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Requirements for Coolants on the Basis of Alternative Freezing Point Depressants

Advanced concepts targeted to increase the performance of combustion engines (for example downsizing or turbocharging) typically result in higher thermal loads which need to be balanced by the coolant. Therefore, potentially suitable freezing point depressants have been investigated regarding their physico-chemical properties and their thermal stability. The investigations took place at the Technische Universität Darmstadt in collaboration with the University of Regensburg.



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1 MOTIVATION

The local surface temperatures in the engine can be up to 260 °C. This is clearly higher than the boiling temperature of common coolants [1]. In addition to water and corrosion inhibitors current conventional coolants normally consist in around 30 to 50 % by volume of the bivalent alcohol monoethylene glycol (MEG), which is added as freezing point depressant [2]. A thermal decomposition of MEG into various carboxylic acids (such as formic acid and glycolic acid) starts to appear already at temperatures of approximately 165 °C, thus well below the peak wall temperatures [3]. The carboxylic acids cause an overall decrease in the pH-value of the coolant, which promotes corrosion in the cooling circuit. In order to counteract this effect, corrosion inhibitors and pH-value stabilisers have to be added to the coolant. These partly dissipate over time, however [4], [5]. An inspection or exchange of the coolant is essential due to the mentioned reasons of thermal instability, combined decomposition, and reduction of ingredients to guarantee the corrosion protection and thus the reliable operation of the cooling system. One possible approach to a solution of the above mentioned technological problems is provided by the use of coolants, which use thermally more stable MEG alternatives as freezing point depressants. Unfortunately, there is no general database about substances, which can be suitably used in combustion engines other than ethylene glycol. Furthermore, there is no information about the physical and chemical substance properties of usable freezing point depressants when mixed with water.

2 SUBSTANCES

In order to make a general assessment of the theoretical application suitability of alternative freezing point depressants, the next step was to conduct research into alternative freezing point depressants. In addition to a literature review, a research in patents of the chemical industry was also performed. In all, more than 140 substances of a wide variety of compound classes were identified, which seem to be suitable candidates for reducing the freezing point of water [6]. In discussion with the project accompanying

committee (PA), substances were selected by meeting the criteria for reduced toxicity in comparison with MEG, solubility in water, and amount of boiling point of the pure substance. The 13 selected substances from the classes of alcohols, carboxylic acid salts, sulfonates and ionic liquids are as follows: 1,2-propanediol, 1,3-butanediol, 1-ethyl-3-methyl-imidazolium ethyl sulfate, diethylene glycol, diglycerol, dimethylsulfoxide (DMSO), glycerin, potassium acetate, potassium formate, potassium propionate, sodium propionate, tetraethylene glycol and triethylene glycol.

3 INVESTIGATION METHODS

3.1 FREEZING POINTS, MIXTURE RATIOS AND THERMAL AGEING

For a comparison of the physico-chemical properties of the selected alternative freezing point depressants among each other and with MEG, all the substances as well as a MEG sample were referenced in a mixture with water at a freezing point of -40 °C. Thus, only binary systems (substance and water) have been studied. The determination of the necessary mixing ratios was based on test method ASTM D1177-12. The thermal ageing of the referenced alternative freezing point depressants was performed in pressure tight reactors made of high-alloy austenitic steel (1.4571). Those have been filled with 400 ml of the relevant liquid while having a total volume of 600 ml. The reactors were locked pressure-sealed under neutral atmosphere and placed for the aging tests for a duration of 336 h at 200 °C in a heating furnace. Throughout the test duration the reactor pressure, as well as the fluid temperature were continuously recorded.

