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Heat capacity, density, surface tension, and contact angle for polyalphaolefins and ester lubricants

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ABSTRACT

Thermophysical properties of lubricants are important to understand which ones are appropriated for the industrial conditions expected. Thermophysical properties of two different families of lubricants were analysed: polyalphaolefins (PAO6, PAO20, PAO32 and PAO40) and four ester-based lubricants. Specific heat capacity, density, surface tension, and contact angle were experimentally determined over a broad temperature range through methods such as μDSC, U-tube vibration, drop volume, and sessile drop method, respectively. A clear difference between the two families was observed due to their structure and composition, grouping by nature. Ester-based lubricants showed lower specific heat capacity but higher surface tension and density than polyalphaolefins. PAO6 clearly has the lowest density and surface tension and presents the highest specific heat capacity of all lubricants, and together with trimethylolpropane trioleate, TMPTO, presents the best wettability. Heat capacity values were used to test the validity of two predictive methods.

1. Introduction

One of the main tasks of lubricants, besides forming a protective film that reduces friction and wear of the machinery moving parts and protects against corrosion, is to remove heat. More efficient heat transfer can result in significant economic and energy savings [1]. Turbine and automotive engines are required to operate at ever increasing temperatures. Uncooled low heat rejection (LHR) engines do not have oil cooler and radiator, being the engine oil the only heat transfer fluid [2,3]. The presence of the lubricant circulating with the operating fluid in reverse Rankine cycle machines or refrigeration systems affects the thermohydraulic processes in the heat exchangers, condenser and evaporator [4]. Lubricant properties, such as heat capacity, surface tension, contact angle and density are important in determining heat-transfer rates for other applications as jet engines, electric drivetrains... [5–7].

The effect of friction and therefore the wear of the pieces are amplified by the increase of temperature [8]. Heat capacity values are needed to know how much thermal energy the lubricant can remove from the friction zone. Lubricants with a large heat capacity, C_p, suffer a smaller temperature increase for the same amount of heat energy absorption [2]. In addition, for improving the load-carrying capacity of the hydrodynamic bearings or analyze the gear losses, volumetric heat capacity of the oils is an essential property [9]. Thus, when the volumetric heat capacity of the lubricating oil is high, the temperatures in the bearing gaps are lower, and consequently the viscosities higher for the same operating conditions [10,11].

The tendency of the lubricants to spread on a solid surface is a very important factor affecting their performance. The wetting ability can be characterized using surface tension and contact angle measurements. Surface tension and contact angle by their effect on spreadability, may also influence the cooling capacity. Poor wettability of surface reduces the heat transfer when phase changes are involved. These properties control the formation and growth of bubbles, and thus play an important role in systems involving boiling and condensation [12]. Besides surface tension is an important parameter in the behaviour of seals, oil spreading rates, foam stability, mist lubrication, wettability of low-energy solids, and lubricant starvation [13–15].

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Nomenclature

PAOs	polyalphaolefins
TMPTO	trimethylolpropane trioleate
TTM	triisotridecyl trimellitate
BIOE	biodegradable polymeric ester
TOTM	tris(2-ethylhexyl) trimellitate
C_p	heat capacity, J g^{-1} K^{-1}
ρ	density, g cm^{-3}
θ	contact angle, °
σ	surface tension, mN m^{-1}
T	temperature, K
AAD	average absolute deviation, %
C	linear correlation parameter, -
λ	linear correlation parameter, -
σ_{SM}	surface tension between the surface and the surrounding medium, mN m^{-1}
σ_{SL}	surface tension between the surface and the liquid, mN m^{-1}
σ_{LM}	surface tension between the liquid and the surrounding medium, mN m^{-1}
S	spreading parameter, mN m^{-1}
W_A	work of adhesion (solid-liquid interface), mN m^{-1}
W_C	work of cohesion (liquid), mN m^{-1}

Oil density, ρ, plays an important role in processes involving heat transfer exchanges. It informs of the basic behaviour of the lubricant, detects the purity of the fluid, and is needed to obtain the volumetric heat capacity. Sanchez [16] proposed an equation relating the surface tension, density and isothermal compressibility based on generalized square-gradient approximation for the free energy density of a two-phase fluid. This equation was verified for 50 polar and non-polar organic liquids. Recently, Pinheiro et al. [17] based on the Sanchez equation found that the logarithm of the surface tension correlated very well with the logarithm of the density for nine waste lubricants.

