Influences of the chemical structure of entrainers on the activity coefficients in presence of biodiesel

A Mäder1,a, A Fleischmann3,a, Ye Fang3,a, W Ruck4,b and J Krahl5,a

1University of Applied Sciences and Arts, Friedrich Streib Str. 2, 96450 Coburg - Ger
2University of Lüneburg – Leuphana, Scharnhornstrasse 1, 2133 Lüneburg - Ger

E-mail:1alexmaeder@me.com,2fleischa@hs-coburg.de,3faye0900@hs-coburg.de,
4ruck@leuphana.de,5krahl@hs-coburg.de

Abstract. In this work we analyzed the strength of the intermolecular forces between biodiesel and the entrainer and their influence on the entrainer’s ability to interact with biodiesel. Furthermore we investigated the influence of the chemical structure of an entrainer to the interaction with biodiesel. For this purpose the activity coefficients \( \gamma^{\infty} \) at infinite dilution of acids, aldehydes, ketones and alcohols in biodiesel were measured with the method of headspace gas chromatography (HSGC). Short-chained acids showed the highest interaction of the analyzed entrainers caused by their ability to build hydrogen bonds with biodiesel. Increased chain length of the acids cause reduced interaction with biodiesel, which is mainly due to the higher obstruction of the acid molecule and therefore the reduced ability to build hydrogen bonds with biodiesel. Aldehydes, ketones and alcohols showed lower interaction with biodiesel compared to the acids. Longer-chained alcohols showed increased interaction with biodiesel due to the raised London Forces and an inductive +I effect of the molecule chain.

Keywords: activity coefficients, headspace gas chromatography, molecular interactions

1. Introduction

Combustion engines equipped with diesel particular filters (DPF) are handicapped by a carry-over of fuel into the engine oil, which leads to oil dilution. The dilution can lead to a decreased oil performance and reduced durability of the engine oil [1]. Diesel fuel can slowly evaporate out of the engine oil and does not remain completely in the oil pan. Compared to diesel fuel, biodiesel remains nearly completely in the engine oil and lead to severe engine oil dilution. Furthermore biodiesel is able to react in different ways in and with the engine oil [2]. This leads to oil sludge formation and can cause damage to diesel engines. The common strategy to solve these problems is to decrease the oil change interval, which also means to increase the overall engine oil consumption.

Several attempts have been published to limit the input of biodiesel in the engine oil by using physical methods, for example to run late injections only in one cylinder [3] or to use control procedures as described in [4], to link the concentration of fuel components in the engine oil with the regeneration periods of the DPF. But there have not been any literature publications in removing biodiesel from the engine oil by using a chemical method.
An elaborated chemical method to remove the biodiesel from the engine oil is the use of entrainers to drag-out the biodiesel out of the engine oil. In this process an entrainer interacts with the biodiesel and forms an azeotrope [5]. Once the azeotrope is formed the entrainer and the biodiesel can be removed from the engine oil at the same time. Generally this happens at lower temperatures, compared to biodiesel distillation without entrainer, if a low-boiling point entrainer is used. The drag-out of biodiesel from the engine oil depends on the chemical interaction between the entrainer and the biodiesel in the mixture. One possible interaction between entrainer and biodiesel can occur over hydrogen bonds. Substances that have polar groups (polar hydroxyl groups or polar oxygen groups) can form strong interactions with the ester group of biodiesel [6] and could be suitable entrainers for biodiesel.

In [7] several entrainers were used and tested successfully to drag-out biodiesel from the engine oil. The method was tested with a one-cylinder test engine and the results showed that the biodiesel was removed successfully from the engine oil while using alcohol as an entrainer. Also other experiments with acids that are able to form strong interactions with biodiesel were tested with positive results. The results showed the ability of alcohols and acids to act as entrainer for biodiesel [8].

However, in all 4.6% of the total amount of biodiesel in engine oil could be removed from the engine oil with this method. Higher efficient entrainers have still to be found, to increase the drag-out of biodiesel. One parameter to express the ability of a substance to act as an entrainer for biodiesel is the activity coefficient of an entrainer with biodiesel. In this work we measured the activity coefficients of potential entrainers in biodiesel and researched the influence of the alternation of the molecule structure of these entrainers to the activity coefficients. The activity coefficients of the investigated substances with biodiesel were also not available in the literature. In addition to the measurement results and the discussion about how the structure of the entrainer influences the activity coefficients, the method of the experimented measurement will be introduced here.