3.2 DETERMINATION OF PH-VALUE, CONDUCTIVITY, REFRACTIVE INDEX AND DECOMPOSITION PRODUCTS

Prior and after the thermal ageing of the mixtures, the pH-values, conductivity as well as refractive indices were determined to identify possible changes of the substances. The pH-values were determined using inoLab pH 720 pH meter. Conductivity was measured using inoLab Cond 720 measuring device. An Abbe-Refractometer by ATG was used to determine the refractive index. All the measurements were performed at constant room temperature of 20 °C. To determine the chemical decomposition of the alternative freezing point depressants mixed with water, the contents of each mixture was determined, prior and after the thermal ageing, using Ion Chromatography (IC) or High Performance Liquid Chromatography (HPLC). The content prior to ageing was adopted here as a reference (100 %). The measurement result after ageing, i.e. the degree of chemical change, was referred to this value in percentage.

3.3 SPECIFIC HEAT CAPACITY, DENSITY AND VISCOSITY

The specific heat capacity of the mixtures was determined by means of a DSC 8000 Apparatus by PerkinElmer. In the temperature range from -35 to 5 °C, the density was measured by means of an Anton-Paar DMA 60/DMA 602 density measuring device. For the temperature range from 5 to 85 °C, an Anton-Paar DMA 5000 M density measuring device was used. The viscosity of the mixtures in the temperature range from -35 to -5 °C was measured by using an Ubbelohde viscometer. For the range of 5 to 95 °C an automated Micro Viscometer (AMVn) manufactured by the company Anton-Paar was used.

3.4 VAPOUR PRESSURE CURVE, BOILING POINT AND EVAPORATION ENTHALPY

For the determination of the vapour pressure curves and the boiling points, an apparatus consisting of a two-neck flask with a reflux condenser and thermometer was used. Pressure regulation was controlled by using a vacuum pump and a pressure gauge. The boiling point of the solution is determined in dependence on the pressure. From the data collected, the boiling point and the evaporation enthalpy were calculated.

4 RESULTS

4.1 THERMAL AGEING OF THE MIXTURES

Using a continuous freezing point determination, the respective substance-related mixing ratios, which adjust a freezing point of $-40\text{ }^{\circ}\text{C}$ in mixture with water, were detected. The finally determined mixing ratios are shown in **TABLE 1**. Subsequently, the thermal ageing was conducted using the mentioned mixing ratios. Several pressures recorded during the thermal ageing inside of the reactors are displayed graphically in **FIGURE 1**. As the result of evaluation shows, the pressure gradients in the mixtures with DMSO, 1-ethyl-3-methyl-imidazolium ethyl sulfate and with potassium formiate are striking. These indicate an obvious increase in pressure during the test, which indicates decomposition or transformation reactions of the aged mixtures as a result of low thermal resistance. An evaluation of the reactors after the test revealed a corrosive attack on the reactor material in the test with 1-ethyl-3-methyl-imidazolium ethyl sulfate. In a test using DMSO a phase separation of the mixture was observed and a biting, broccoli-like smell was also recorded. Together with potassium formiate, which also showed an excessive pressure increase during thermal ageing, these three substances were subsequently excluded from further studies since they were not found to be suitable alternatives to MEG because of their lack of thermal stability. The pressure gradients of the tetra- and triethylene glycol mixtures are also remarkable. These also show pressure increases after 144 or 240 h test duration, which fall or

Mixture with ...	Compound class	Mixing ratio [% m/m]	Freezing point [$^{\circ}\text{C}$]
Monoethylene glycol	Alcohol	52.23	-40.2
1.2-Propanediol	Alcohol	53.20	-40.2
1.3-Butanediol	Alcohol	61.32	-40.2
Diethylene glycol	Alcohol	58.13	-40.1
Triethylene glycol	Alcohol	60.01	-40.7
Tetraethylene glycol	Alcohol	60.96	-40.3
Glycerin	Alcohol	61.26	-40.4
Diglycerol	Alcohol	66.49	-40.4
Potassium acetate	Carboxylic Acid Salt	38.41	-40.1
Potassium formiate	Carboxylic Acid Salt	42.73	-39.8
Potassium propionate	Carboxylic Acid Salt	38.93	-40.0
Sodium propionate	Carboxylic Acid Salt	36.08	-40.6
1-Ethyl-3-Methyl-Immidazolium ethyl sulfate	Ionic Liquid	65.86	-40.7
Dimethyl sulfoxide (DMSO)	Sulfoxide	46.99	-40.3

Standard deviation of 1.2 Propanediol, Triethylene glycol, Tetraethylene glycol = $1.2\text{ }^{\circ}\text{C}$, others = $0.6\text{ }^{\circ}\text{C}$

TABLE 1 Determined mixing ratios and freezing points

remain on the same level afterwards. This indicates thermally induced reactions, too. However, it seems that formed out gases gradually dissipate over time (pressure fall) or no further reactions appear (remaining on the same level).