In this work, surface tension, density and contact angle for temperatures from 283.15 K to 323.15 K and specific heat capacities in the temperature range (283.15–353.15 K), of four polyalphaolefins of different molecular weight, PAO6, PAO20, PAO32, PAO40, and four ester-based lubricants were measured. These esters are trimethylolpropane trioleate, TMPTO, triisotridecyl trimellitate, TTM, a biodegradable polymeric ester, BIOE, and tris(2-ethylhexyl) trimellitate, TOTM. This last compound is a high-temperature, high-pressure, high-viscosity standard [18]. PAOs are one of the most used lubricants and ester-based lubricants are looking up to substitute them, so to find an ester that could match their characteristics would be ideal. PAO lubricant bases are usually synthesized by multi-step process: ethylene is polymerized to 1-decene and then oligomerized to obtain bigger structures; in the final step, these oligomers are hydrogenated to produce a fully saturated, very stable hydrocarbon mixture. In comparison with mineral lubricants, PAOs have very high oxidation and hydrolytic stabilities, high viscosity index, low pour point, good inherent lubricity. They are used in engine crankcase, compressor, turbine or gear oils, and as hydraulic, dielectric, brake, metalworking or automatic transmission fluids as well as heat transfer media, gels for coating optical fibers, off-shore drilling, shock absorbers, and space applications [19,20]. The usual properties of ester oil bases are high viscosity index, biodegradability, excellent lubricity and low toxicity [21]. The values of density and surface tension obtained in this work were used to test the Pinheiro et al. [17] equation. In addition, heat capacity experimental values were used to test the prediction capability of the group-contribution methods of Rùzicka and Domalski and Ceriani et al. [22,23]. We selected these models as they are simple and provide estimates within the limits of accuracy required in industrial applications.

2. Experimental section

2.1. Materials

Table 1 shows the source, main characteristics and the analytical methods used to characterize the different lubricants. Samples of four polyalphaolefins of different molecular weight (PAO6, PAO20, PAO32, and PAO40) have been provided by REPSOL (PAO20 and PAO32 are mixtures of PAO40 with small amounts of PAO6). Characterization of the PAO6 sample (NMR, FTIR spectrum and MALDI-TOF mass spectroscopy) were reported by Guimarey et al. [24]. In the case of PAO40 sample, Liñeira del Río et al. [25] reported the FTIR spectrum. PAO32 sample is a mixture of PAO40 (89 wt%) and PAO6 (11 wt%), its FTIR and Raman spectra were recently reported by Nasser et al. [26]. PAO20

Table 1
Source, weight average molecular weight, M_w, molecular mass, polydispersity index, purity and analytical methods used to characterize the lubricants.

Chemical name	Source	M_w/g mol^{-1}	Polydispersity index	Analytical method
PAO6[a]	Repsol	604.29	1.043	NMR [24] FTIR spectrum [24] MALDI-TOF mass spectroscopy [24]
PAO20[a]	Repsol	627.34	1.031	MALDI-TOF mass spectroscopy, SM[f]
PAO32[a]	Repsol	667.79	1.075	MALDI-TOF mass spectroscopy, SM[f] FTIR spectrum [26] Raman spectrum [26]
PAO40[a]	Repsol	699.21	1.020	MALDI-TOF mass spectroscopy, SM[f] FTIR spectrum [25]

Chemical name	Source	Molecular mass/g mol^{-1}	Purity (mole fraction)	Analytical method
TMPTO[b]	Croda	926.79	0.683[g]	HPLC–ESI-Q-TOF-MS analysis [28] FTIR spectrum [25, 28]
TTM[c]	Verkol	746.64	0.454[h]	UHPLC–APCI-TOF-MS analysis, SM[f] FTIR spectrum [27]
TOTM[d]	Sigma-Aldrich	546.79	0.99[i]	
BIOE[e]	Verkol	337.75	0.95	HPLC–ESI-Q-TOF-MS analysis, SM[f] FTIR spectrum [27]

Chemical name	Source	Molecular mass/ g mol^{-1}	Purity (mole fraction)	Analytical method
Squalane	Sigma-Aldrich	422.81	0.99 [i]	–
n-Decane	Sigma-Aldrich	142.28	0.99 [i]	–
n-Heptane	Sigma-Aldrich	100.20	0.99 [i]	–

[a] PAOs = polyalphaolefins.
[b] TMPTO = trimethylolpropane trioleate.
[c] TTM = triisotridecyl trimellitate.
[d] TOTM = tris(2-ethylhexyl) trimellitate.
[e] BIOE = biodegradable polymeric ester.
[f] SM = Supplementary material. Figs S1-S10
[g] 68.3% of TMPTO, 27.6% of a compound with a C=C bond more than TMPTO, and a 4.1% of a compound with two C=C bonds more than TMPTO [28] (% composition in mole fraction).
[h] 45.4% of TTM, 35.2% of a compound with a methylene group (CH_2) less than TTM, and a 19.4% of a compound with two methylene groups (CH_2) less than TTM (composition given in wt%).
[i] Determined by the supplier.

is a mixture of PAO40 (65 wt%) and PAO6 (35 wt%).

