Active Control of Boundary Lubrication of Ceramic Tribo-Pairs in Sodium Dodecyl Sulfate Aqueous Solutions

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Abstract
The objective of the study is to actively control friction between engineering ceramics in underwater applications. By designing a proper electrode system and applying an external electric field, the active control of friction between Al2O3 plate and ZrO2 ball in sodium dodecyl sulfate (SDS) aqueous solutions has been realized, which is different from the previous studies of potential-controlled boundary lubrication where at least one part of tribo-pairs is a conductor. Reversible change of friction coefficient has been observed in the range from 0.12 to 0.35. An indirect electric field-assisted adsorption/desorption model has been proposed to explain the observed phenomena. The addition of inorganic salts containing counterions to the SDS solution or increasing the concentration of SDS can shorten the response time of friction to the variation of the applied electric field by facilitating the formation of SDS micelles. This opens a new way to realize the active control of friction for insulative tribo-pairs without corrosion.

Graphical Abstract

Keywords Water-based lubrication · Surfactant · Ceramic friction pairs · Boundary lubrication · Potential-control

1 Introduction
Since 1980s, engineering ceramics have been increasingly employed for structures and components of machine systems because of their excellent properties such as high corrosion resistance, high wear resistance, high melting point, and low density [1]. Oxides, nitrides, and carbides ceramics including Al2O3, ZrO2, Si3N4, and SiC offer many possibilities
of producing components with beneficial combinations of properties with good tribological performance [2].

Recently, researches on tribology of ceramic/metal and ceramic/ceramic pairs in sliding contact become important for a lot of engineering applications, including roller bearings, journal bearings, seal rings, valves, and parts for internal combustion engines [3]. For example, Aronov and Mesyef [4] investigated wear mechanisms in sliding contact of partially stabilized zirconia rubbed against itself and against different kinds of steels at high temperatures and exhaust gas environment in combustion systems. Johannes et al. [5] found that advanced ceramics show potentials to increase heat transfer and improve power density of lubricated clutch systems. Yamamoto et al. [6] focused on rolling contact fatigue life of ceramic bearings in water and found that all ceramic (Si₃N₄, ZrO₂, SiC) bearings possess 15–70 times longer rolling fatigue life than all AISI 440C steel bearings and, thus, could be especially applicable to corrosive environment in various cleaning equipment for manufacturing semiconductors integrated circuits and liquid crystal display panels, food processing machinery, chemical plants, etching equipment, and so on.

Another advantage of the ceramic/metal and ceramic/ceramic tribo-pairs in sliding contact is their compatibility with environmentally friendly lubricants [7], especially water-based lubricants, which are regarded as the perfect candidate compared with conventional oil and grease lubricants, owing to the excellent properties of ecofriendly, high fluidity and superb thermal conductivity. Water-based lubricants have been widely researched and applied in the fields of ship propulsion system [8], marine transportation, oil and coal mining [9], deep-seabed mining robot vehicles, and so on. At low speed and high load conditions, additives including surfactants [10] or nanoparticles [11] are added to improve boundary lubrication of water. In addition, some laboratory studies have shown that ultra-low friction or superlubricity could be achieved with ceramic–ceramic tribo-pairs under acidic aqueous solutions [12–14]. Up to now, the anti-friction mechanisms involved in the water-based lubrication of ceramic tribo-pairs have included adsorbed boundary films, tribochemical reactions [14], hydration lubrication, double electric layer repulsion, and hydrodynamic lubrication effect [15].

Like oil lubrication and solid lubrication, reducing friction is not the sole objective of water-based lubrication. For the past decades, many researchers have been pursuing active control of friction and wear [16, 17], in which some special external mechanical, thermal, optical, electrostatic, or electrochemical stimuli are imposed to tribo-systems in order to actively tune the magnitude of friction in situ. Particularly, effects of an electric field on tribological behavior of materials have been mostly studied in various aqueous and nonaqueous solutions with or without additives of various kinds of salts [18], surfactants [19], ionic liquids [20], nanoparticles [21, 22], and antiwear additives [23–25]. This emerging technology is usually called as potential-controlled boundary lubrication or potential-controlled friction. At present, the basic mechanisms of potential-controlled boundary lubrication have been almost clarified, including the potential-assisted reversible tuning between adsorption and desorption [26], morphology transition of the responsive constituents of additives at relatively mild electric field conditions, and the electrochemical or triboelectrochemical reactions at strong electric fields, such as electrolysis of solutions [27, 28], oxidation, or selected oxidation of metal substrates [29].

