Electronic Supplementary Information for

A Dual-Responsive Microemulsion with Macroscale Superlubricity and Largely Switchable Friction

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S1: Experimental Section

Synthesis of Cationic Emulsifiers

Materials for preparing magnetic cationic emulsifiers including didodecyldimethylammonium chloride (DDACl), cerous chloride ($CeCl_3$), ferric chloride ($FeCl_3$) and gadolinium chloride ($GdCl_3$) were purchased from Aladdin Biochemical Technology Co. Ltd., China. All the chemicals have a purity above 98% and were used as sources. Magnetic cationic surfactants didodecyldimethylammonium tetrachlorocerate (DDACe), didodecyldimethyl-ammonium tetrachloroferrate (DDAFe) and didodecyldimethylammonium tetrachlorogadolinate (DDAGd) were synthesized by mixing an equal molar amount of DDABr with $CeCl_3$, $FeCl_3$ and $GdCl_3$, respectively, in methanol and stirring overnight at room temperature.[1, 2] The solvents were then evaporated and the products were dried under reduced pressure at 80 ºC overnight, yielding white, orange and white solids for DDACe, DDAFe and DDAGd, respectively.

Sample Preparation

Aqueous solutions of different cationic surfactants were mixed with EG and an equal volume of n-hexane at desired amounts and stoichiometric ratios in glass serum bottles at room temperature. The mixtures were stirred at 2500 rpm for 10 min to achieve homogenization. All the samples were kept at 20 ± 0.5 ºC and their phase behaviour was recorded after one-month storage. Both the oil and glycol were received from Sinopharm Chemical Reagent Co. Ltd., China and have a purity ≥99%. Ultrapure water (ρ = 18.25 mΩ·cm) was employed to prepare all the sample solutions and microemulsions (MEM).

Sample Characterizations

Electrical conductivity measurements for obtaining the cmc and β of cationic surfactants as well as the conductivity of a MEM were carried out using a DDS-307A analyzer. The magnetism of different cationic surfactants was characterized by a MPMSXL SQUID magnetometry (Quantum Design, USA). The type of various MEM was determined using drop tests after

stained with a hydrophilic dye methylene blue. The internal size distribution and zeta potential of different MEM and emulsions (EM) were analysed by a Nano ZS90 potential analyser (Malvern, UK) equipping with parallel-plate platinum black electrodes spaced 5 mm apart and a 10 mm path-length rectangular organic glass cell. The interfacial tension of DDACe and DDACe/EG mixture at the n-hexane/water interface at different temperatures was examined by a TX-500C spinning drop interface tensiometer (CNG, USA). The freezing point of n-hexane, DDACe MEM and aqueous solutions of DDACe and EG was measured using a DSC 204 differential scanning calorimeter (NATZSCH, Germany) at a cooling rate of 5 °C min^{-1}.

Friction and Wear Tests

The tribological performance of different MEM and EM were determined by a friction and wear tester designed and constructed by Lanzhou Institute of Chemical Physics using a sliding ball-on-disc configuration with steel ball (AISI 52100, Diameter: 3 mm, Hardness: 61-65 HRC) and substrate (AISI 52100, Diameter: 24 mm, Thickness: 8 mm, Hardness: 61-65 HRC, Roughness (R_a): 13 nm) as counterparts.[3, 4] Both the ball and substrate had been cleaned ultrasonically in petroleum ether and methanol before the measurements. The testing temperature range was between -60 and 60 °C, the sliding velocity range was set to be between 0.005 and 0.5 m s^{-1}, the applied normal loads were 2, 4, 6, 8 and 10 N, corresponding to average effective contact normal pressures of 1.4, 1.6, 1.8, 2.0 and 2.2 GPa, respectively, the testing time was 30 min. All the measurements were repeated for at least three times to ensure a reproducibility, the average CoF values were calculated from multiple reproducible measurements. In each measurement, the environmental temperature was rigorously maintained at a target value of ±0.5 °C using an electrothermostatic controller to avoid any possible temperature variations from the friction between two contacting steel surfaces. The switchable frictional behaviour of the DDACe/n-hexane/water/EG mixture was tested by alternately varying system temperatures between 20 and 50 °C *in situ* for closely simulating the scenario in practical applications where the temperature usually changes in real-time.

The wear volume of a steel disc after the frictional tests was determined using a MicroXAM 800 3D surface profiler (KLA-Tencor, USA). The wear tracks on steel substrates after lubricated with different materials were characterized by a JSM-7610 field emission SEM (JEOL, Japan), a MicroXAM 800 3D surface profiler (KLA-Tencor, USA) and an Axioscope 5 optical microscopy (OM, Zeiss, Germany), respectively. The tribochemical reactions of a DDACe MEM or EM during the lubrication process were examined by a K-Alpha XPS (Thermo Scientific, USA). The ECR of n-hexane, water, EG, DDACe solution and the DDACe/EG/n-hexane/water mixture at 20 and 50 °C was measured by an SRV-IV oscillating friction and wear tester (Optimol, Germany).

Molecular Dynamics Simulations

Classical molecular dynamics (MD) simulations were implemented by creating a MD box with dimensions of 40 × 40 × 160 $Å^3$, where Fe substrates with a thickness of ~20 Å and (100) surface was placed at the bottom of the box while a mixture of 1000 EG molecules, 40 DDA^+ and 40 $[CeCl_4]^-$ ions was placed above the Fe substrate. Periodic boundary conditions were imposed on the two orthogonal (*i.e.*, *x* and *y*) directions to mimic infinite planar iron substrate and a wall-boundary condition was exerted on the out-of-plane direction. Polymer Consistent Force Field (PCFF) was used to describe the atomic interactions with atomic partial charges of the EG/DDA^+/$[CeCl_4]^-$ mixture assigned according to the QEq charge.[5] For the non-bonded atomic interactions, 12-6 Lennard-Jones (LJ) potential with a cutoff distance of 10.0 Å was applied to describe the van der Waals forces between atoms, whereas standard Coulomb potential was employed to mimic the electrostatic interactions evaluated with the particle-particle particle-mesh (PPPM) algorithm. For the Ce atom in the $[CeCl_4]^-$ ion, the 126- LJ parameters were taken from a recent study by Kanhaiya et al..[6]

Specifically, energy minimizations were firstly conducted to relax the system with an energy and force tolerances of 0.00001 Kcal mol^{-1} and 0.00001 Kcal mol^{-1} $Å^{-1}$, respectively. Then MD simulations with 100,000 timesteps were carried out to further relax the systems

under canonical ensemble at temperatures of 20 and 50 °C. At last, MD simulations with 10,000,000 timesteps were performed to capture the structural properties of the EG/DDA^+/$[CeCl_4]^-$ mixture that was in contact with the Fe substrate. During the whole simulation process, the movement of atoms was controlled by the classical Newton's motion, in which the velocity-Verlet algorithm with a timestep of 1.0 fs was applied to integrate the classic Newton's equation. The temperature was controlled by the Nose-hoover thermostat.