Verkol Lubricantes provided the synthetic esters (triisotridecyl trimellitate, TTM, and the biodegradable polymeric ester, BIOE) whereas the base oil trimethylolpropane trioleate (TMPTO, CAS: 57675-44-2, molecular mass 926.79 g mol^{-1}) was kindly provided by Croda. An aliquot of the TTM (CAS: 2583122-54–5; molecular mass 746.64 g mol^{-1}) sample was characterized previously [27] through FTIR and mass spectrum. TTM characterization was completed by an Ultra-High Performance Liquid Chromatography, UHPLC, coupled with an APCI-TOF mass spectrometer (Fig. S8). An aliquot of the TMPTO sample was characterized by Liñeira del Río et al. [28] using FTIR spectrum, and HPLC–ESI-Q-TOF-MS analysis. Guimarey et al. [27] provided a FTIR spectra of BIOE (molecular mass of 337.75 g mol^{-1}). The sample of tris (2-ethylhexyl) trimellitate ester (TOTM, CAS 3319-31-1) studied in this work was supplied by Sigma-Aldrich. It has a mole fraction purity higher than 0.99 and a molecular weight of 546.79 g mol^{-1}, and has been characterised by Liñeira del Río et al. [29].

2.2. *Thermophysical and surface characterization techniques*

Density at atmospheric pressure of the samples was measured from (283.15 to 323.15) K by using a vibrating tube densimeter (Anton Paar DSA 5000, Austria). Calibration was performed using mechanically degassed ultrapure water (Elix 3 purification system, Millipore Corp.) and dry air as density standards. The upper limit for the standard uncertainty of density measurements (samples with viscosity higher than 100 mPa s) is 0.0002 g cm^{-3}. For samples with a viscosity lower than 30 mPa s, a standard uncertainty of 0.00004 g cm^{-3} is obtained [24, 30].

Equilibrium surface tensions were measured with a Lauda drop volume tensiometer (TVT 2 model, Germany) using the standard mode. A syringe of 2.5 ml attached to a steel capillary with an inner radius of 1.345 mm, furnished between 50 and 60 drops of each sample. Calibration was performed using ultrapure water (Elix 3 purification system, Millipore Corp.). Both the equipment and the procedure were described in detail in the past [31–33]. Depending on the working temperature (283.15 to 323.15) K, the surface tension was determined with a combined expanded uncertainty ranging from 0.2 to 0.4 mN m^{-1} at the 95% confidence level. The temperature of the external bath to which the measurement cell is connected was controlled within ±0.01 K.

The wetting behaviour of the eight base oils was evaluated using a contact angle analyser, Phoenix MT(A), at different temperatures (from 293.15 to 323.15 K). Method validation was performed using a certified drop calibration reference tool made of glass, which includes three images of sessile drops with nominal contact angles of 30°, 60° and 120°. Before the static contact angle measurements, the surface was rinsed with ethanol and dried in a stream of hot air. The surface material selected to determine the wettability behaviour of the base oils was AISI 420 stainless steel, which is frequently used for tribological tests. One drop of lubricant sample was dropped on the steel surface using a syringe. To obtain the value of the average steady-state contact angle, a period of 5 s was waited to stabilize the droplet and at least three measurements were replicated for each base oil. For the determination of the static contact angle, the expanded uncertainty is 1° (level of confidence of 95%). In addition, spreading parameter was calculated using surface tension and contact angle measurements.

Specific heat capacities were obtained using the isothermal step method with a Micro DSCIII differential scanning calorimeter from Setaram, France. Calibration was performed using a Joule effect calibration vessel (Setaram) and checked using n-decane and squalane (Sigma-Aldrich ≥99%) as heat capacity standards, their C_p values being taken from the literature [34,35]. Background noise of the Micro DSCIII was less than 3 μW. The experimental technique has previously been described [30], and the standard uncertainty in C_p experimental values is estimated to be 0.002 J g^{-1} K^{-1}. Fig. S11 shows the comparison between the measured heat capacity for n-decane and squalane and literature data and Table S1 (Supplementary material) shows the C_p values obtained for n-decane and squalane in the temperature range (283.15–353.15) K. Table S2 includes the calculation of the different contributions to the uncertainty associated with the determination of the specific heat capacity. For this calculation, squalane was used as the calibration substance, n-heptane as the sample and the chose temperature was $T = 298.15$ K.

