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Surface Tension of Low-viscous Lubricants in High Pressure Carbon Dioxide Atmospheres

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ABSTRACT

The optimization of refrigeration systems can be achieved by increasing the isentropic efficiency of the compressor. One possible way is the reduction of the friction and leakage losses which occur at the piston rings. The viscosity and the surface tension of the lubricant must be known for this purpose. From the literature only a small amount of measured values for the surface tension of commonly used lubricants are known. Additionally natural refrigerants like R-744 are more common according to the latest (i.e. European) environmental regulation. The thermophysical properties of lubricant-refrigerant-mixtures can currently only be calculated by generalized calculation methods. For specific mixtures, these equations need to be confirmed by measurements. In this paper the measurement results of the surface tension of different low-viscous lubricants are shown. A test bench was designed to measure the surface tension of different liquids especially under high pressure atmospheres. The investigation was performed by using the pendant drop method and analyzing the results with new algorithms for the solution of the Young-Laplace equation. Effects of the geometry of the used capillaries are discussed which leads to possible optimizations of this measurement method. Dilution effects on the surface tension of the lubricants in carbon dioxide atmospheres are shown and discussed. The effect of higher pressures and different temperatures on the surface tension is shown as well as a comparison of the measurements with generalized methods.

1. INTRODUCTION

With increasing pressure and lower temperatures refrigerants are soluted in the compressor lubricants which leads to a significant change of the thermophysical properties of the lubricant. Especially the transport properties viscosity, thermal conductivity and surface tension are interesting for technical applications. These properties are important for the process of lubrication and sealing in the compressor, i.e. on the piston rings. Studies from (Di Nicola & Moglie, 2011) and (Di Nicola & Pierantozzi, 2013) show that the surface tension of refrigerants can be precalculated by using corresponding generalized methods. However especially the critical parameters of the fluids, the critical temperature, pressure, volume, the normal boiling point and the acentric factor need to be known. (Di Nicola & Pierantozzi, 2013) also show that the surface tension of refrigerant mixtures can be calculated by adjusting one specific parameter of the binary fluid mixture. For this purpose the surface tension and its temperature dependency must be known for both fluids. This isn’t usually the case for lubricants. Studies from (Zhelezny P., Zhelezny, Proenko, & Ancherbak, 2007) and (Zheleznya, Sechenyhb, Ivcenkkoa, & Yury, 2014) show that the surface tension of refrigerant-oil-mixtures (ROS) can be calculated when the vapor pressure of the refrigerant lubricant mixture is known for different temperatures and concentrations. These calculations can be used for reduced critical temperatures up to 0.7. This leads to limitations, when fluids like R744, R170, R23, R290, R32 or R1234yf are used, which have critical temperature lower than 373 K. Certain compressor parts and thus the lubricant can have significant higher temperatures in refrigeration or heat pump systems. Also the precalculating according to (Zheleznya, Sechenyhb, Ivcenkkoa, & Yury, 2014) leads to problems when the temperature is lower than the critical temperature of the refrigerant but the pressure is higher than the pseudo critical pressure of the lubricant. This is often the case, as the critical pressure of a lubricant is typically rather low, and it can especially be the case for mixtures of R744 with lubricants. On the other side especially for low temperature applications with R744 or R23 low-viscous lubricants with an high viscosity index (VI) must be used to ensure the lubricant transport through the evaporator. To calculate the friction losses and the thickness of the lubricant film inside the evaporator and compressor the surface tension must be known.
2. THEORETICAL APPROACH

2.1 Surface tension of pure fluids calculated with the Young-Laplace equation

When a liquid drop is in equilibrium to its gas phase at a specific pressure and temperature, it can be described by a balance of forces. Referencing the forces to the surface of the drop, the equilibrium can also be described as a pressure equilibrium. The equilibrium of a pendant drop can be described by the Young-Laplace equation (1).

\[
\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \Delta p \equiv p_1 - p_2 - z \cdot g \cdot (\rho'' - \rho')
\]