2. Theoretical background
In ideal mixtures the interactions between the molecules are equal. These mixtures can be described with equation (1), with the partial pressure \( p_i \), the vapour pressure \( p_{0i} \), the substance \( i \) and the mole fraction \( x_i \) in the liquid.

\[
p_i = p_{0i} \times x_i
\] (1)

If the interaction between the substances in the mixture gets stronger, this mixture becomes non-ideal and equation (1) must be corrected with equation (2).

\[
p_i = p_{0i} \times x_i \times \gamma^i
\] (2)

The activity coefficient \( \gamma^i \) is a correction factor for the summary of all intermolecular forces like dipol-dipol forces, London forces also known as van der Waals forces, and hydrogen bondings between two substances [9]. Ideal mixtures without any interaction between the substances \( \gamma^i \) can alternatively expressed with \( \gamma^i = 1 \), but most mixtures are non-ideal and for that reason the activity coefficient must be \( \gamma^i \neq 1 \). Generally a lower \( \gamma^i \) express higher interaction. The interaction between molecules is also influenced by the polarity and the structure of the molecules itself. Nonpolar molecules, for example alkanes, generally show a lower interaction compared to polar molecules. The interaction can be stronger if polar groups like carboxyl-groups or hydroxyl-groups are present. These groups have the ability to interact for example with hydrogen bonds [9]. If the structure of a molecule is obstructed, and the polar groups are handicapped to build interaction to other molecules, the interaction also can be decreased.

Further, the activity coefficient is always a function of temperature and composition of the liquid fraction. Therefore, the activity coefficient at infinite dilution \( \gamma^{\infty} \) is often discussed in literature. At infinite dilution the activity coefficient in equation (2) is defined by equation (3).

\[
\gamma^{\infty} = \frac{p_i}{p_{0i}}
\] (3)
The mole fraction $x_l$, which is needed for an infinite dilution was suggested by Horvaka et al. [10] and is usually in the range of 0.0005 to 0.005 mole fractions of the lower-boiling component in the mixture. In order to improve the extrapolation accuracy we measured in the mole fraction range of 0.0001 to 0.05 of the entrainer.

To calculate the activity coefficient with equations (2) and (3) the partial pressure $p_l$ and the vapor pressure $p_{0l}$ of the used substances must be known. The vapour pressure $p_{0l}$ of the pure substance can be calculated with the Antoine-Equation (4), which contains the temperature and the component-specific constants $A$, $B$ and $C$.

$$\log_{10} p_{0l} = A - \frac{B}{C + T}$$

(4)

The constants $A$, $B$ and $C$ are accessible in databases for thermodynamic properties like the Dortmund Data Bank or the NIST Database. The data that is measured in the headspace gas chromatography (HSGC) is the composition of a gas phase. Partial pressure of the substances cannot be measured directly by that method. Therefore, the HSGC must be calibrated to the used substances to measure $p_l$.

2.1. Calibration of the HSGC

The composition measurement of a gas phase by HSGC can be expressed by equation (5), where $A_l$ is the peak area of the detector signal and $RF$ is the response factor of the HSGC system.

$$A_l = RF * p_l$$

(5)

$RF$ is constant for a given HSGC system but $p_l$ depends on the used substances, the mixture and temperature of the mixture. To calibrate the HSGC to the used substances the vapor pressure $p_{0l}$ of the pure substance at specific temperature is calculated with equation (4) and the pure substance is measured at temperatures above room temperature, and below the boiling point of the substances by HSGC. A typical calibration chart for these measurements is illustrated in figure 1.

![Figure 1](image)

**Figure 1.** Typical calibration chart for a pure substance measured by HSGC. The x-axis shows the calculated vapour pressure $p_{0l}$ of the substance, the y-axis shows the integrated peak area $A_l$ of the detector signal.

