Applications (PTT , Polyurethane , Cosmetic , Personal Care & Home Cleaning & Others) & Geography - Global Market Trends & Forecasts to 2021. [online]. 2015. [Accessed 3 February 2018]. Available from: http://www.marketsandmarkets.com/Market-Reports/1-3-propanediol-pdo-market-760.html
83. GRAND VIEW RESEARCH, Inc. 1,3 Propanediol (PDO) Market Analysis By Application (Polytrimethylene Terephthalate (PTT), Polyurethane, Personal Care & Detergents) And Segment Forecasts To 2022. *Report ID: 978-1-68038-385-0* [online]. 2015. Available from: https://www.grandviewresearch.com/industry-analysis/1-3-propanediol-pdo-market
84. DUPONT TATE&LYLE. Susterra® 1,3-Propanediol, High-Performance, Biobased Glycol Antifreeze and Coolant. *Engine Coolants* [online]. 2016. [Accessed 2 May 2018]. Available from: http://www.duponttateandlyle.com/susterra/engine_coolant_glycol_antifreeze

CURRICULUM VITAE

František Mikšík

The Institute of Chemistry and Technology of Environmental Protection
Faculty of Chemistry
Brno University of Technology, Brno

Education

Duration	October 2016 – present
Degree	Ph.D.
Subject	Heat storage and heat transfer, adsorption material properties
Institution	Kyushu University, Fukuoka, Japan
Duration	September 2011 – present
Degree	Ph.D.
Subject	Chemistry, environmental protection technology, renewable sources of energy, solar thermal systems.
Institution	Brno university of Technology, Brno, Czech Republic
Duration	September 2008 – August 2010
Degree	Ing. (Master degree in engineering)
Subject	Chemistry, environmental protection technology, chemical engineering, analytical chemistry, organic chemistry, renewable sources of energy,
Institution	Brno university of Technology, Brno, Czech Republic
Duration	September 2005 – 26 August 2008
Degree	Bc.
Subject	Chemistry and technology of environmental protection, general chemistry, environmental chemistry
Institution	Brno university of Technology, Brno, Czech Republic

Work Experience

Duration	April 2016 – present
Occupation and position	Research Fellow
Main activities and responsibilities	Heat storage and heat transfer research, adsorption material properties, development of heat storage device based on adsorption materials
Employer	International institute for Carbon-Neutral Energy Research, Kyushu University, Ito, Japan
Duration	July 2017 – August 2017
Occupation and position	Research Training
Main activities and responsibilities	Preparation of mesoporous adsorption materials based on mesoporous silica, properties analysis, advanced chemistry
Employer	National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

Duration	April 2016 – September 2016
Occupation and position	Research Student
Main activities and responsibilities	Heat storage and heat transfer research, adsorption material properties
Employer	Kyushu University, Fukuoka, Japan
Duration	September 2015 – December 2015
Occupation and position	Intern
Main activities and responsibilities	Research on renewable sources of energy. Hydrogen production and storage. Peatland research on contact properties measurement by HF/AC
Employer	University of Highlands and Islands, Stornoway, Scotland, UK
Duration	February 2015 – May 2016
Occupation and position	Specialist for heat sharing
Main activities and responsibilities	Developing of measurement device for routine measurements in laboratory for heat transport, data analysis
Employer	Brno university of Technology, Brno, Czech Republic
Duration	Jun 2008 – August 2012 (part time/fulltime)
Occupation and position	IT Developer, programmer, IT technic
Main activities and responsibilities	Development of web applications and database systems. Leading small team (2-3 persons), responsible for workflow and timeline.
Employer	KAPERT s.r.o., Břeclav, Czech Republic

Personal Skills

Mother language **Czech**

Other languages

	Understanding				Speaking				Writing	
	Listening		Reading		Spoken interaction		Spoken production			
English	C2	Proficient	C2	Proficient	C2	Proficient	C2	Proficient	C2	Proficient
German	A2	Basic	A2	Basic	A2	Basic	A2	Basic	A2	Basic
Japanese	B1	Independent	B1	Independent	B2	Independent	B2	Independent	A1	Basic