In equation (1) \(\sigma\) is the surface tension, \(R_1\) and \(R_2\) are the significant radii of the drop, \(p_1\) the internal pressure of the drop, \(p_2\) the pressure in the gas phase, \(g\) is the gravitational acceleration and \(\rho'\) and \(\rho''\) are the densities of the liquid and gaseous phase. Since the internal pressure difference of the drop \(\Delta p\) is difficult to measure it is more common to measure to geometric parameters of the drop. As shown in publications from (Davida, Sefiane, & Tadristb, 2007), (Saad, Policova, & Neumann, 2011), (Berry, Neeson, Dagastine, Chan, & Tabor, 2015) especially the equivalent spherical radius \(R_0\) can be used. To solve equation (1) it can be assumed that when a specific sphere is found which has the same geometric behavior it should have the same balance of forces which leads to the surface tension. The internal pressure force \((\pi \cdot R_0^2 \cdot p_1)\), the outer pressure force \((\pi \cdot R_0^2 \cdot p_2)\) and the interfacial tension \((2\pi \cdot R_0^2 \cdot \sigma)\) have to cancel each other (2), see Figure 1.

\[
\pi \cdot R_0^2 \cdot p_1 = \pi \cdot R_0^2 \cdot p_2 + 2\pi \cdot R_0^2 \cdot \sigma
\]

Since equation (2) still needs the difference of the internal and outer pressure of the drop the Bond-Number Bo was defined (3) which can be interpreted as a geometrical index of the drop.

\[
Bo \equiv \frac{(\rho' - \rho'') \cdot g \cdot R_0^2}{\sigma} = f(\phi, s)
\]

The solution of equation (3) is shown in detail by (Berry, Neeson, Dagastine, Chan, & Tabor, 2015). Since equation (3) is only a function of the drop shape the detection and calculation of the edge function is essential. Since the density difference \((\rho' - \rho'')\) is not always known by from measurements also the Laplace constant \(a\) can be used (4) for comparing the measurements with other tabulated values.

\[
a \equiv \sqrt{\frac{\sigma}{(\rho' - \rho'') \cdot g}} = \frac{R_0}{\sqrt{Bo}}
\]

In the literature like (Zhelezny P., Zhelezny, Proenko, & Ancherbak, 2007) and (Zhelezny, Semenyuk, Ancherbak, Grebenkov, & Beliayeva, 2007) also the capillary constant \(\alpha^2\) is used (5).

\[
\alpha^2 = \frac{2 \cdot \sigma}{(\rho' - \rho'') \cdot g} = 2 \cdot a^2 = 2 \cdot \frac{R_0^2}{Bo}
\]

2.2 Literature survey on surface tension of refrigerants and refrigerant-lubricant mixtures

Only a few measurements and methods for the calculation of the surface tension of lubricants are known from the literature. Generalized and semi-empirical methods are shown by (Reid, Prausnitz, & Poling, 1987) where at least the surface tension of the normal boiling point and the critical parameters of the fluid have to be known. Analysis from (Di Nicola & Moglie, 2011) and (Di Nicola & Pierantozzi, 2013) led to the same results. Since often the database of the lubricants is small these methods have a high uncertainty. Also group contribution methods like
UNIFAC or UNIQUAC cannot be used since the chemical structure of the lubricant and the additives are often unknown.

A new approach was investigated by (Zheleznya, Sechenyh, Ivchenko, & Yury, 2014) who used a special form of the corresponding state method to calculate the surface tension of lubricants and lubricant refrigerant mixtures. The basic idea was to use the vapor pressure data of the lubricant refrigerant mixtures and approximate the surface tension with universal coefficients and pseudo critical data of the mixtures. Analysis from (Zhelezny P., Zhelezny, Procenko, & Ancherbak, 2007), (Zhelezny, Semenyuk, Ancherbak, Grebenkov, & Beliayeva, 2007) and (Semenyuk, Zhelezny, Ivchenko, & Geller, 2011) show that these methods can be applied for the surface tension calculation of different refrigerant lubricant combinations. However as discussed by (Vetere, 1992), (Yokozeki, 2001) or (Zhelezny, Zhelezny, & Scripov, 2003) still a lot of data like the liquid density, the compressibility factor, pTx-data of the refrigerant lubricant mixture and others are unknown. The method shown by (Di Nicola & Pierantozzi, 2013) has the advantage that the temperature and liquid phase concentration dependency can be described with simple semi-empirical equations which can be fitted to surface tension measurements and only solubility data are required. However at temperatures or pressures higher than the critical values of the refrigerant, the model reaches its limits considering that the surface tension of supercritical states is not defined.