S2: Supplementary Figures and Tables

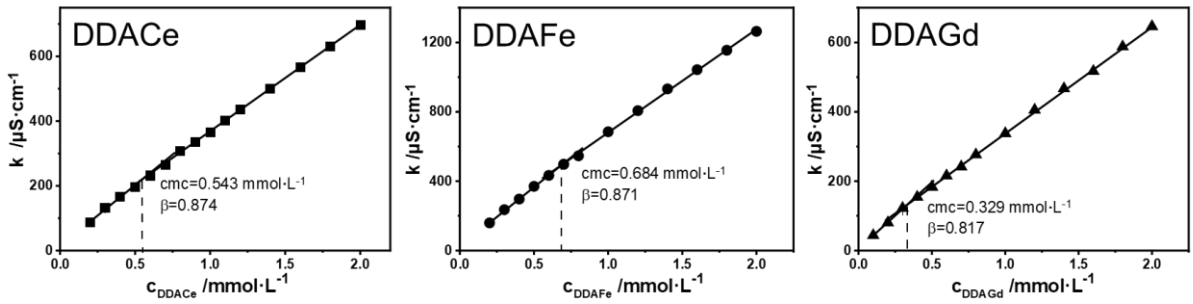


Figure S1. Electrical conductivity measurements of surfactant DDACe, DDAFe and DDAGd. T = 20 ºC.

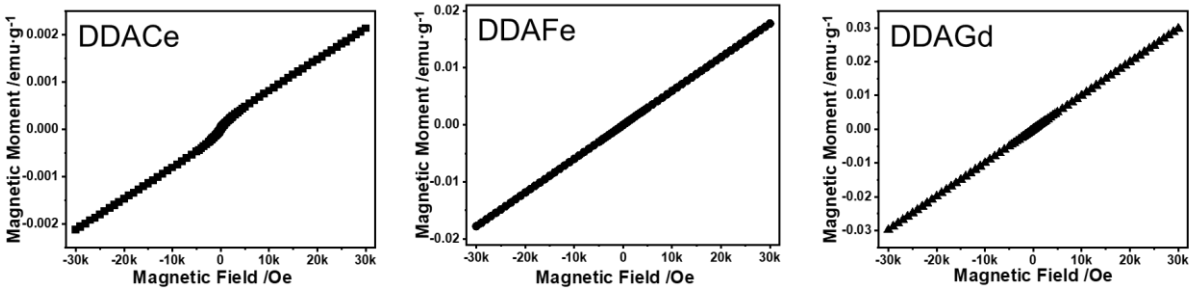


Figure S2. SQUID magnetometry results of DDACe, DDAFe and DDAGd. T = 20 ºC. The magnetic moment generally followed a linear relationship with the strength of an applied magnetic field, indicative of a paramagnetic nature of the three kinds of surfactants.[1, 2]

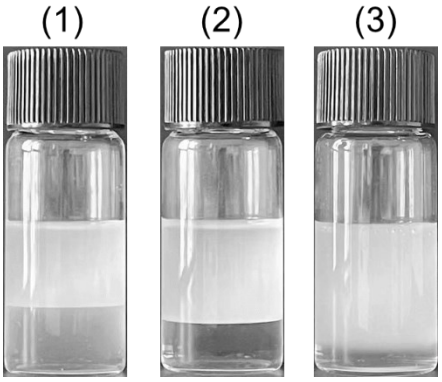


Figure S3. Photographs of turbid EM formed by the DDACe/EG/water/n-hexane mixture at different stoichiometric ratios: *(1)* 47.78 wt% DDACe solution, 13.18 wt% EG, 39.04 wt% n-hexane; *(2)* 37.42 wt% DDACe solution, 13.75 wt% EG, 48.83 wt% n-hexane; *(3)* 16.84 wt% DDACe solution, 12.07 wt% EG, 71.09 wt% n-hexane. T = 20 ºC.

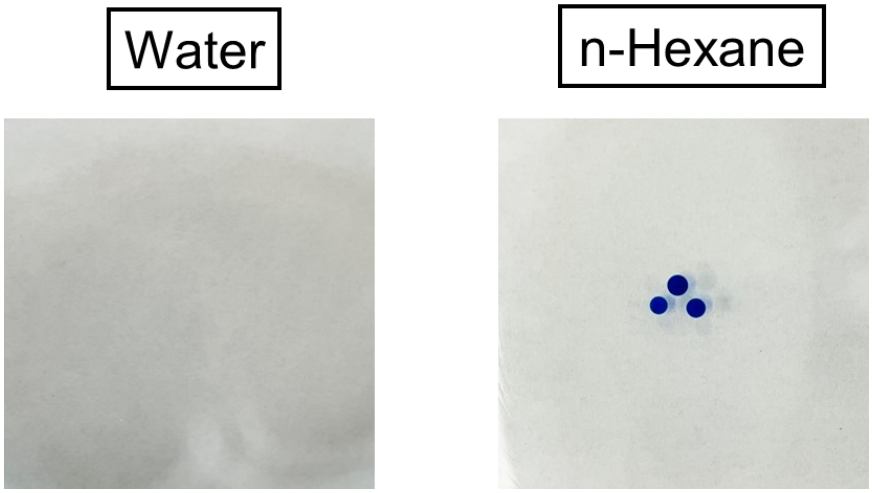


Figure S4. Photographs of ~5 μL DDACe MEM droplets (stained with methylene blue) after added into water and n-hexane, respectively. T = 20 ºC.