Once the calibration for a substance is done, $p_l$ can be calculated with equation (5) and the calibration chart. If the calibration chart shows linearity for a substance, equation (2) can be written as
equation (6) with the area $A_{0i}$ of the integrated detector signal, the compressibility factors $z^{oi}$ for the infinite substance solution and $z^{0i}$ for the pure substance, the solute fugacity coefficients in the equilibrium gas-phase $\phi^{0i}$ and $\phi^{oi}$ for infinitely dilution. In this case equation (3) and (6) can be used to calculate $\gamma^{0i}$ for a substance at infinite dilution.

$$A_i = A_{0i} \cdot x_i \cdot \gamma^{0i} \cdot \frac{z^{0i} \cdot \phi^{0i}}{z^{oi} \cdot \phi^{oi}}$$\hspace{1cm} (6)$$

The compressibility factors and the fugacity coefficients correct the ideal gas-law to account for the real gas behaviour in the presence of air [10]. For low pressures and temperatures $z^{oi}, z^{0i}, \phi^{oi}$ and $\phi^{oi}$ are close to the ideal behaviour of a gas and incline to one [11]. In our experiments we can assume the ideal behaviour of the gas phase because of the small pressure and the low temperature of 70°C used in the sample vial. This assumption doesn’t have a significant influence to the error in the activity coefficient calculation [12].

3. Methods and Materials

Figure 2 depicts an overview of the used measurement system. The HSGC system consists of a headspace sampler (HS) Hewlett Packard 7190 and a 7890 Agilent gas chromatography (GC) with mass spectrometry (GC/MS). The GC/MS is equipped with two electronic pressure control modules (EPC) that controls the gas flow to the headspace sampler for the vial pressure and carrier gas for sample transfer. For the sample transfer from the HS to the GC/MS a transfer-line links the two systems. The transfer-line is always heated 20°C above the oven temperature in order to prevent the condensing of the gas phase, that can cause significant measurement errors. The HS can hold up to six sample vials in the heated oven at a temperature range of 35°C to 200°C with a precision of ±0.1°C.

![Figure 2. Overview over the used HSGC System with Headspace Sampler and GC/MS.](image)

For the measurement of the activity coefficients a mixture of entrainer and biodiesel is prepared with a 1µL gas-tight syringe and checked for correct mass of the entrainer gravimetrically. The sample is sealed within a 20mL inert glass vial and the content of the vial is stirred well. The vial is transferred into the HS and maintained a period of time by a specific temperature until a thermodynamic equilibrium is achieved. After that, an inflation needle cuts off the vial, EPC2 opens the gas flow and inert gas (helium) passes into the vial in order to pressurize the vial. The pressurized vial is relaxed into a heated sample loop for conditioning the gas phase. After that EPC1 opens the gas flow and the content of the sample loop is injected over the transfer-line into the Split/Splitless-Injektor (SSL) of the GC/MS. This method ensures that always the same amount of gas-phase from a vial is collected and therefore the peak areas $A_i$ and $A_{0i}$ are highly reproducible. In order to avoid errors in measurement pre-examinations of the charge quantity of the vial, the needed equilibration time and the optimum equilibration temperature have to be figured out.
3.1. Determination of the optimal charge quantity
For the experiment we used 20 mL inert glass vials and 1 mL, 5 mL and 10 mL of the sample. The measured peak areas $A_t$ and $A_{0t}$ should be independent from the amount of the used sample. Also, it’s an advantage to use a smaller sample amounts due to a shorter equilibration time. Our results show no significant difference in $A_t$ and $A_{0t}$ for the different used sample amounts. In order to reduce the equilibration time and improve the sample throughput we used the appropriate amount of 1mL for the maximum vial charge quantity.

3.2. Determination of the equilibration time of the sample
For the measurement of activity coefficients it is important to achieve a thermodynamic equilibrium of the sample inside the vial. Therefore the sample has to be maintained at a constant temperature for a specific period of time until a stable equilibrium is reached. To maximize the sensitivity of the measurements the peak areas $A_t$ and $A_{0t}$ should be maximized and saturated for a sample. We did measurements with an equilibration time of 30, 60, 90 and 120 minutes to determine the optimum time of equilibration. The results show a stable peak area for $A_t$ and $A_{0t}$ for an equilibration time of 60 minutes. To improve the measurement accuracy we choose an equilibration time of 90 minutes for all samples. This ensures that a stable equilibration of the gas phase is reached under any circumstances.