2.3 High pressure effects on the surface tension of lubricants

Measurements from (Eggers & Jaeger, 1994), (Chun & Wilkinson, 1995) and (Bachu & Bennion, 2009) show that the close to the critical state of carbon dioxide, some fluid mixtures lead to ‘special’ behavior. This behavior can be explained with the temperature and pressure dependency of the pure fluids. The temperature dependency can be described with equation (6) where the saturation temperature $T_s$ can also be described by a function of the vapor pressure like the Clausius-Clapyeron equation. When the temperature or pressure gets close to the critical state, the
surface tension becomes zero, which leads to problems using the equations of (Di Nicola & Pierantozzi, 2013) for binary fluid mixtures. However this problem can be solved when the critical state of the mixture is known as a function of the concentration.

\[ \sigma(T_s) = \sigma_{ref} \cdot \left(1 - \frac{T_s(T_s)}{T_c}\right)^n \]  \hspace{1cm} (6)

In equation (6) \( \sigma_{ref} \) is the surface tension at a reference state point, \( T_s \) is the saturation temperature as a function of the saturation pressure \( p_s, T_c \) is the critical temperature and \( n \) is a fluid specific exponent. For technical applications it is more common to measure the pressure and temperature and calculate other thermophysical properties. If we consider a system of a lubricant and carbon dioxide without a miscibility gap, the correlation from (Di Nicola & Pierantozzi, 2013) can be used for subcritical temperatures as a function of the concentration \( x \) (7).

\[ \sigma_{mix}(p, T) = \left(\sigma_1(T) \cdot x_1(p, T)\right)^r + \left(\sigma_2(T) \cdot x_2(p, T)\right)^r \]  \hspace{1cm} (7)

The surface tension of the mixture \( \sigma_{mix} \) depends on the temperature (7). With the assumption of an ideal solubility and with the application of Dalton’s Law, the pressure dependency can be described. Considering that the lubricant vapor pressure is almost zero the one dimensional equation (8) can be formulated.

\[ x(p, T_s) = \frac{p}{p_s(T_s)} \]  \hspace{1cm} (8)

Applying equation (8) on (7) for binary systems of pure gas phases and close to an ideal liquid phase equation (9) is resulting.

\[ \sigma_{mix}(p, T) = \left(\sigma_1(T) \cdot \frac{p}{p_s(T_s)}\right)^r + \left(\sigma_2(T) \cdot \left(1 - \frac{p}{p_s(T_s)}\right)^r \right) \]  \hspace{1cm} (9)

Using equation (9) and (4) or (5) it can be assumed that also the Laplace constant and the capillary constant should be a function of pressure and temperature. Equation (9) can also be expressed as a polynomial function for the Laplace constant \( a=f(p, T) \) because of the following assumptions

- the surface tension is a power function,
- the density of the liquid phase is approximately a linear function of the temperature and
- the vapor density is in first approximation a polynomial function of pressure and temperature.

3. EXPERIMENTAL TEST SETUP AND MEASUREMENT

3.1 Experimental test setup

A test bench was designed to measure the surface tension of lubricants in high pressure atmospheres. It is shown in Figure 3. The key part is a high pressure stainless steel cell. This high pressure cell includes two high pressure sight glasses with an optical distortion of almost zero. From the top of the cell a pipe with a small capillary at the end, two PT-100 resistance thermometers and an additional small diameter pipe are connected to the cell. The drops are generated with by means of the capillary tube. The two resistance thermometers measure the temperature of the lubricant and inside the measuring cell to ensure that they have the same temperature. Through the small pipe gas can flow into the measuring cell to generate a specific pressure. On the one side of the sight glasses a monochrome and collimated LED is used for the lightning of the measuring cell. The whole apparatus is placed in a temperature chamber. On the other side of the sight glasses a camera is installed to photograph the drops. A Nikon D7000 with a macro lens for high quality resolute pictures is used. To reduce effects of scattered light a circular polarization filter was used. Additionally the experimental apparatus includes:

- different valves for controlling the gas and lubricant flow,
• a vacuum pump for degassing the lubricant and removing air and moisture from the measuring cell,
• a pressure tank where the lubricant is stored and
• Two pressure sensors, one for the measuring cell and one for the pressure tank.

The apparatus was designed for pressure from 0 up to 170 bar and a temperature range from 220 up to 400 K. The principle design of the apparatus is shown in Figure 3 and Figure 2.