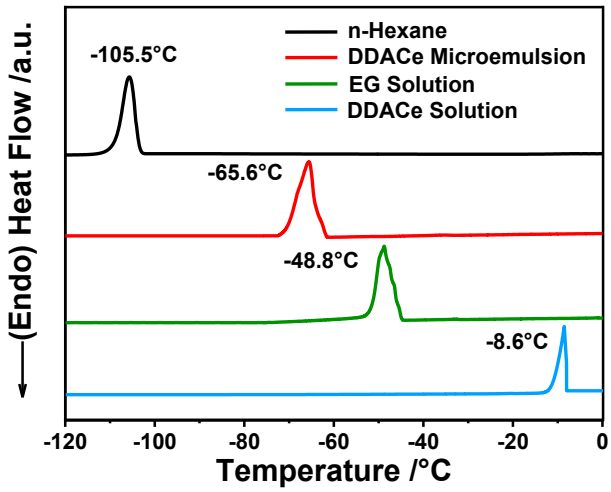


Figure S5. Differential scanning calorimetry (DSC) spectra of n-hexane, 15 mmol L^{-1} DDACe and 40 wt% EG solutions, and a MEM consisting of 35.43 wt% DDACe solution, 26.03 wt% EG and 38.54 wt% n-hexane, a surfactant concentration of 15 mmol L^{-1} and a volume ratio of water-to-oil = 1:1 in a temperature range between -120 and 0 ºC. The results suggest an excellent anti-freezing property of the DDACe MEM.

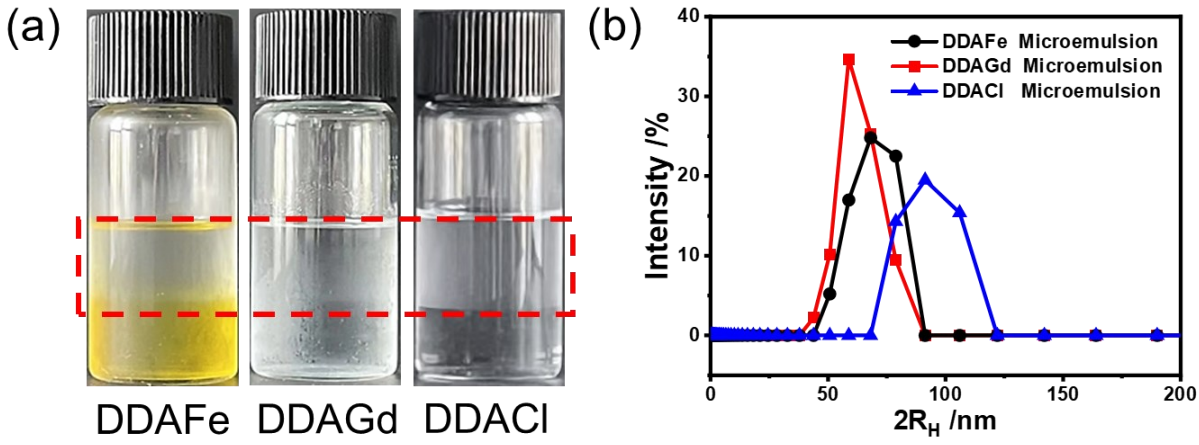


Figure S6. (a) Photographs and (b) internal size distribution of representative DDAFe, DDAGd and DDACl MEM. All the MEM contained 35.43 wt% surfactant solution, 26.03 wt% EG and 38.54 wt% n-hexane. The surfactant concentration was 15 mmol L^{-1}, and the volume ratio between the aqueous and oil phases was 1:1. T = 20 °C.

Table S1. Phase behaviour and colloidal stability of the surfactant/EG/water/n-hexane mixtures with a constant amount of EG, water and oil (*v*:*v*:*v* = 0.36:1:1) but different surfactant concentrations at 20 °C. The results suggest a highest thermodynamic stability of the DDACe MEM.

Concentration ($mmol \cdot L^{-1}$)	DDACe	DDAFe	DDAGd	DDACl
25×10^{-3}	○	○	○	○
21×10^{-3}	○	○	○	○
20×10^{-3}	●	⦿	⦿	⦿
15×10^{-3}	●	⦿	⦿	●
12×10^{-3}	●	○	●	●
11×10^{-3}	○	○	○	○
5×10^{-3}	○	○	○	○
0×10^{-3}	×	×	×	×

● Stable MEM;

⦿ Unstable MEM;

○ EM;

× No formation of EM.

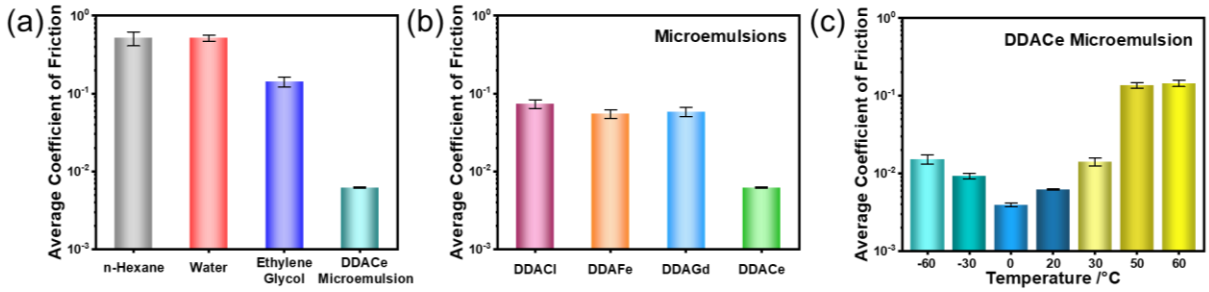
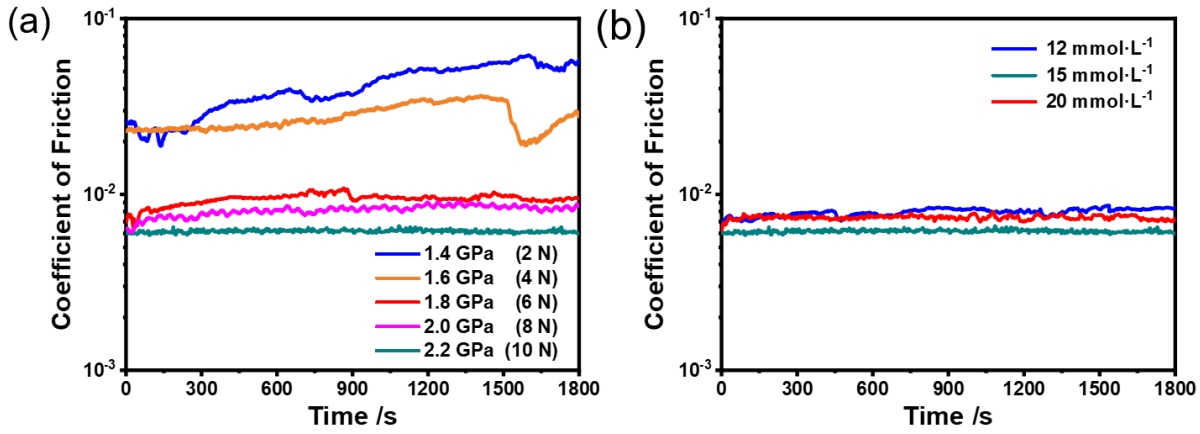