3.3. Determination of the equilibration temperature
In order to avoid boiling of the used substances, the equilibration temperature should be below the boiling point of the used sample. A boiling sample could lead to pressure-induced leakages, which may cause measurement errors. Also, the temperature should be high enough to ensure that the substance is concentrated sufficiently in the gas phase and can be detected by GC/MS. Common temperatures are 10°C below the boiling point of the substances. Lower temperatures are possible as long the peak areas $A_t$ and $A_{0t}$ are stable and the signal to noise ratio is high enough to avoid errors in the measurement. For the experiment we choose 70°C. This temperature fits all substances boiling points and the signal to noise ratio of the detector signal is also very high for all the used samples.

The measurement results of infinite dilution coefficients can differ between HSGC systems. This can be caused for example by different sample purities, different sample preparation steps or different calibration setups for the HSGC system. For example in [12] and [10] the infinite dilution coefficient of 2-Methyl-1-Propanol in water were measured with different HSGC systems. The results show a deviation between the measurements of $\Delta \gamma^\infty = 2.1$.

In order to minimize the measurement errors of our system the overall HSGC settings like the flow rate, vial pressurizing time and inject time of the samples were optimized and checked by comparing literature data to prove the optimal settings for the HSGC. Also the used capillary column has been chosen to fit all the used substances and the GC/MS settings as well the method to determine the peak area of the substances has been optimized for best results. To benchmark the optimization steps we measured five times the well-known activity coefficient of ethanol in water at infinite dilution and compared it with literature data for reproducibility. Table 1 shows the measurement of the activity coefficient at infinite dilution for ethanol in water for our measurement setup compared with literature data.

| Experiment     | $\gamma^\infty$ |
|----------------|-----------------|
| Our experiment | 7.57            |
| Reference [14]| 7.05            |
| Reference [15]| 7.24            |
The correlation with the literature data showed an overall deviation of \( \Delta y^{\infty} = 0.52 \) for reference [14] and \( \Delta y^{\infty} = 0.33 \) for reference [15]. Therefore, our HSGC system is able to measure activity coefficients at infinite dilution with high accuracy and reproducibility. Table 2 lists the substances used for the activity measurements. The substances are supplied from Merck Chemicals with the highest purity available. The used biodiesel is according to DIN1412 [13]. The carrier gas (Helium 5.0) for the HSGC was supplied from the LINDE GROUP and has a purity of 99.999%.

Table 2. Overview over the used substances for the activity measurements.

| Substance       | Purity |
|-----------------|--------|
| Formic Acid     | > 99%  |
| Valeric Acid    | > 99%  |
| Propionic Acid  | > 99%  |
| Acetic Acid     | > 99%  |
| Butanoic Acid   | > 99%  |
| Ethanol         | > 99%  |
| 1-Butanol       | > 99%  |
| 1-Propanol      | > 99%  |
| 1-Hexanol       | > 99%  |
| 1-Octanol       | > 99%  |
| Butanal         | > 99%  |
| Butanone        | > 99%  |

4. Results and Discussion

The HSGC system described in this work produced reproducible and accurate results for all the measured substances. The results for the measurement of the alcohols in biodiesel can be found in table 3. Comparing the values for the different substances a decrease of \( y^{\infty} \) is recognizable if the chain length of the alcohol is increased. This means the interaction of the alcohols is increasing with larger chain length of the alcohol. Also, there is a tendency for \( y^{\infty} \) to go into saturation. In figure 3 we plotted the length of the alkyl group \( N \) of the alcohol in counter current to \( y^{\infty} \).

Table 3. Activity coefficients \( y^{\infty} \) of alcohols in biodiesel at infinite dilution at a temperature of 70°C.

| Substance | \( y^{\infty} \) |
|-----------|-----------------|
| Ethanol   | 35.53           |
| 1-Propanol| 9.14            |
| 1-Butanol | 4.03            |
| 1-Hexanol | 2.97            |
| 1-Octanol | 2.92            |
Increased London forces between biodiesel and the entrainer can explain the shape of figure 3, but the saturation of $\gamma^\infty$ with increased $N$ must be further discussed.

$$U_{\text{dispersion}} = -\frac{1}{(4\pi\varepsilon_0)^2} \frac{3\alpha_1 \alpha_2}{2r^6} \frac{l_1 l_2}{l_1 + l_2}$$ (7)