In the previous potential-controlled boundary lubrication experiments, however, it is required that at least one part of the tribo-pairs to be controlled is a conductor and serves as the working electrode [16, 30], which means it is not applicable to the tribo-pairs made of insulators such as ceramic–ceramic, polymer–polymer or ceramic–polymer pairs. In addition, in water-based lubrication, the surface potential acted on the sliding surfaces should be strictly limited to the range of electrochemical window for prevention of excessive corrosion of the working electrode. In this work, an alternative design of electrochemical cell, where the working and counterpart electrodes are completely separated from the sliding pairs, is proposed and, thus, can be applied to all tribo-pairs made of any kinds of materials.

**Fig. 1** Schematic of the testing module combining an electrochemical workstation (or a DC power supply) and a tribometer.
demonstrate the effect of the new design, tribology tests on ZrO2 ball on Al2O3 plate in sodium dodecyl sulfate (SDS, a common surfactant) aqueous solution were conducted under varying electric field conditions. It has been discovered that the friction coefficient can be tuned in a relative wide range as like in the cases of ceramic balls on metal plates reported previously [19], but with a longer response time. An indirect adsorption model has been proposed to explain the observations. Furthermore, it is found that adding inorganic salts or increasing the concentration of SDS can shorten the response time. The mechanism has been elucidated by analyzing the state of SDS micelles at the solid–liquid interface.

2 Experimental Details

2.1 Materials

Sodium dodecyl sulfate (SDS, 95%, Beijing Solarbio Science & Technology Co., Ltd.) was selected as the anti-friction additive in water in this work. The SDS and NaCl (99.5%, Sinopharm Chemical Reagent Beijing Co., Ltd.) were dissolved in the deionized water (DI water) with resistivity of 18.2 MΩ cm in the concentration range of 0 mM to 10 mM. The prepared aqueous solutions were used in the tribology tests.

ZrO2 balls with diameter of 6.35 mm and surface roughness Ra of ~20 nm were used as the upper friction pair. Al2O3 plates (10 × 20 × 2 mm3) were used as the lower friction pair, and its Ra was about 3 μm measured on a 3D optical surface profilometer (Zygo NexView, USA). A steel ball holder was designed and served as the working electrode, and a steel plate (20 × 20 × 2 mm3) placed aside the Al2O3 plate was used as the counter electrode, as shown in Fig. 1. In the three-electrode system, an Ag/AgCl electrode was used as the reference electrode with \( E_0 = 0.2224 \text{ V} \) relative to the standard hydrogen electrode.

2.2 Friction Tests and Electrochemical Measurements

Figure 1 shows the experimental setup, which merges a tribometer (UMT-3, Bruker, Germany) with either an electrochemical workstation (PGSTAT302N, Auto, Switzerland) or a direct current (DC) power supply. Before friction tests, both the upper and lower specimens were cleaned in an ultrasonic bath with acetone, ethanol, and DI water sequentially, and dried with compressed air. The force applied to the ball-on-flat surface was 3 N, corresponding a pressure of 0.98 GPa. Tests were performed at the sliding speed of 10 mm/s over a 5 mm track. The reciprocating frequency was set at 1 Hz. All the tests were carried out at room temperature about 25 °C.

An external electric field was applied on either with a two-electrode system or a three-electrode system. The inner and outer diameters of the bottom ring for the ball holder (stainless steel, worked as the working electrode in the electrochemical measurements) were 4.9 mm and 9.9 mm, respectively. During the friction tests and electrochemical measurements, the submergence of the ball holder into the SDS solution was kept in the range between 1 and 2 mm, while the counter electrode steel plate was always immersed in the solution. For the three-electrode system, a reference electrode of Ag/AgCl was placed close to the ball holder with a gap about 1 mm. A negative value of voltage (in both of the two-electrode and three-electrode systems) means that the working electrode is connected to the negative pole of the DC supply or the electrochemistry workstation, and vice versa.