![Image of the apparatus](image.png)

**Figure 2 – high pressure cell with connected pipes and wires**

### 3.2 Surface tension measurement procedure

The lubricant is charged to the pressure tank (A) (see Figure 3) by means of a filling spout which is closed afterwards. A vacuum pump evacuates the entire system to pressures lower than $10^{-3}$ mbar for at least 10 hours. After that, the system is sealed again and the gas from the gas cylinder (C) is charged into the system. For the tests carbon dioxide with a purity of 99.9% was used. The purity was validated by a gas chromatographic analysis. The pressure drop in the system, which is caused by the solution of gas in the lubricant, needs to be considered. After about 90 minutes the lubricant is saturated with the gas. The high pressure cell is located in a temperature chamber. Afterwards the valve (D) in the gas pipe to the high pressure cell is closed. The pressure inside the lubricant tank is slightly increased by letting a small amount of gas into the tank. The pressure difference is about 0.05 to 0.1 bar. After that the flow control valve (E) is opened carefully and the lubricant flows to the high pressure cell due to the small pressure difference. The system is observed by an optical camera until a drop was generated. The drop is held long enough so that the saturation state of the drop is in equilibrium with the gas phase. According to measurements from e.g. (Davida, Sefiane, & Tadrist, 2007) the saturation state is reached in a few seconds. This can be explained by the small volume of the drop where only a small amount of gas molecules can be solved. A picture of the drop is taken and the drop is drained by opening the flow control valve (E) carefully. After that the procedure is repeated until at least 20 drops are generated at a specific pressure and temperature. After that the pressure was changed for the next operation point and the system was given a time of at least 1.5 hours for saturation.
3.3 Computational analysis of the surface tension with the pendant drop method

For the analysis of the drops a computational algorithm for the solution of the Young-Laplace equation was used. The solution of the algorithm is well described by (Berry, Neeson, Dagastine, Chan, & Tabor, 2015) who also developed an open source analysis program called “OpenDrop”. The basic idea of the program is the detection of the edge of a binarized picture and to calculate the volume and shape of the drop by using dimensionless variables. An example of the analysis is shown in Figure 4. At first the pictures are trimmed, so that the drop and the capillary are shown, see Figure 4, picture 1. The picture is then binarized so that the edges of the drop and the capillary are shown as black contours, picture 2. Since the histograms of the pictures, see Figure 4, picture 1, have two maxima with a few values in between them, the data loss is minimal. Tests have shown that a different threshold value of ±10 % of the original value for the binarisation leads to uncertainties of the analysis lower than 0.5 % of the surface tension.
After the binarisation the program “OpenDrop” needs the input areas for the drop, see Figure 4, picture 3, and the capillary, picture 4, which are shown as a green rectangles. The outer diameter of the capillary is also an initial value for the calculation of the drop dimensions. Besides this the density values of the liquid and the gas phase have to be known. These parameters however are just used for the calculation of an absolute value of the surface tension of the liquid phase. After all parameters are entered the edge of the drop is detected and the dimensionless parameters are calculated as shown by (Berry, Neeson, Dagastine, Chan, & Tabor, 2015). The calculated shape of the drop is shown to the user as a dotted line for control purposes (Figure 4, Picture 5). As shown by the analyses of (Berry, Neeson, Dagastine, Chan, & Tabor, 2015) only drops with a high Bond- and Worthington-Number lead to a low scattering and high certainty of the measured values which means that drops with a high volume have to be produced. Only drops with a Bond-Number higher than 0.5 and a Worthington-Number higher than 0.7 were used for their analysis. For pressures near the critical pressure of carbon dioxide the drops become much smaller so that the Bond-number decreases. That is why also drops with lower Bond-numbers were used in this investigation.