An overview of all the values for pH, conductivity and refractive index can be seen in **TABLE 2**, both before and after the thermal exposure of the mixtures. The same applies for the determined level

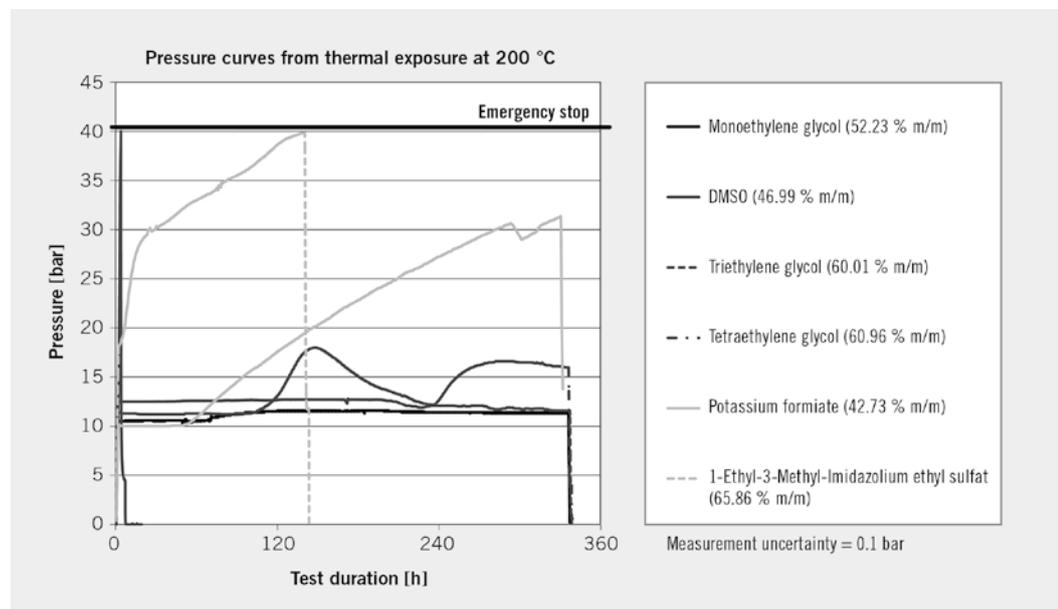


FIGURE 1 Recorded pressure gradients of selected substances in comparison with MEG (© TU Darmstadt)

Mixture with ...	pH-Value [-]		Conductivity [$\mu\text{S}/\text{cm}$]		Refractive index [-]		Decomposition [%]
	Before testing	After testing	Before testing	After testing	Before testing	After testing	–
Monoethylene glycol (52.23 % m/m)	5.24	3.4	1.3	33.3	1.387	1.3875	0.9
1,2-Propanediol (53.20 % m/m)	6.58	3.25	0.5	46.5	1.392	1.3885	15.2
1,3-Butanediol (61.32 % m/m)	5.56	4.79	1.6	3.1	1.4053	1.405	6.5
Diethylene glycol (58.13 % m/m)	6.4	4.03	0.4	11.1	1.442	1.4446	0
Triethylene glycol (60.01 % m/m)	4.42	4.18	2.4	3.4	1.4242	1.4242	0
Tetraethylene glycol (60.96 % m/m)	4.55	4.58	3.1	7.4	1.4142	1.4141	0
Glycerin (61.26 % m/m)	5.52	2.76	1	46.7	1.4162	1.4149	5.32
Diglycerol (66.49 % m/m)	4.25	3.15	1.3	13.3	1.4329	1.4331	7.86
Potassium acetate (38.41 % m/m)	9.2	8.88	150×10^3	150×10^3	1.3798	1.3803	0.48
Potassium formiate (42.73 % m/m)	12	9.91	289×10^3	272×10^3	1.3788	1.3809	–
Potassium propionate (38.93 % m/m)	10.02	9.23	117×10^3	118×10^3	1.3851	1.3869	3.6
Sodium propionate (36.08 % m/m)	9.2	8.64	53.5×10^3	50.8×10^3	1.3862	1.3879	0
1-Ethyl-3-Methyl-Immidazolium ethyl sulfate (65.86 % m/m)	7.31	1.8	33.9×10^3	32.2×10^3	1.424	1.4308	–
Dimethyl sulfoxide (46.99 % m/m)	6.64	–	0.9	–	1.404	–	–