Considering that the open-circuit potential (OCP) of the steel holder (working electrode in Fig. 1) in SDS aqueous solution was about −0.023 V versus Ag/AgCl; during the experiments, the surface potential of the holder was set either as −0.6 V or +0.2 V when the three-electrode system was used. In general, ad- and desorption behaviors (physical process) and electrochemical behaviors (chemical process) are distinguished by thermodynamic potential window. Here, we present the C–V curves (electric current versus surface potential) by sweeping surface potentials from 0 to +2 V, then to −2 V, and back to 0 V. According to the results shown in Fig. 2, when the surface potential is in the range of −0.6 to +0.2 V, the current is less than 0.2 mA. The current increases exponentially outside of the thermodynamic potential window, indicating that electrochemical reactions occur under overpotentials. When switched to the two-electrode system, 2 V was applied on either negatively or positively, which was a little bit higher value compared with that in the three-electrode system. The surface potential or voltage ranges was so selected in the following experiments that profound electrolysis of the test SDS solution was prevented. After friction tests, the morphologies spected on an optical microscope (Keyence, Japan) and a 3D optical surface profilometer (Zygo NexView).

2.3 Characterization of Adsorption Behavior at Solid–Liquid Interface

A quartz crystal microbalance (QCM, Q-sense E4 system, Biolin Scientific, Sweden) was used to measure adsorption/desorption of SDS molecules on solid surfaces. The changes of both resonance frequency (\( \Delta f \)) and dissipation (\( \Delta D \)) due to the mass variations of ions or molecules on the Al2O3-coated quartz crystal sensors per unit area were recorded by the QCM. The adsorption measurements were performed in the following 4 steps. The first step is to start measurement in air to find the base resonance frequencies till approaching relatively stable values. The second step is
to inject pure water into the testing module by an external pump with the speed of 200 μL/min through a PTFE tubing of 0.75 mm in inner diameter and 22.5 cm in length, monitoring the variations of $\Delta D$ and $\Delta f$ in water till they keep on stable values for at least 180 s. The third step is to switch the injection from pure water to the SDS solution to be tested, recording the changes in resonance frequencies and dissipation caused by adsorption or desorption of the

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**Fig. 2** Measurements of $C$–$V$ curves at room temperature in aqueous solution with 1 mM SDS and 10 mM NaCl by using steel plate as counter electrode, ball holder (steel) as work electrode, and Ag/AgCl as the reference electrode. **b** Is a partial enlargement of **a**

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**Fig. 3** Friction coefficient of the Al$_2$O$_3$ plate vs. ZrO$_2$ ball versus time with the mixed solution of 1 mM SDS and 10 mM NaCl working as the lubricant under different applied potentials in two-electrode system
ions or surfactants for the third, fifth, seventh, and ninth overtones at 298 K. The final step is to re-inject pure water into the testing module for cleaning the conduit and vessel.

If the measured value of $\Delta D$ is smaller than $10^{-6}$, then the adsorbed film can be regarded as rigid, and Sauerbrey equation can be used to calculate the adsorbed mass changes ($\Delta m$) according to the frequency changes, as shown in Eq. (1) [31, 32]:

$$\Delta m = - C_0 \frac{\Delta f}{N},$$

where $C_0$ is a constant of 17.7 ng/Hz cm$^2$, which is related to the properties of the quartz crystal, and $N$ is the overtone of the oscillations. In this work, the fifth overtone was used for the calculation because of its better signal-to-noise ratio among the different overtones.

### 3 Results and Discussion

#### 3.1 Active Control of Friction Between Ceramics Under Water Lubrication Conditions

Figures 3 and 4 show the friction test results with two-electrode and three-electrode systems, respectively. After a running-in period lasting 800 s, the applied voltage (Fig. 3) or the
surface potential (Fig. 4) was periodically changed between +2 and −2 V (Fig. 3) or between +0.2 V and −0.6 V (Fig. 4). We can see that the coefficient of friction (COF) goes up to about 0.35 in the periods of negative voltage or negative surface potential. When the voltage or potential is switched to positive, the COF restores to or slightly below the initial value of 0.12～0.13. In the last stage of 2000～2200 s, the power supply is off, and the COF goes down to 0.12. There is no doubt that the friction coefficient between the ceramic ball and plate has been modulated by the applied electric field with either the two-electrode or three-electrode method.