3. Results and discussion

Densities and surface tensions for the eight base-oils in the range of temperatures from 283.15 to 323.15 K are reported in Table 2. Both properties decrease linearly with temperature. Densities of several of the studied base-fluid lubricants have been previously published. Guimarey et al. [27] (from the same provider) and Otero et al. [36] published density values of BIOE and TTM with an average absolute deviation (AAD%) of 0.2% and 0.03% from 283.15 to 333.15 K, and of 0.3% and 0.004% at 20 °C, respectively. Liñeira del Río et al. [37] reported the density of TTM from the same provider obtaining a deviation of 0.03%. Density of TMPTO published by Otero et al. [36] deviates by 0.09%. Mia et al. [38] measured PAO32 density at 15 °C obtaining a deviation of 2.2% with our results. Besides, Nasser et al. [26] measured density of PAO32 with a deviation of 0.06%. Liñeira del Río et al. [25] obtained the density value for PAO40 at 313.15 K of 0.8346 g cm^{-3}. Table S3 shows the AAD% between the experimental densities and previously published values measured by our experimental group. The only base oil that presents a difference greater than 0.06% is BIOE. The difference (0.24%) with the results of reference [28] may be due to the use of different lots of this compound. Fig. 1 shows the deviations between the experimental density values of Table 2 for the reference fluid TOTM and literature data [29,39–43].

As can be seen in Fig. 2, there is a clear difference between the behaviour of polyalphaolefins and that of ester based lubricants. PAO6 is the one with lower molecular mass among the PAOs, presenting the lowest density and surface tension of all samples. PAO40 is the one with higher density and surface tension, while PAO20 and PAO32 show very similar properties once they are blends of PAO40 with small amounts of PAO6 to obtain intermediate viscosities.

Synthetic esters are interesting due to their high polarity and biodegradability; their properties depend on the ramification of the alcohol and the size of the acid that composes them, which allows tailoring properties by molecular design. Alkylated aromatic ester lubricants' properties are defined mainly by the aromatic component [44], therefore TOTM and TTM, both trimellitates, are homologous and possible to compare. TOTM with lower molecular weight presents higher density and surface tension as expected. TMPTO shows the highest surface tension of all samples, a result of its higher polarity.

The linear dependence between ln (σ) and ln (ρ) was analysed through the correlation proposed by Pinheiro et al. [17]:

$$\ln(\sigma / \mathrm{mN{\cdot}m^{-1}}) = C + \lambda \ln(\rho / \mathrm{kg{\cdot}m^{-3}}) \tag{1}$$

where C and λ are parameters of the linear regression, stated in Table 3. In Fig. 2, the linear behaviour is perceived for all lubricants. There is an obvious separation in two classes: alkanes and esters, two different natures of lubricants with different chemical composition and physical behaviour.

As regards to wettability, the contact angle, θ, is defined as the angle that the surface of a liquid forms when it comes into contact with a solid surface. The value of the contact angle depends mainly on the relationship between the adhesive forces of the liquid and the solid and the cohesive forces of the liquid itself.

Fig. 3 shows the contact angles measured for all lubricants in the range of temperatures from 293.15 to 323.15 K. Several attempts to determine the contact angle of the base oils were made at 283.15 K, but the results obtained were discarded due to water condensation on the steel surface interfering with the contact angle value. For the

Table 2
Density, ρ[a], and surface tension, σ[b], for the analysed lubricants in the range of temperatures, T[c], from 283.15 K to 323.15 K, and at pressure $p = 0.0991$ MPa[d].

T/K	ρ/g cm^{-3} PAO6	σ/mN m^{-1}	ρ/g cm^{-3} PAO20	σ/mN m^{-1}	ρ/g cm^{-3} PAO32	σ/mN m^{-1}	ρ/g cm^{-3} PAO40	σ/mN m^{-1}
283.15	0.83016	30.24	0.84424	30.63	0.84851	30.94	0.85268	31.38
288.15	0.82702	29.84	0.84118	30.35	0.84560	30.55	0.84949	30.89
293.15	0.82389	29.46	0.83811	29.92	0.84269	30.13	0.84628	30.42
298.15	0.82075	29.08	0.83504	29.51	0.83979	29.80	0.84328	30.00
303.15	0.81763	28.70	0.83199	29.10	0.83690	29.38	0.84028	29.57
308.15	0.81450	28.27	0.82899	28.71	0.83401	28.98	0.83729	29.17
313.15	0.81137	27.91	0.82598	28.32	0.83111	28.59	0.83430	28.78
318.15	0.80824	27.54	0.82297	27.96	0.82817	28.18	0.83131	28.40
323.15	0.80512	27.17	0.81996	27.61	0.82524	27.82	0.82833	28.00
	TMPTO		BIOE		TOTM		TTM	
283.15	0.92352	33.44	0.95253	32.74	0.99562	31.61	0.96144	31.40
288.15	0.92023	33.04	0.94906	32.30	0.99194	31.21	0.95796	30.90
293.15	0.91692	32.70	0.94554	31.88	0.98825	30.80	0.95437	30.40
298.15	0.91360	32.36	0.94202	31.49	0.98454	30.42	0.95090	30.03
303.15	0.91030	31.97	0.93873	31.10	0.98096	30.03	0.94761	29.63
308.15	0.90699	31.64	0.93544	30.72	0.97735	29.67	0.94432	29.28
313.15	0.90368	31.28	0.93217	30.38	0.97366	29.34	0.94101	28.84
318.15	0.90038	30.92	0.92890	30.04	0.97011	28.99	0.93769	28.57
323.15	0.89709	30.57	0.92563	29.69	0.96648	28.63	0.93443	28.17