Computer skills	Professional: Windows XP, 7, 10 Advanced: MS Word, MS Excel, MS PowerPoint, CAD – Autodesk Inventor Intermediate: Windows server 2000, 2003, 2008, MatLab, Anysys
Programming skills	Professional (more than 10-year experience): C, MySQL, SQL 602, PHP, HTML, XML, XPath Advanced: JavaScript, Java Intermediate: C++
Electro technic skills	Microcontroller megaAVR series programming (more than 10-year experience), Development and programming of data logging devices, measuring devices. Development of digital systems for regulation and control. Systems for PC control. Design and assembly of PCB.
Other skills	Driving licence – regular for manual transmission (more than 20000 km) Hobbies: Reading, softball, travelling, movies

LIST OF PUBLICATIONS

MIKŠÍK, F.; SKOLIL, J.; KOTLÍK, J.; ČÁSLAVSKÝ, J.; MIYAZAKI, T.; KOYAMA, S.; PŮČKOVÁ, H.; LEVEK, P. Antifreeze heat transfer fluid based on Propane-1,3- diol. Proceedings and Program. Fukuoka, Japan: Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 2017. s. 117-120.

MIKŠÍK, F.; MIYAZAKI, T.; KOYAMA, S.; KOTLÍK, J. Adsorption and desorption of water on mesoporous silica for energy storage. Tokyo, Japan: ISHPC, 2017.

PŮČKOVÁ, H.; KOTLÍK, J.; MIKŠÍK, F.; LEVEK, P.; VÁVROVÁ, M.; MIYAZAKI, T.; KOYMA, S. Accumulation of water and energy in environment by short rotation coppice plantations. Fukuoka, Japan: Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 2017. s. 75-78.

PŮČKOVÁ, H.; KOTLÍK, J.; MIKŠÍK, F.; LEVEK, P. Kombinované systémy OZE v RD - energeticky rovnovážné soustavy. In Zborník: Situácia v ekologicky zaťažených regiónoch Slovenska a strednej Európy.XXV. Vedecké sympózium s mezinárodnou účasťou. Košice 2016: Slovenská banícka spoločnosť ZSVTS, Základná organizácia pri Ústave geotechniky SAV, 2016. s. 84-88. ISBN: 978-80-89883-00- 4.

PŮČKOVÁ, H.; KOTLÍK, J.; KOTLÍKOVÁ, S.; MIKŠÍK, F. Rychlerostoucí dřeviny a životní prostředí. In XXIV. Vedecké sympózium s mezinárodnou účasťou. Košice 2015: Slovenská banícka spoločnosť ZSVTS, Základná organizácia pri Ústave geotechniky SAV, 2015. s. 44-48. ISBN: 978-80-970034-8- 7.

MIKŠÍK, F. Zapojení studentů doktorského studijního programu do přípravy nových laboratorních úloh. Purkyňova 118, 612 00 Brno: VUT v Brně, Fakulta chemická, 2014. s. 1-2.

MIKŠÍK, F.; KOTLÍK, J. Degradation and corrosion inhibitors for heat transfer fluids based on polyols. Book of Abstracts CEITEC Annual Conference "Frontiers in Material and Life Sciences". Brno (Czech Republic): Masaryk University, 2014. s. 182-182. ISBN: 987-80-210-7159- 9.

MIKŠÍK, F.; KOTLÍK, J. Degradation of glycol based heat transfer fluids. EMEC15 Book of abstracts. Brno: Brno University of Technology, 2014. ISBN: 978-80-214-5073- 8.

MIKŠÍK, F.; KOTLÍK, J. Teplonosné kapaliny na bázi glykolů v životním prostředí. In XXIII. VEDECKÉ SYMPÓZIUM - ZBORNÍK - HRÁDOK 2014. Košice: Slovenská banícka spoločnosť ZSVTS, Základná organizácia pri Ústave geotechniky SAV, 2014. s. 73-77. ISBN: 978-80-970034-7- 0.

MIKŠÍK, F.; KOTLÍK, J. Perspektivy využití kombinovaných solárních systémů v rodinných domech. Energetika, 2013, roč. 63, č. 01, s. 30-32. ISSN: 0375- 8842.

MIKŠÍK, F.; KOTLÍK, J. Kombinované solární systémy v RD - energeticky rovnovážná soustava. In 34. NEKONVENČNÍ ZDROJE ELEKTRICKÉ ENERGIE. Blansko: Česká elektrotechnická společnost, 2013. s. 104-109. ISBN: 978-80-02-02458- 3.