Figure S7. (a) Average CoF of n-hexane, water, EG and DDACe MEM at room temperature. (b) Average CoF of MEM prepared with different surfactants at 20 ºC. (b) Average CoF of DDACe MEM in a temperature range from -60 to 60 ºC. All the MEM (or EM) were constituted of 35.43 wt% surfactant solution, 26.03 wt% EG and 38.54 wt% n-hexane, a constant surfactant concentration of 15 mmol L^{-1} and a volume ratio of water-to-oil = 1:1.



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153 **Figure S8.** Effect of (a) applied normal load pressure (or normal load) and (b) surfactant

154 concentration on the CoF of a DDACe MEM (containing 35.43 wt% DDACe solution, 26.03

155 wt% EG and 38.54 wt% n-hexane, c_{DDACe} = 15 mmol L^{-1}, v_{water}:v_{oil} = 1:1). T = 20 ºC.

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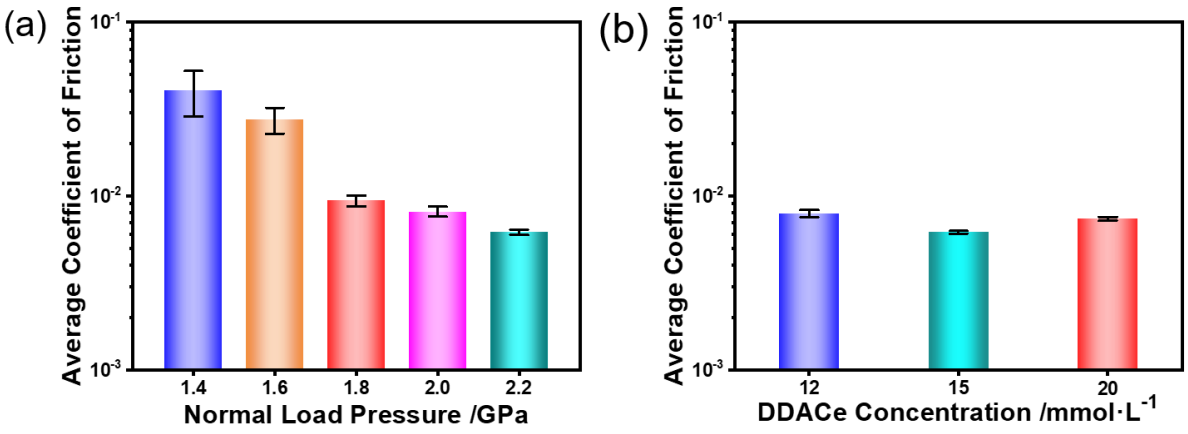

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158 **Figure S9.** Average CoF of a DDACe MEM (consisting of 35.43 wt% DDACe solution, 26.03

159 wt% EG and 38.54 wt% n-hexane, c_{DDACe} = 15 mmol L^{-1}, v_{water}:v_{oil} = 1:1) at different normal

160 load pressures (a) and surfactant concentrations (b). T = 20 ºC.

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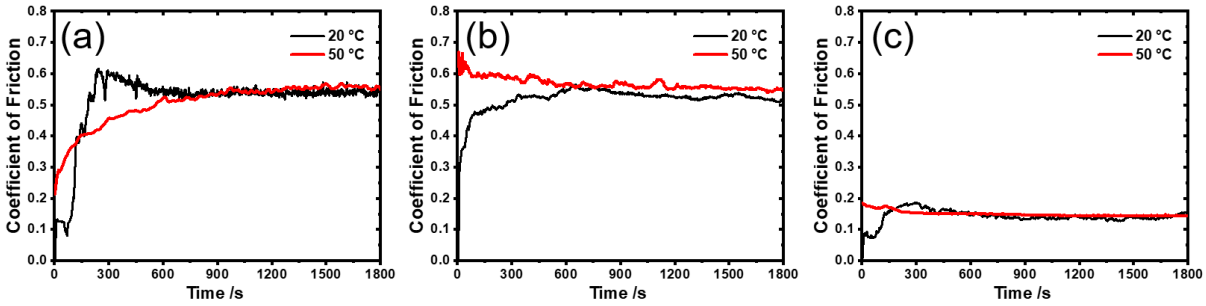


Figure S10. CoF of (a) n-hexane, (b) water and (c) EG at 20 and 50 °C under an applied normal load pressure of 2.2 GPa (*i.e.*, 10 N normal load) and sliding velocity of 0.1 m s^{-1}.