[a] Combined expanded density uncertainty is $U_c(\rho) = 4 \times 10^{-4}$ g cm^{-3}.
[b] Combined expanded surface tension uncertainty is $U_c(\sigma) = 0.4$ mN m^{-1}
[c] Expanded temperature uncertainty is U(T) = 0.02 K.
[d] Expanded pressure uncertainty is U(p) = 0.0005 MPa (0.95 level of confidence).

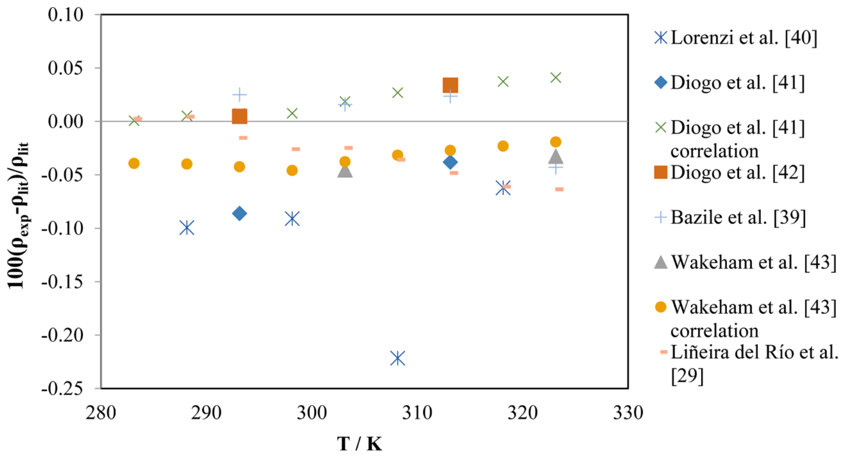

Fig. 1. Deviations between density literature data at atmospheric pressure and TOTM experimental data of Table 2.

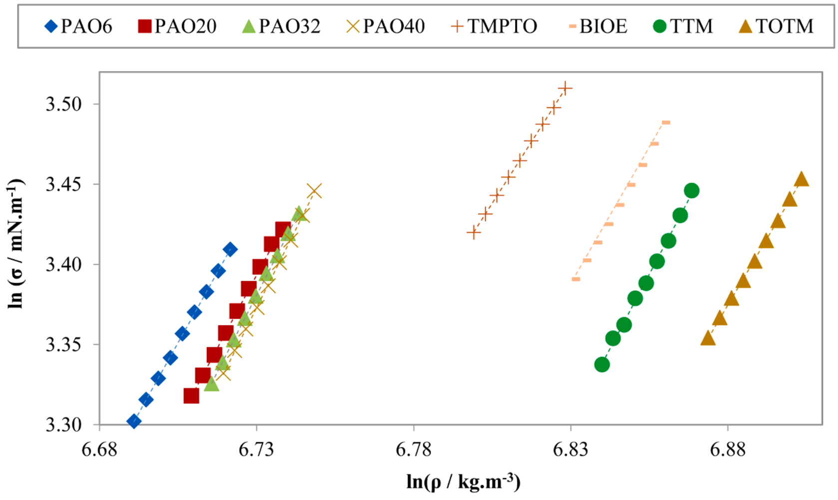

Fig. 2. Linear correlation between ln (σ) and ln (ρ) for the base-fluids.

Table 3
Linear correlation parameters of Eq. (1) for the different lubricants.