TABLE 2 Determined pH-values, conductivities, refractive indices and levels of decomposition

of decomposition. The results show (with the exception of tetraethylene glycol) a general decrease of the pH-values after the end of the ageing process. This corresponds with the acidification of the individual mixtures, caused for example by decomposition products. The highest levels of reduction by amount in the pH-values were found in the mixtures containing 1-ethyl-3-methyl-immidazolium ethyl sulfate, potassium formiate, 1,2-propanediol and glycerol. The increased conductivity of the mixtures, which was also generally found after the tests, can be caused by a corresponding increase in the acidification of conductive ions or could be explained by corrosion of the reactor material in the test with 1-ethyl-3-methyl-immidazolium ethyl sulfate. The results show that the thermal resistances of 1,2-propanediol, 1,3-butanediol, glycerine and diglycerol were the lowest overall. Diethylene glycol, triethylene glycol and sodium propionate, however, have a thermal resistance, which is comparable to that of MEG or even surpasses it.

4.2 DETERMINATION OF THE PHYSICO-CHEMICAL SUBSTANCE DATA

Selected results of the physico-chemical substance data determination are shown as a function of temperature in **FIGURE 2**. The selected substances show striking different properties in comparison with MEG regarding the respective investigation. This may cause advantages and disadvantages when used in engine coolants. In comparison to monoethylene glycol, the mixtures with 1,2-propanediol, 1,3-butanediol and sodium propionate are char-

acterised by their increased specific heat capacity. Based on a real cooling system of an internal combustion engine, this would have a positive impact on the heat dissipation, e.g. from the thermally highly stressed areas of cylinder head. Mixtures with 1,3-butanediol and 1,2-propanediol show lower densities compared to mixtures of monoethylene glycol. With regard to their possible use in cooling circuits of internal combustion engines, weight could be saved in this way, which in turn would have a positive effect on fuel consumption and emission. Overall, the mixtures with potassium acetate and diglycerol have the highest densities in the tests. Even in relation to monoethylene glycol, especially in the low temperature range, mixtures with potassium propionate are characterised by having a similar viscosity and mixtures with potassium acetate by having a lower viscosity. With rising temperature, these values, however, continue to approach those for MEG or may even show higher viscosity. Overall, a low viscosity of heat transfer medium is requested for use in the cooling circuit because at the same flow rates lower pumping energy is necessary.

TABLE 3 shows the measured boiling points (at 760 Torr = 1.013 bar) as well as the evaporation enthalpy corresponding to the mixture. In direct comparison to mixtures with monoethylene glycol, mixtures with glycerin and potassium acetate show slightly higher boiling points. Mixtures with 1,2-propanediol and tetraethylene glycol, however had recognisably lower boiling points. In practice, a boiling point which is different to MEG can directly

effect the cooling strategy and the positive impact of the evaporation cooling on so called hot spots and has to be considered.