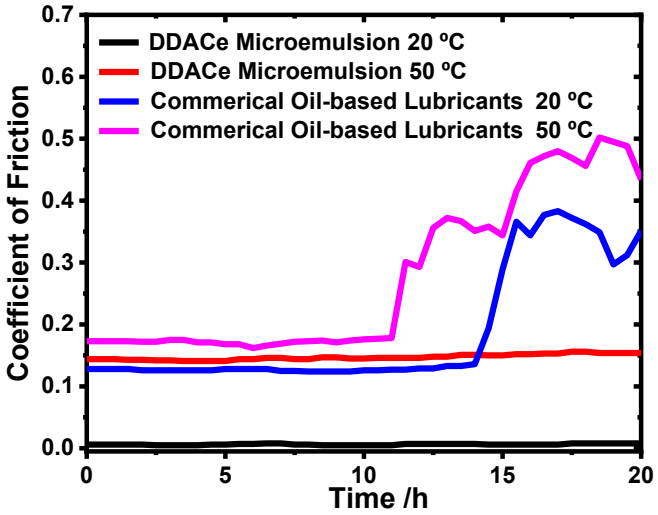


Figure S11. Comparison in the CoF between DDACe microemulsion and a commercially available general-purpose oil-based lubricants (a mixture consisting of liquid paraffin and additives) during a continuous measurement for 20 h at 20 and 50 °C. The applied normal load pressure was 2.2 GPa (*i.e.*, 10 N normal load) and the sliding velocity was 0.1 m s^{-1}.

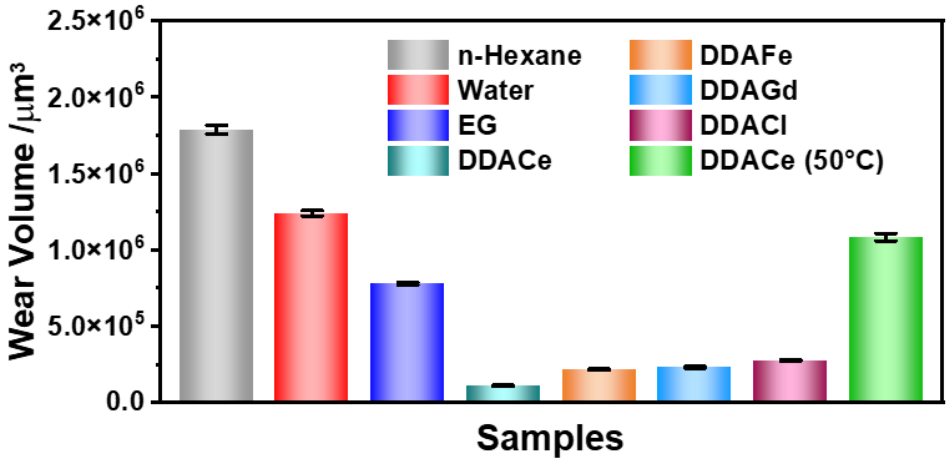


Figure S12. Wear volume of steel substrates after lubricated with n-hexane, water, EG and MEM (or EM) stabilized by different surfactants.

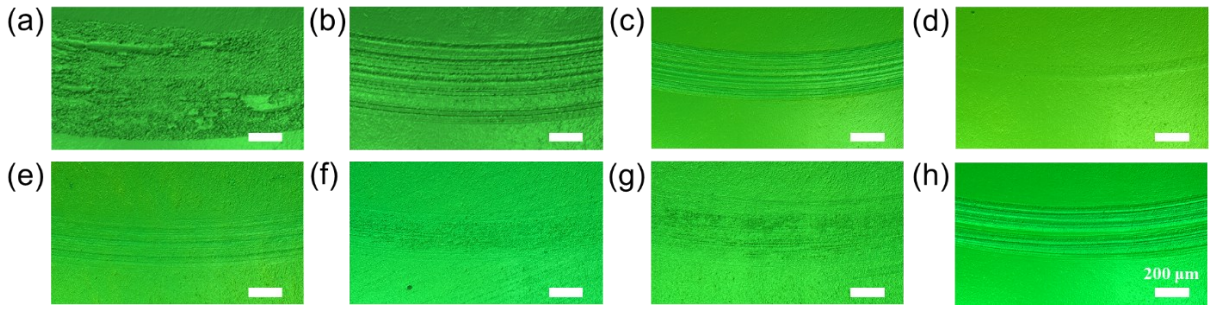


Figure S13. Surface topography of steel substrates after lubricated with (a) n-hexane, (b) water, (c) EG, (d) DDACe MEM, (e) DDAFe MEM, (f) DDAGd MEM, (g) DDACl MEM and (h) 50 ºC DDACe EM using 3D surface profilometer. All the MEM (or EM) contained 35.43 wt% surfactant solution, 26.03 wt% EG and 38.54 wt% n-hexane, a constant surfactant concentration of 15 mmol L^{-1} and a volume ratio of water-to-oil = 1:1.

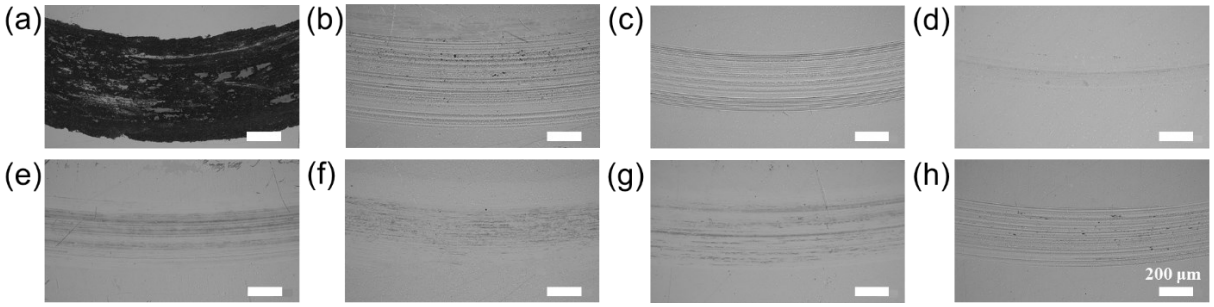


Figure S14. Optical micrographs of steel substrates after lubricated with (a) n-hexane, (b) water, (c) EG, (d) DDACe MEM, (e) DDAFe MEM, (f) DDAGd MEM, (g) DDACl MEM and (h) 50 ºC DDACe EM. All the MEM (or EM) were constituted of 35.43 wt% surfactant solution, 26.03 wt% EG and 38.54 wt% n-hexane, a constant surfactant concentration of 15 mmol L^{-1} and a volume ratio of water-to-oil = 1:1.