	C	*λ*	R^2
PAO6	−20.184	3.5102	0.9998
PAO20	−21.170	3.6498	0.9990
PAO32	−22.459	3.8395	0.9996
PAO40	−22.965	3.9135	0.9997
TMPTO	−17.486	3.0748	0.9998
BIOE	−19.854	3.4030	0.9996
TOTM	−19.507	3.3258	0.9995
TTM	−22.066	3.7141	0.997

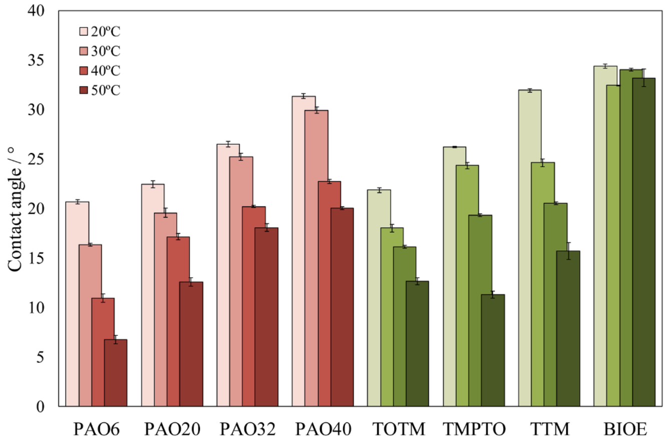

Fig. 3. Contact angles for the eight base oils with a steel surface of a plate at temperatures from 293.15 to 323.15 K.

temperatures tested, high wettability was revealed for all base oils obtaining small contact angles (<< 90°). The better wettability behaviour was obtained for PAO6 and TMPTO base oils with contact angle values of 6.8° and 11.3° at 323.15 K, respectively. An increase can be observed in the contact angle as the degree of polymerisation of the PAOs increases. This can be explained by their surface tension. The contact angle is related by Young's equation with the surface tensions at the different interfaces as follows [45]:

$$\cos(\theta) = \frac{\sigma_{SM} - \sigma_{SL}}{\sigma_{LM}} \tag{2}$$

where σ_{SM} is the surface tension between the surface and the surrounding medium (air), σ_{SL} is the surface tension between the surface and the liquid and σ_{LM} is the surface tension between the liquid and the surrounding medium. Therefore, as the σ_{LM} increases, the cosine of the contact angle decreases, in other words, the contact angle of that liquid increases. Thus, the results obtained for both surface tension and contact angle for polyalphaolefins are consistent. However, this is not the case with ester-based lubricants. There is no direct relationship between the surface tension of these lubricants and the contact angles they form on the stainless steel surface. This may be due to the different composition of these lubricants, which affects the adhesive force of the liquid and the surface (σ_{SL}). The wetting behaviour for most base oils with regard to temperature variation was as expected. It should be noted that no variation with the temperature was observed for the BIOE oil, the differences are within the limits of error of the measurements. For all other base oils, the contact angle decreases as the temperature rises, this trend is the same as for the surface tension. The variations of contact angles range from 1.2° to 16.3° for BIOE and TTM, respectively, in a temperature range of 30 K.

The effect of wettability on lubrication is typically characterized using the spreading parameter, *S*, which can be defined as [46]:

$$S = \sigma_{SM} - (\sigma_{SL} + \sigma_{LM}) \tag{3}$$

Combining Eqs. (2) and (3) the spreading parameter can be described as the difference between the adhesion work between the liquid and the surface (W_A) and the cohesion work between liquid molecules (W_C) [47]:

$$S = \sigma_{LM}\cos\theta - \sigma_{LM} = \sigma_{LM}(\cos\theta - 1) \tag{4}$$

Therefore, adhesive and cohesive forces can be estimated as:

$$W_A \approx \sigma_{LM}(\cos\theta + 1) \tag{5}$$

$$W_C = 2\sigma_{LM} \tag{6}$$

Thus, spreading parameter can be expressed approximately as:

$$S = W_A - W_C \approx \sigma_{LM}(\cos\theta + 1) - 2\sigma_{LM} \tag{7}$$

When $S>0$, $WC<WA$, the liquid spreads completely over the surface in order to decrease its surface energy. When $S<0$, $WC>WA$, the liquid forms a drop on the surface due to cohesive forces between oil molecules which are attracted more strongly to each other.

The spreading parameter values determined by Eq. (7) from experimental surface tension and contact angle for the eight base oils were gathered in Table 4. It can be observed that *S* is negative for all cases studied; this means that the cohesive forces of base oils are higher than the adhesive forces in the solid-liquid interface. As mentioned above, as the temperature increases, the contact angle and surface tension of the liquid decreases. This is because the cohesion work, W_C, that takes place between the molecules of the liquid becomes weaker with an increase of molecular thermal activity and therefore, *S* increases towards zero.