MIKŠÍK, F.; KOTLÍK, J. Kombinované solární systémy v RD - energeticky rovnovážná soustava. Energetika, 2013, roč. 63, č. 12, s. 716-719. ISSN: 0375- 8842.

KOTLÍK, J.; MIKŠÍK, F. Teplonosné kapaliny na bázi propan-1,3- diolu pro termické solární systémy. In XXI. vedecké sympózium s medzinárodnou účasťou SITUÁCIA V EKOLOGICKY ZAŤAŽENÝCH REGIÓNOCH SLOVENSKA A STREDNEJ EURÓPY. Košice: Slovenská banícka spoločnosť ZSVTS, Základná organizácia pri Ústave geotechniky SAV, 2012. s. 70-73. ISBN: 978-80-970034-4- 9.

MIKŠÍK, F.; KOTLÍK, J. Kombinované solární systémy a jejich řízení v rodinných domech. Elektrotechnický magazín, 2012, roč. 2012, č. 5, s. 18-20. ISSN: 1210- 5422.

MIKŠÍK, F.; KOTLÍK, J. Kombinované solární systémy a jejich řízení v rodinných domech. In 33. NEKONVENČNÍ ZDROJE ELEKTRICKÉ ENERGIE. Hrotovice: Česká elektrotechnická společnost, 2012. s. 21-26. ISBN: 978-80-02-02372- 2.

LIST OF ACTIVITIES

KOTLÍK, J.; MIKŠÍK, F.; VUT v Brně,Antonínská 548/1, 601 90 Brno: Ruční kapková mikropipeta. 24086, užitný vzor. (2012)

MIKŠÍK, F.; KOTLÍK, J.: Automatický rheometr; Automatický rheometr. laboratoř. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.: Data SD; Dataloger SD. VUT FCH, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.: Dataloger SDM; Dataloger SDM. VUT FCH, Purkyňova 118, Brno. (prototyp)

KOTLÍK, J.; MIKŠÍK, F.: Techno SDM; Technologie výroby datalogeru SDM. VUT FCH, Purkyňova 118, Brno. (ověřená technologie)

KOTLÍK, J.; MIKŠÍK, F.: Rheometr LT; Rheometr LT. VUT FCH, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.: Hydrogen; Zařízení pro odběr vzorků spalin. VUT v Brně, ÚCHTOŽP, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.; KOTLÍKOVÁ, S.: Classic alfa; Ekoterm solar CS. VUT FCH, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.; KOTLÍKOVÁ, S.: Classic beta; Ekoterm vaku CS. VUT FCH, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.; KOTLÍKOVÁ, S.: Classic gama; Ekoterm solar plus CS. VUT FCH, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.; BLAHA, R.: Forline LED12AP; Forline LED AP 12prizma. VUT FCH, Purkyňova 118, Brno; HELIOS GROUP s.r.o. ,Haškova 17, Brno. (prototyp)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.; KOTLÍKOVÁ, S.: Classic delta; Ekoterm spirit CS. VUT FCH, Purkyňova 118, Brno. (funkční vzorek)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.: Classic alfa P; Ekoterm solar CSP. VUT FCH, Purkyňova 118, Brno,;CLASSIC Oil s.r.o.,Oty Peška 343,Kladno. (prototyp)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.: Classic beta P; Ekoterm vaku CSP. VUT FCH, Purkyňova 118, Brno,;CLASSIC Oil s.r.o.,Oty Peška 343,Kladno. (prototyp)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.: Classic gama P; Ekoterm solar plus CSP. VUT FCH, Purkyňova 118, Brno,;CLASSIC Oil s.r.o.,Oty Peška 343,Kladno. (prototyp)

KOTLÍK, J.; MIKŠÍK, F.; SKOLIL, J.: Classic delta P; Ekoterm spirit CSP. VUT FCH, Purkyňova 118, Brno,;CLASSIC Oil s.r.o.,Oty Peška 343,Kladno. (prototyp)

KOTLÍK, J.; MIKŠÍK, F.; BLAHA, R.: Forline LED48AP; Forline LED AP 48prizma. VUT FCH, Purkyňova 118, Brno; HELIOS GROUP s.r.o. ,Haškova 17, Brno. (prototyp)

KOTLÍK, J.; SKOLIL, J.; MIKŠÍK, F.; LEVEK, P.; PŮČKOVÁ, H.: Zařízení pro zrychlené stárnutí; Geron. laboratoř. (funkční vzorek)