4. EXPERIMENTAL RESULTS

4.1 Surface tension of different lubricants in carbon dioxide atmosphere

As shown in equation (9) the surface tension can be calculated for different boundary conditions. Since especially the effect of higher pressures on the surface tension of mixtures is not well discussed in the literature isothermal measurements of the surface tension for different pressures were initiated. The carbon dioxide had a purity of 99.9%. Three different POE (polyolefin ester) lubricants were used. Lubricant A and C were POE of ISO-VG 32 and lubricant B a POE of ISO-VG 22. The results are shown in Figure 5. The Laplace constant and the capillary constant can be expressed as a second-order polynomial function of the pressure. The extrapolation shows a reasonable behavior so that it can be assumed that the constants can be precalculated with a low number of measured values. As shown in Figure 5 the difference between the three analyzed lubricants is small. The lubricants A and C with a higher viscosity do not tend to a much different Laplace or capillary constant than lubricant B. The variations of the measurements of the Laplace and capillary constant for constant pressures are also small, see Figure 5. The relative differences of the measurements are smaller than 1 % for Lubricant B. For Lubricant A and C especially at pressures higher than 50 bar the differences increase. Lubricant A has a maximum deviation of lower than 1 % for the Laplace constant and smaller than 2 % for the capillary constant for pressure lower than 50 bar. For higher pressures the deviations increase up to 6 % for the Laplace constant and up to 11 % for the capillary constant (see also Figure 5). Lubricant A has also a maximum of the Laplace constant at about 5 bar which is assumed that this caused by the wetting effects of the capillary at this pressure. Lubricant C has a maximum deviation of 0.5 % for the Laplace constant and 0.9 % of the capillary constant at pressures lower than 50 bar. At higher pressures the deviation increases up to 13 % for the Laplace constant and 2.6 % for the capillary constant. As shown in equation (9), the behavior of the mixtures can be described with simple polynomial functions. However the temperature effect still needs further investigation, since the solubility of the gas in the lubricant decreases with higher temperatures. The differences of the Laplace constants and capillary constants for the three analyzed lubricants are small. That is why only density data of the lubricant carbon dioxide mixtures is needed to calculate the surface tension of the mixtures, see equation (4) and (5).
Figure 5 – Laplace and capillary constant as functions of pressure for different pressures at 293.15 K

4.2 Uncertainty of the measurements

Commercial lubricants were used for the measurements. Thus production-related variations of the properties are possible. Additionally the amount of anti-foam additives in the lubricant is not known which means that the surface tension of the base oil can lead to other results. Other effects that were observed while measuring the surface tension of the pure lubricant at different temperatures were the wetting of the capillary, as shown in Figure 6 A to E, and so called “melting” of the drop at low temperatures, as shown in Figure 6 I to V. As shown in A to B the drop is rising on the outside of the capillary upwards. The drop is then growing on the outside of the capillary (C). This leads to problems when analyzing pictures like D or E because the outer diameter of the wet capillary is unknown. When this effect occurred, the capillary was removed and cleaned with a cleaning solvent. At lower temperatures effects like a melting drop, I to V in Figure 6, were observed. The kinematic viscosity is about 50 times higher than at room temperature and the density is about 8% higher. Since these effects could not be observed at higher temperatures, it can be assumed that at high viscosities the flow resistance increases and internal Reynolds-Number of the drop decreases so that the drop is not stable anymore, see Figure 6. Calibration measurements with water, ethanol and acetone show maximum deviation at different temperatures of about 5% compared to values from (Lemmon, Huber, & McLinden, 2013) for temperatures from 243 up to 373 K. The wetting effects occurred more frequently with small outer diameters of the capillary. Especially at high pressures Bond and Worthington numbers greater than 1 were observed. These values were not used since Worthington numbers are defined as equal or lower than 1.
Another uncertainty is the quality of the edge detection of the drops. To reduce the effect of different Bond numbers drops with different radii $R_0$ and different Worthington numbers should be analyzed.

Figure 6 – Wetting and melting effects with the pendant drop method

5. CONCLUSIONS

The measurement and the calculation of the surface tension for different low viscose lubricants in carbon dioxide atmospheres are explained in this paper. The functional dependency of the surface tension and the Laplace constant are discussed and compared to measurements. The measurements show that the Laplace constant and the capillary constant can be easily described for isothermal data sets. With the developed test bench the effects of other gas and lubricant combinations can be analyzed at different temperatures and pressures. Further investigations are required to confirm the dependencies for different boundary conditions. Effects of wetting capillaries and melting drops need further investigation about how to measure the surface tension and of possible effects on the lubrication in compressors.

NOMENCLATURE

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<th>Symbol</th>
<th>Description</th>
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<td>$a$</td>
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<td>(m²)</td>
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<tr>
<td>$\alpha^2$</td>
<td>Capillary constant</td>
<td>(mm²)</td>
</tr>
<tr>
<td>$Bo$</td>
<td>Bond-Number</td>
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<td>$\phi$</td>
<td>Drop tangent angel</td>
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<tr>
<td>$s$</td>
<td>Arc length</td>
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<tr>
<td>$\sigma$</td>
<td>Surface tension</td>
<td>(N·m⁻¹)</td>
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<tr>
<td>$r$</td>
<td>Adjustable parameter for mixtures</td>
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</tr>
<tr>
<td>$R$</td>
<td>Radius</td>
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<td>(Pa)</td>
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<td>$x$</td>
<td>Mole fraction refrigerant in liquid phase</td>
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**Subscript**

- $c$: critical state point
- $mix$: mixture
REFERENCES