Finally, the specific heat capacity for the base oils in the temperature range (283.15 – 353.15 K) are reported in Table 5. As Fig. 4a shows, there is a clear difference between polyalphaolefins and the rest of the base-oils. PAO40, PAO32, and PAO20 show very similar specific heat capacity (note that PAO32 and PAO20 are mixtures of PAO40 with small amounts of PAO6). PAO6 and PAO40 heat capacity has been reported from 273.15 to 323.15 K by Rudnick [19] with an AAD of 6.8% and 1.3%, respectively. Likely, this average deviation is due to the different sample (PAO6 are oligomers of dimers, trimers and tetramers). For the ester-based lubricants, the two aromatic esters (TTM and TOTM) have the lowest heat capacity as the ring bonds contribute less to the heat

Table 4
Experimental data of the contact angle, θ[a], and spreading parameter, *S*, at different temperatures, *T*[b], and at pressure $p = 0.0991$ MPa[c].

T / K	θ/°	$S \pm u(S)$[d] /mN m^{-1}	θ/°	$S \pm u(S)$ /mN m^{-1}	θ/°	$S \pm u(S)$ /mN m^{-1}	θ/°	$S \pm u(S)$ /mN m^{-1}
	PAO6		PAO20		PAO32		PAO40	
293.15	20.7	−1.9 ± 0.2	22.5	−2.3 ± 0.2	26.5	−3.2 ± 0.2	31.4	−4.5 ± 0.3
303.15	16.4	−1.2 ± 0.1	19.6	−1.7 ± 0.2	25.3	−2.8 ± 0.2	30.0	−3.9 ± 0.3
313.15	10.9	−0.5 ± 0.1	17.2	−1.3 ± 0.1	20.2	−1.8 ± 0.2	22.7	−2.2 ± 0.2
323.15	6.8	−0.2 ± 0.1	12.6	−0.7 ± 0.1	18.1	−1.4 ± 0.2	20.1	−1.7 ± 0.2
	TMPTO		TOTM		TTM		BIOE	
293.15	26.2	−3.4 ± 0.3	21.9	−2.2 ± 0.2	32.0	−4.6 ± 0.3	34.4	−5.6 ± 0.3
303.15	24.4	−2.9 ± 0.2	18.0	−1.5 ± 0.2	24.7	−2.7 ± 0.2	32.5	−4.9 ± 0.3
313.15	19.4	−1.8 ± 0.2	16.2	−1.2 ± 0.1	20.5	−1.8 ± 0.2	34.1	−5.2 ± 0.3
323.15	11.3	−0.6 ± 0.1	12.6	−0.7 ± 0.1	15.7	−1.0 ± 0.1	33.2	−4.9 ± 0.3

[a] Expanded contact angle uncertainty is U(θ) = 1°.
[b] Expanded temperature uncertainty is U(T) = 0.2 K.
[c] Expanded pressure uncertainty is U(p) = 0.0005 MPa. (0.95 level of confidence).
[d] Standard uncertainty for spreading parameter.

Table 5
Specific heat capacity, C_p[a], of the base-fluids at different temperatures, T[b], and at pressure $p = 0.0991$ MPa[c].

T / K	C_p /J g^{-1} K^{-1}			
	PAO6	PAO20	PAO32	PAO40
283.15	2.236	2.128	2.124	2.121
293.15	2.275	2.157	2.152	2.143
303.15	2.301	2.187	2.185	2.186
313.15	2.328	2.218	2.215	2.217
323.15	2.362	2.251	2.246	2.246
333.15	2.396	2.280	2.278	2.281
343.15	2.420	2.314	2.314	2.312
353.15	2.479	2.350	2.348	2.351
	TOTM	TTM	TMPTO	BIOE
283.15	1.831	1.879	1.965	1.972
293.15	1.862	1.908	1.986	1.995
303.15	1.881	1.939	2.014	2.023
313.15	1.910	1.966	2.032	2.045
323.15	1.931	1.996	2.057	2.070
333.15	1.956	2.026	2.084	2.095
343.15	1.983	2.049	2.113	2.122
353.15	2.005	2.092	2.138	2.151

[a] Expanded specific heat capacity uncertainty is U(C_p) = 0.004 J g^{-1} K^{-1}.
[b] Expanded temperature uncertainty is U(T) = 0.2 K.
[c] Expanded pressure uncertainty is U(p) = 0.0005 MPa (0.95 level of confidence).