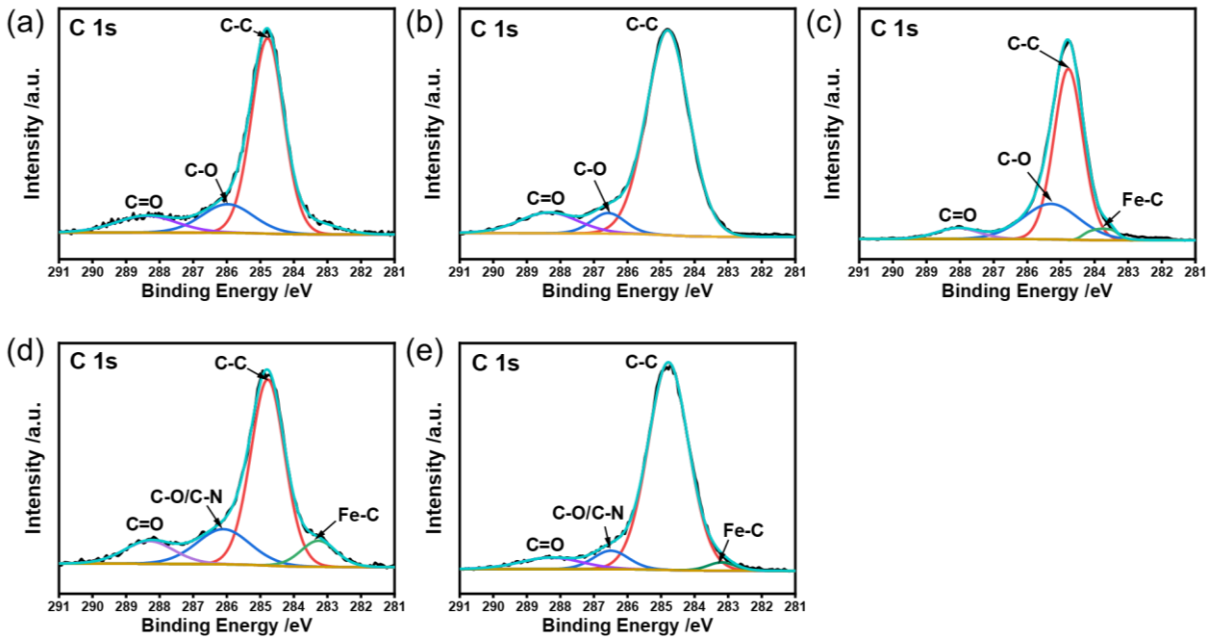
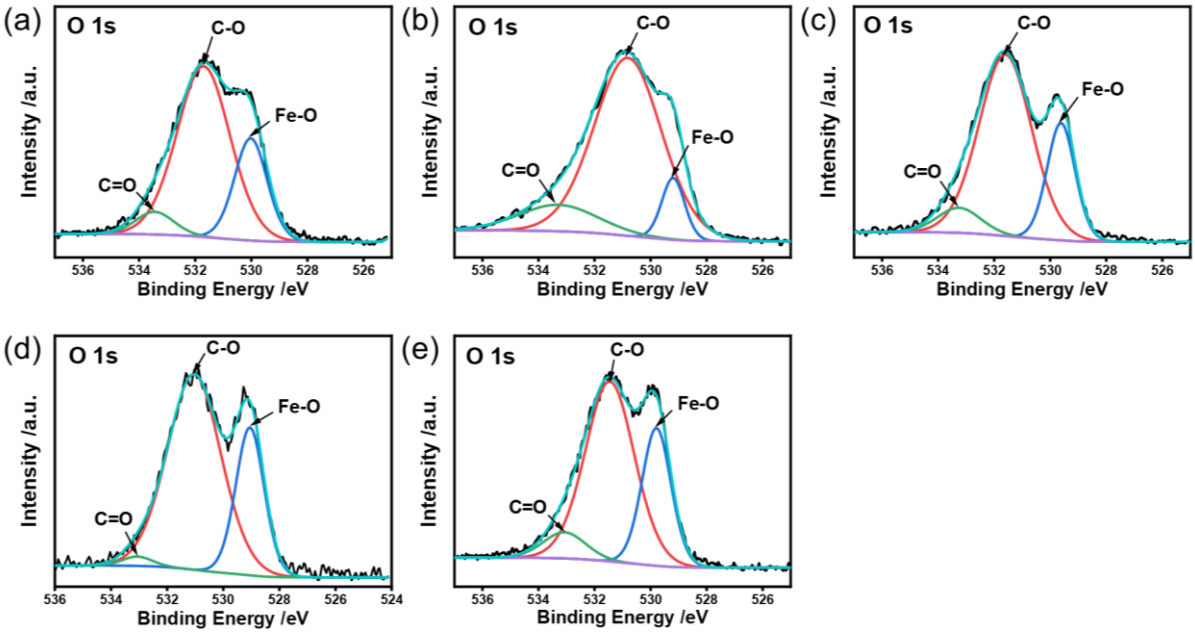


Figure S15. XPS C 1s spectra of (a) n-hexane, (b) water, (c) EG, (d) DDACe MEM and (e) 50 ºC DDACe EM. All the MEM (or EM) were constituted of 35.43 wt% DDACe solution, 26.03 wt% EG and 38.54 wt% n-hexane, a constant DDACe concentration of 15 mmol L^{-1} and a volume ratio of water-to-oil = 1:1.



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197 **Figure S16.** XPS O 1s spectra of (a) n-hexane, (b) water, (c) EG, (d) DDACe MEM and (e) 50

198 ºC DDACe EM. All the MEM (or EM) consisted of 35.43 wt% DDACe solution, 26.03 wt%

199 EG and 38.54 wt% n-hexane, a constant DDACe concentration of 15 mmol L^{-1} and a volume

200 ratio of water-to-oil = 1:1.

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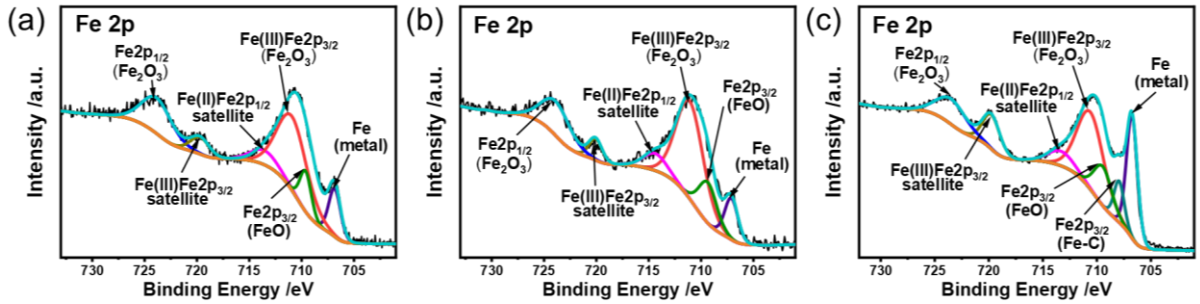

Figure S17. Additional XPS Fe 2p spectra of (a) n-hexane, (b) water and (c) EG.