5 RANKING

With regard to the project goal, to find a freezing point depressant, which is potentially suitable for use in internal combustion engines

and which is superior to monoethylene glycol in terms of increased thermal stability, a ranking was performed. In consultation with the PA, the degree of decomposition was selected as the main evaluation criterion during thermal ageing. A subsidiary criterion was the change in pH-value which also occurs during the thermal ageing. The resulting ranking of substances is shown in **TABLE 4**. It is apparent from this, that mixtures with triethylene glycol, sodium propionate, diethylene glycol and potassium acetate demonstrate clear advantages compared to monoethylene glycol in terms of the thermal stability and the associated change in the pH-value. The named substances seem to be the most suitable alternative freezing point depressants for use in coolants for internal combustion engines.

6 SUMMARY

It was the project goal to identify potentially suitable freezing point depressants for use in cooling circuits of internal combustion engines, which offer improved thermal stability and otherwise comparable or better properties compared to MEG. For this, 140 substances were researched and 13 potential substances were selected for further investigations. Following this, both the thermal stability as well as the physico-chemical properties of these substances have been determined in mixture with water. To ensure the comparability of the substance properties, all the mixtures were referenced to a freezing point of -40 °C. The determination

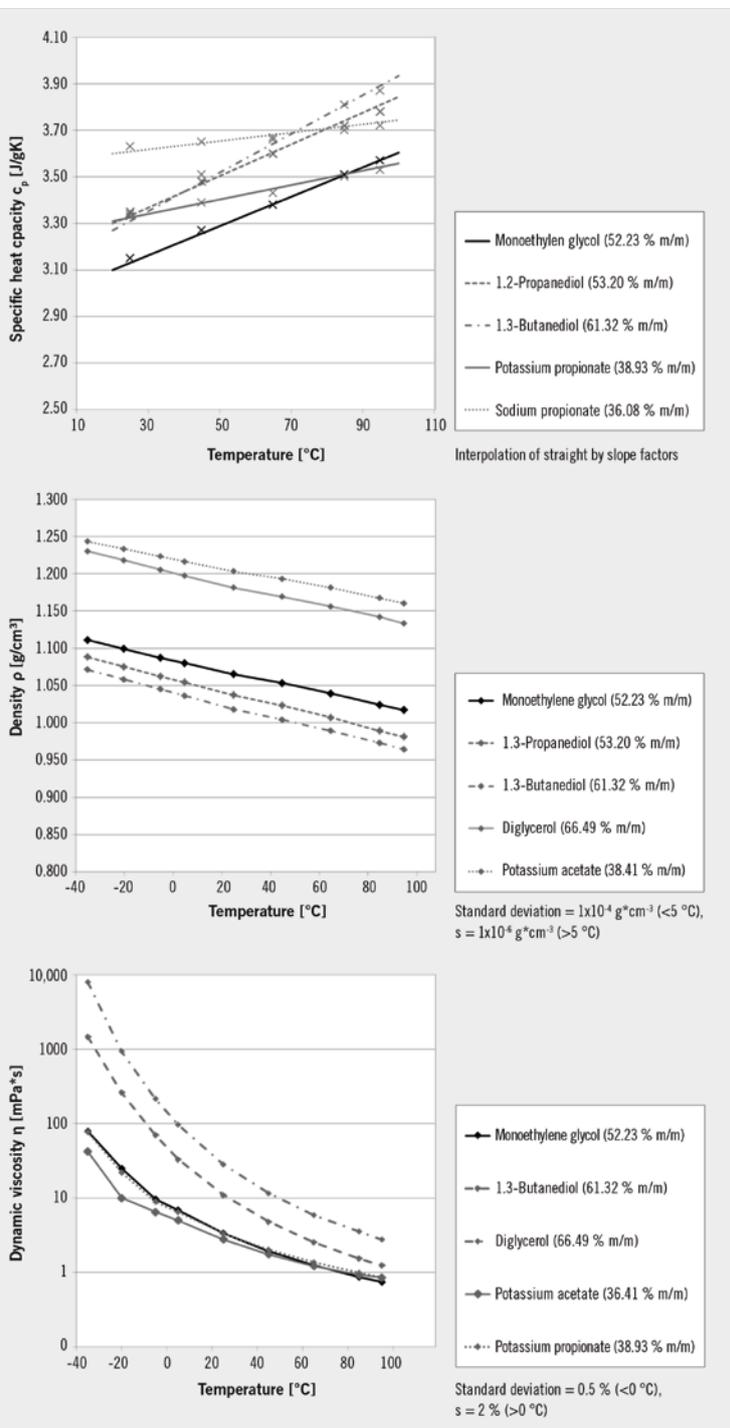


FIGURE 2 Determined specific heat capacities, densities and dynamic viscosities of selected substances in comparison with MEG dependent on temperature (© TU Darmstadt)

Mixture with ...	Boiling Point at 760 Torr [°C]	Evaporation Enthalpy [kJ/mol]
Monoethylene glycol (52.23 % m/m)	109.3	43.6
1.2-Propanediol (53.20 % m/m)	105.9	43.1
1.3-Butanediol (61.32 % m/m)	106.3	44.4
Diethylene glycol (58.13 % m/m)	108.8	42.7
Triethylene glycol (60.01 % m/m)	106.2	43.4
Tetraethylene glycol (60.96 % m/m)	105.4	43.9
Glycerin (61.26 % m/m)	110.7	43.0
Diglycerol (66.49 % m/m)	108.3	43.9
Potassium acetate (38.41 % m/m)	109.8	43.9