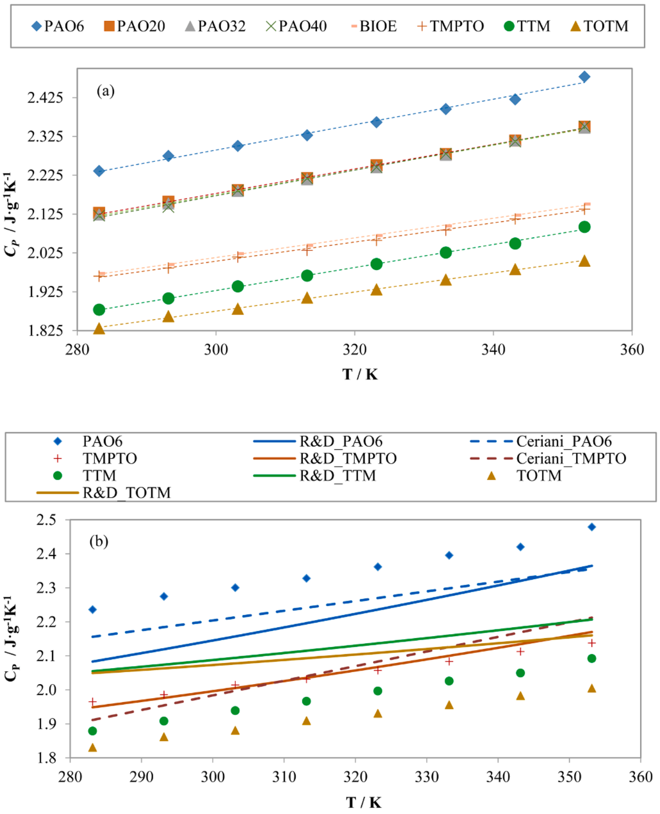

Fig. 4. Specific heat capacity of the base oils: (a) Experimental values, (b) Comparison with the predictions of the group contribution methods of Rùzicka & Domalski [23,49] and Ceriani et al. [22]. The dashed line in Fig. 4a is a guide to the eye.

storage [23]. TTM with higher molecular mass than TOTM presents higher heat capacity. Esters show lower specific heat capacity, due to carbon double bonds and aromatic rings fewer possibilities for heat storage [48]. The carboxylic group is more complex, according to Rùzicka and Domalski [23, 49], C=O bonds have a very good contribution in storage but the –O– contributes negatively due to the lack of vibration modes for this bond. Even though TMPTO as a triester was expected to have a much higher C_p than BIOE, the presence of carbon double bonds lowered its heat capacity near BIOE's values as a diester. TOTM heat capacity has been reported from 297.91 to 368.80 K by Bazile et al. [39] with an AAD of 2.8%.

In Fig. 4b the experimental C_p values of the analyzed liquids with known structures (PAO6, TMPTO, TTM, TOTM) were compared with the data obtained with the group contribution method proposed by Rùzicka and Domalski [23,49] in all the temperature range. The method proposed by Ceriani et al. [22] was only applied to PAO6 and TMPTO because the group parameters for aromatic bonds were not reported. The best predictions were obtained for TMPTO with AAD% of 0.72% for the first group contribution method and 1.89% for the second. For the other compounds, the deviations range from 4% (PAO6 with Ceriani et al.) to 10% (TOTM with Rùzicka and Domalski).

4. Conclusion

In this work, the thermophysical and surface properties of several base oils have been determined experimentally to check if ester-based oils could replace polyalphaolefins in their industrial applications. The following points could be concluded:

Double bonds and aromatic rings raise density because they compact the molecule, so, as expected, ester-based lubricants present higher density than polyalphaolefins. Among esters, trimellitates showed higher density.

The highest surface tensions are observed for ester-based lubricants, this is due to their higher polarity resulting in higher cohesive forces and higher contact angle, which means less wettability. As expected TMPTO has the highest surface tension due to its high polarity.

All base oils studied on the stainless steel surface showed negative values of spreading parameter, but their wettability behaviour improved with increasing temperature. The increase of contact angle for polyalphaolefins was linear with the increase of surface tension and of molecular weight. On the other hand, ester-based lubricants had more controversial contact angle results with no relation to the surface tensions probably due to the oxygen atom and the double bonds in their structure. Comparing between the two trimellitate molecules, TTM is the largest and presents lower surface tension and higher contact angle, resulting in lower wettability than TOTM.

PAOs show higher specific heat capacity, due to the large saturated hydrocarbon structures, than ester-based lubricants. As expected, the trimellitate esters have the lowest specific heat capacity due to their aromatic rings.

PAO6 clearly has the lowest density and surface tension and presents the highest specific heat capacity of all lubricants.

Declaration of Competing Interest

The authors report no conflict of interest.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.tca.2021.178994.

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