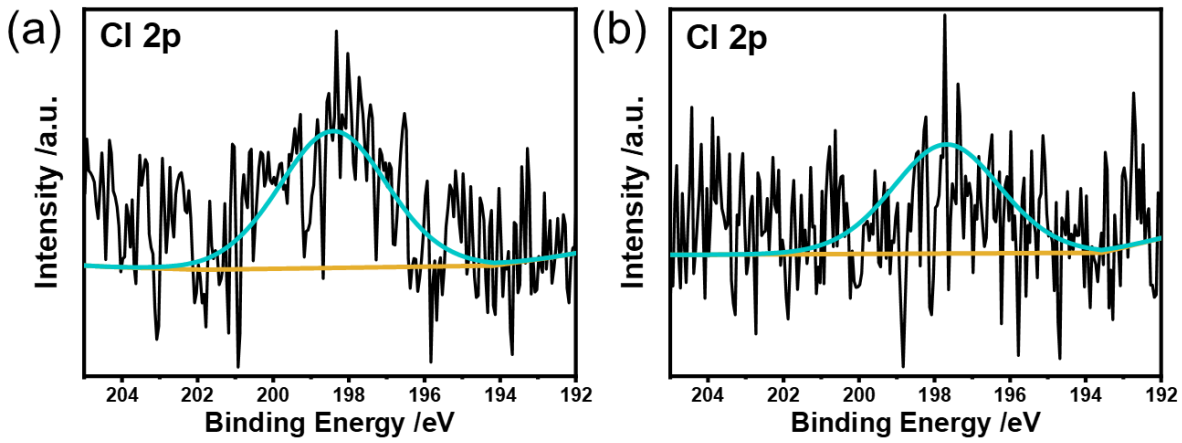

Figure S18. XPS Cl 2p spectra of (a) DDACe MEM and (b) 50 ºC DDACe EM. Both the MEM and EM consisted of 35.43 wt% DDACe solution, 26.03 wt% EG and 38.54 wt% n-hexane, a constant DDACe concentration of 15 mmol L^{-1} and a volume ratio of water-to-oil = 1:1.

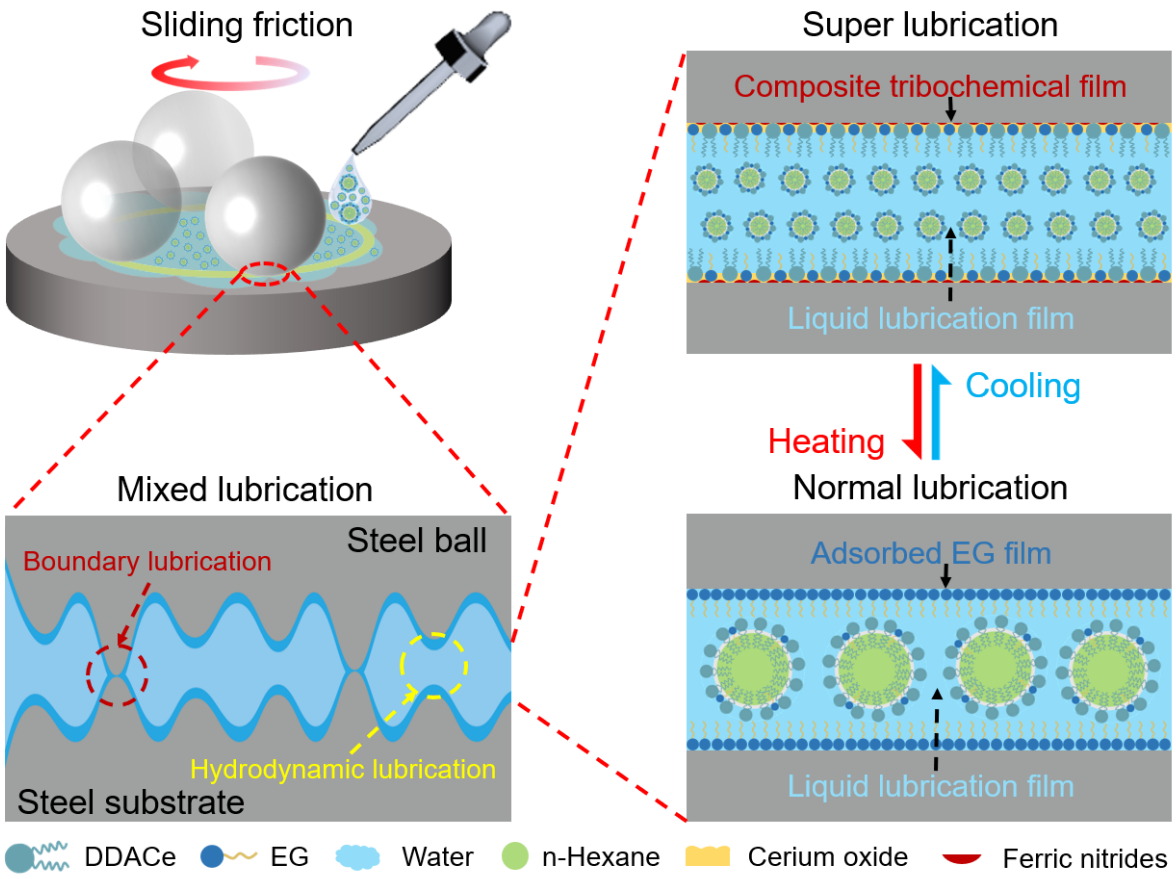

Figure S19. Schematic illustration of possible mechanism for thermally responsive superlubrication of the DDACe/EG/n-hexane/water mixture.