Potassium propionate (38.93 % m/m)	107.1	44.0
Sodium propionate (36.08 % m/m)	107.6	44.2
Standard deviation = 0.9 °C		

TABLE 3 Determined boiling points and evaporation enthalpies

Rank	Mixture with ...	Mixing ratio [% m/m]	Decomposition level [%]	pH value change [%]	Specific heat capacity at 20 °C [J/(g K)]	Density at 25 °C [g/cm ³]	Dyn. viscosity at 25 °C [mPa*s]	Boiling point at 760 Torr [°C]	Evaporation enthalpy [kJ/mol]
–	Monoethylene glycol	52.23	0.90	35.11	3.10	1.06	3.35	109.30	43.60
1	Triethylene glycol	60.01	0.00	5.43	3.03	1.09	8.29	106.20	43.40
2	Sodium propionate	36.09	0.00	6.09	3.60	1.17	6.79	107.60	44.20
3	Diethylene glycol	58.13	0.00	37.03	3.05	1.08	7.27	108.80	42.70
4	Potassium acetate	38.41	0.48	3.48	2.90	1.20	2.77	109.80	43.90
5	Tetraethylene glycol	60.96	3.30	-0.66	3.07	1.09	11.60	105.40	43.90
6	Potassium propionate	38.93	3.60	7.88	3.31	1.16	3.33	107.10	44.00
7	Glycerin	61.26	5.32	50.00	2.94	1.15	9.13	110.70	43.00
8	1.3-Butanediol	61.32	6.50	13.85	3.27	1.02	10.93	106.30	44.40
9	Diglycerol	66.49	7.86	25.88	2.83	1.18	28.08	108.30	43.90
10	1.2-Propanediol	53.20	15.20	50.61	3.30	1.04	5.96	105.90	43.10

TABLE 4 Ranking

of the thermal mixture stability was performed by using Ion Chromatography or High Performance Liquid Chromatography. The investigation of the physico-chemical properties (specific heat capacity, density, dynamic viscosity, boiling point, evaporation enthalpy) has been carried out by appropriate measurement units.

Finally, all test results were compared to each other and MEG in a ranking. The main criteria for the ranking were the thermal stability as well as the pH-value changes during the thermal ageing. The aim was to identify the potentially most suitable alternative freezing point depressants for use in cooling circuits of internal combustion engines. The results of the ranking show that triethylene glycol, sodium propionate, diethylene glycol and potassium acetate appear to be best suited for this purpose. Especially in relation to a reference mixture of MEG and water, enhanced thermal stability can be derived. Therefore, the project results can provide a basis for the further development and testing of new, thermally more stable coolants.

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