The energy of London forces can be expressed with equation (7) [16], where $\alpha_1$ and $\alpha_2$ are the polarizabilities, $l_1$ and $l_2$ are the ionization potentials and $r$ the clearance of the two different molecules [17]. As a result of the $\alpha_1$ and $\alpha_2$ terms in equation (7) dispersion forces increase with the molecular volume and the number of polarizable electrons. The tendency of figure 3 to go into saturation with increasing $N$ leads to the conclusion that the London forces are involved into the interaction of alcohols with biodiesel but are not the main interaction. If London forces would be the main interaction between alcohols and biodiesel the forces should become, as expected, stronger with increasing $N$ according to equation (7), but $\gamma^\infty$ should not go into saturation. Our conclusion is an inductive +I effect from the alkyl groups that increases the electron density of the hydroxyl groups of the alcohol, which can lead to a stronger interaction with biodiesel, for example over hydrogen bonds. The effective range of the inductive effect is limited in space [18] and therefore the saturation of $\gamma^\infty$ can be explained by this limitation. In our experiment the range of the +I effect shows no more significant influence to the activity coefficient after four alkyl groups.

Table 4 shows the activity coefficients of the acids at infinite dilution in biodiesel at $70^\circ$C. Compared to figure 3 the activity coefficient increase with the length of the alkyl group $N$. For $N \geq 3$ there is a significant increase of $\gamma^\infty$ that is depict in figure 4.

**Table 4.** Activity coefficients $\gamma^\infty$ of acids in biodiesel at infinite dilution at a temperature of $70^\circ$C.

| Substance          | $\gamma^\infty$ |
|--------------------|------------------|
| Formic Acid        | 0.36             |
| Acetic Acid        | 0.70             |
| Propanoic Acid     | 0.65             |
| Butanoic Acid      | 4.29             |
| Valeric Acid       | 20.02            |
Figure 4. Activity coefficients $\gamma^\infty$ of acids in biodiesel vs. length of the alkyl group $N$ of the used acid at a temperature of 70°C.

The distinct increase of $\gamma^\infty$ after three alkyl groups is similar to the significant decrease of the used alcohols. But in case of the acids the increased London forces cannot explain this effect. With increased $N$ the London forces are also increased according to equation (7), and therefore $\gamma^\infty$ should be decreased. We assume the increase of the activity of the acids with ascending $N$ is caused by steric reasons of the acid group. With larger $N$ the steric obstruction of the strong polar acid group is higher. Therefore the interaction with the biodiesel can be disturbed and $\gamma^\infty$ is increased in that case. Overall, the acids show the opposite behaviour of the alcohols, larger acids molecules lead to less interaction with the biodiesel.

Generally, substances possessing hydroxyl groups or other groups with a hydrogen atom bound to an electronegative atom are strongly associated to form hydrogen bonds [16]. In this case, Butanal and 1-Butanol should form stronger hydrogen bonds and should possess low activity. Butanon should possess higher activity compared to 1-Butanol or Butanal, according to the lack of a hydrogen atom bond to an electronegative atom.

Table 5 shows the measured activity coefficients of 1-Butanol, Butanal and Butanone in biodiesel at 70°C. As assumed, compared to Butanone the activity of Butanal and 1-Butanol is lower and therefore the interaction with biodiesel is stronger. Therefore the ketone group of Butanone has not the ability to build as strong hydrogen bonds with biodiesel as the aldehyde group of Butanal or the alcohol group of 1-Butanol. Compared to Butanal, 1-Butanol shows similar activity with biodiesel but the activity is lower caused by a single hydrogen atom bound to a strong electronegative oxygen atom.

Table 5. Activity coefficients $\gamma^\infty$ of alcohols, aldehydes and ketones in biodiesel at infinite dilution at 70°C.

| Substance | $\gamma^\infty$ |
|-----------|----------------|
| 1-Butanol | 4.03           |
| Butanal   | 4.68           |
| Butanone  | 8.38           |

According to these results the main interaction of these substances with biodiesel over hydrogen bonds can be assumed. Also acids with a hydrogen atom bound to a strong electronegative oxygen atom should therefore interact over hydrogen bonds according to [16].
5. Conclusion
The knowledge of activity coefficients at infinite dilution can help to find efficiently suitable entrainers for biodiesel. For this reason we described a method to measure activity coefficients of acids, aldehydes, ketones and alcohols at infinite dilution using headspace gas chromatography. Activity coefficients of these possible entrainers in biodiesel were measured in order to determine the interaction with biodiesel.