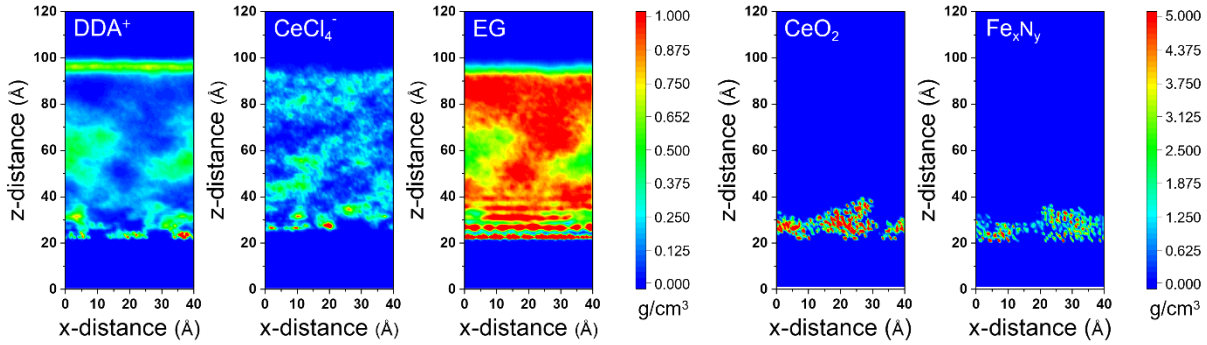

Figure S20. 2D density profiles of the DDACe/EG mixture and its tribochemical products in the MD box at 20 °C. The scale bar indicates the density of different compounds in the studying distance range.

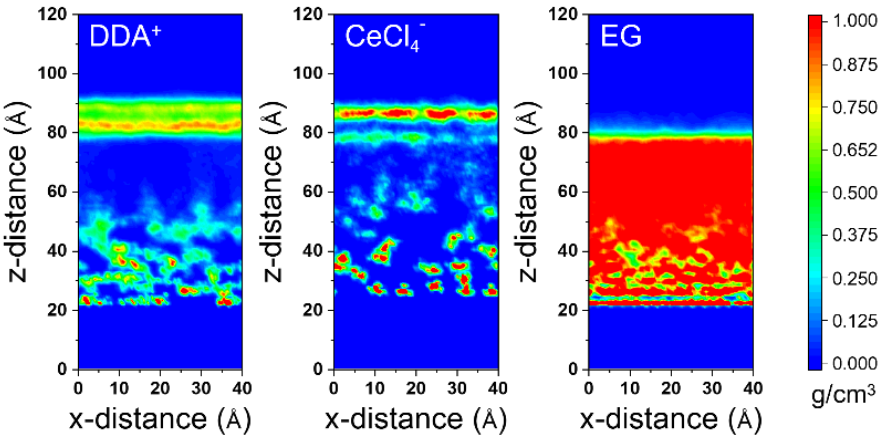

Figure S21. 2D density profiles of the DDACe/EG mixture in the MD box at 50 °C. The scale bar indicates the density of different compounds in the studying distance range.

S3: Supplementary Text

Calculation of The Thickness of Liquid Lubrication Films

The thickness of liquid lubricating films between the two contacting steel surfaces was calculated according to the Hamrock-Dowson formula:[7, 8]

$$H_c^* = \frac{h_c}{R_x} = 2.69 \frac{G^{*0.53} U^{*0.67}}{W^{*0.067}} (1 - 0.61e^{-0.73k}) \quad \text{(Eq. S1)}$$

$$G^* = \alpha E \quad \text{(Eq. S2)}$$

$$W^* = \frac{w}{E R_x^2} \quad \text{(Eq. S3)}$$

$$U^* = \frac{\eta u}{E R_X} \quad \text{(Eq. S4)}$$

$$\frac{2}{E} = \frac{1-\mu_1^2}{E_1} + \frac{1-\mu_2^2}{E_2} \quad \text{(Eq. S5)}$$

$$k = 1.03 \left(\frac{R_x}{R_y}\right)^{0.64} \quad \text{(Eq. S6)}$$

$$\frac{d}{2} = \left(\frac{3Rw}{4E}\right)^{\frac{1}{3}} \quad \text{(Eq. S7)}$$

$$R = \frac{Ed^3}{6w} \quad \text{(Eq. S8)}$$

Here H_c^* and h_c are the dimensionless and dimensional central film thickness, respectively; G^* and E are the dimensionless and equivalent elastic moduli, respectively; α (4 GPa^{-1}) refers to the viscosity-pressure coefficient of lubricants; W^* and w (10 N) are the dimensionless and dimensional loads, respectively; U^* and u (0.10 m s^{-1}) represent the dimensionless and dimensional sliding velocity; η (90 mPa·s at 20 °C and 138 mPa·s at 50 °C) is the viscosity of the liquid lubricants. μ_1 (0.3) and E_1 (206 GPa) are the Poisson's ratio and elastic modulus for the steel ball, while μ_2 (0.3) and E_2 (206 GPa) are the Poisson's ratio and elastic modulus for the steel disc. k is the ellipticity. According to the Hertzian contact theory (Eq. S7), the equivalent radius (R) of a steel ball can be calculated from the diameter of a wear scar (112 μm at 20 °C and 239 μm at 50 °C) using Eq. S8, i.e., $R=R_x=R_y$ (5.3 mm at 20 °C and 51.3 mm at

245 50 °C) DDACe EM. As a consequence, the thickness of liquid films between the tribopair was
246 calculated to be ~32 nm for DDACe MEM at 20 °C and ~123 nm for DDACe EM at 50 °C.
247 The thickness-roughness ratio (λ) of liquid lubrication films was further calculated to
248 probe the physical lubricating mechanism of MEM or EM lubricants:
249 $$\lambda = \frac{h_c}{\sqrt{\sigma_1^2+\sigma_2^2}}$$ (Eq. S9)
250 Where σ_1(18 nm at 20 °C and 32 nm at 50 °C) and σ_2 (18 nm at 20 °C and 32 nm at 50 °C)
251 are the surface roughness of a worn steel ball and disc, respectively. The lubrication nature can
252 be evaluated according to: 1) λ<1 for boundary lubrication; 2) 1≤λ≤3 for mixed lubrication; and
253 3) λ>3 for hydrodynamic lubrication, respectively.
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References

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