As assumed, the interaction of the entrainer with biodiesel is influenced by the molecule structure of the entrainer. Short-chained acids show high interaction with biodiesel. With growing chain length of the acid the interaction with biodiesel is stronger influenced by steric obstruction of the longer alkyl chain and the interaction with the biodiesel is decreased (Figure 4). Alcohols show raising interaction with increasing length of the alkyl chain (Figure 3). Increased London forces and an inductive +I effect of the molecule chain, that increases the electron density around the alcohol group, can explain the higher interaction. Overall, short acids show the highest interaction with biodiesel of all the analyzed entrainers (Table 4). Short-chained alcohols, ketones and aldehydes show lower interaction compared to acids or long-chained alcohols (Table 5, Table 3). According to the results the majority of the interaction with biodiesel of alcohols, aldehydes and ketones should occur over hydrogen bonds.

The results affirm the assumed suitability of short-chained acids and long-chained alcohols to act as entrainer for biodiesel according to the strong interaction with biodiesel. In summary, the knowledge about activity coefficients may enable the design of entrainers for biodiesel.

References
[1] Thornton M J, Alleman T L, Luecke J and McCormick R L 2009 Impacts of Biodiesel Fuel Blends Oil Dilution on Light-Duty Diesel Engine Operation Soc. of aut. eng. Conf. International Powertrains Fuels and Lubricants Meeting NREL/CP-540-44833
[2] Fang H and McCormick R 2006 Spectroscopic study of biodiesel degradation pathways Soc. of aut. eng. 2006-01-3300
[3] Ford AG 2007 Reduce of Oil Dilution Eur. Pat. Appl. 1744022A1
[4] Toyota Motor Corporation 2007 Fuel injection control device of internal combustion engine Jap. Pat. Off. 2007071121A
[5] Christen D S 2005 Practical knowledge of chemical engineering: Handbook for chemists and chemical engineers (Berlin: Springer)
[6] Bieker T 1995 A contribution for the choice of consumables and consumables-mixtures for the extractive- and azeotrope rectification (Verlag Shaker)
[7] Krahl J, Munack A, Haupt J and Bockey D 2009 Methods and substance-compositions for the reduction of the oil dilution of combustion engines Ger. Pat. Trad. Off. DE102008024382 A1
[8] Mäder A 2011 Research of the interaction of engine oil with new fuels and methods for extension of the oil chance interval Innovative Automotive Engineering vol 2 (Germany: Expert Verlag) pp16-22
[9] Behr A, Agar D W and Jörissen J 2010 Technical Chemistry (Heidelberg: Spektrum Akademischer Verlag)
[10] Hovorka S, Dohnal V, Roux A H and Roux-Desgranges G 2002 Determination of temperature dependence of limiting activity coefficients for a group of moderately hydrophobic organic solutes in water Flu. Ph. Equ. 201 pp 135–164
[11] Sandler S I 2006 Chemical, Biochemical, and Engineering Thermodynamics vol 4 (John Wiley & Sons)
[12] Whitehead P G and Sandler S I 1999 Headspace gas chromatography for measurement of infinite dilution activity coefficients of C4 alcohols in water Flu. Pha. Equ. 157 pp 111–120
[13] DIN EN 14214 Automotive fuels 2009 Fatty acid methyl esters (FAME) for diesel engines - Requirements and test methods German Institute for Standardization. e. V.
[14] Wittig R, Lohmann J and Gmehling J 2003 Vap. Liq. Equ. UNIFAC Group Contribution vol 6

9
Revision and Extension Ind. Eng. Chem. Res. 42 pp 183-188
[15] Mertl I 1972 Collect. Czech.Chem.Commun. 37 p 366
[16] Reichardt C 2004 Solvents and solvent effects in organic chemistry (Weinheim: Wiley-VCH)
[17] Nelson W M 2000 Choosing Solvents that Promote Green Chemistry Symp. ACS 767 313 Green Chemical Syntheses and Processes Chem. Abstr. 133
[18] Ansyln E V and Dougherty D A 2006 Modern physical organic chemistry (University Science Books)