Differing from the electrically tunable friction between ceramic balls and metal plates reported by the authors previously [19, 26], both parts of the ceramic tribo-pairs in this study are insulator, the surface potential of which could not be changed by the electrode system shown in Fig. 1. Why is the friction between ceramics responsible to the changes in the applied voltage or surface potential on the steel holder? It should be noted that the steel holder is placed in a position so close to the contact area (with a gap of 1 mm) that the change in the distribution of SDS molecules or ions in the solution, which depends on the electric field between the working electrode and the counter electrode, indirectly affects the adsorption of lubrificous SDS anions on the contact surface, and thus the boundary lubrication state. This is probably the mechanism responsible to the reversible changes in friction coefficient shown in Figs. 3 and 4. The response behavior can be displayed some extent behind the applied voltage or potential as shown in Eq. (3). The observed characteristics of wear under different surface potentials accord with that of the COF.

It is worth noting that the changes in COF delayed in some extent behind the applied voltage or potential as shown in Figs. 3 and 4. The response behavior can be displayed more clearly in a shorter time scale in Fig. 6. Figure 6a and b presents the variations of COF with time when the surface potential was switched from +0.2 to −0.6 V or 0 V and from −0.6 to +0.2 V or 0 V, respectively. Both of the pictures show that there is a time lag of 10 s or more behind the surface potential. Furthermore, the COF takes several tens of seconds (60～80 s) to reach a relatively stable value.

On the other hand, the changes in the current were almost synchronous with the surface potential as shown in Fig. 6c and d. In Fig. 6d, the current is at the maximum value at the beginning of switching and gradually approaches to −0.13 mA after 5 s. The insert indicates that there exists a small cyclic fluctuation of current with the frequency of 1 Hz, which is considered to be caused by the reciprocating motion of the Al2O3 plate. When the surface potential was switched from the negative value of −0.6 V to zero or the positive value of +0.2 V, the current decayed from sub-mA to μA rapidly in 2 s and then further decreased to about 0.3 μA and 0.1 μA for the cases of +0.2 V and 0 V surface potentials respectively, as shown in Fig. 6d. According to the fact that the current dropped rapidly and remained stable at a minor value, it is considered that the measured current is caused by electron transportation across the electrode-adsorbate interface, rather than electrochemical reaction process. The charging current is understandable, just like what happens in a capacitor. After the discharging process, weak current across an electrode-liquid interface is feasible at the presence of an external biased potential without electrochemical reactions. For example, charge transfer had been observed across a single molecular, like benzene-1,4-dithiol [33].

Comparing Fig. 6a and c with Fig. 6b and d, it is evident that the change of COF is behind of the current, or the electromigration of ions in the solution under the electric field between the electrodes. The time lag, in the order of tens of seconds, is much longer than that in the cases of ceramic/metal contacts found previously [19], in which the response time is just a few seconds or less.
Fig. 6 Relationship between the COF, electric current, and time, when the surface potential was controlled and changed by electrochemical workstation. The COF over time when the surface potential was changed from +0.2 to −0.6 V at 0 s shown in a and from −0.6 to +0.2 V or 0 V at 0 s shown in b. The current over time when the surface potential was changed from +0.2 to −0.6 V at 0 s shown in c and from −0.6 to +0.2 V or 0 V at 0 s shown in d.

Fig. 7 Friction coefficient of the Al₂O₃ plate vs. ZrO₂ ball versus time with pure H₂O or single solution working as the lubricant under different applied potentials of the working electrode near the contact area.
3.2 Effect of the SDS Concentration

In the above experiments, the mixture solution of 1 mM SDS and 10 mM NaCl was used as the lubricant. In order to explore the effects of the additives and their components on the lubrication behaviors, the following experiments have been carried out.

Firstly, pure water, pure SDS solutions with different concentrations, as well as 10 mM NaCl solution were compared as the lubricant of the ceramic tribo-pairs. The friction results are shown in Fig. 7. In pure water or in the 10 mM NaCl solution without SDS, the COF is relatively high, about 0.45. The addition of NaCl makes the COF more stable, rather than decreases it effectively. However, when the SDS concentration is greater than or equal to 1 mM, the COF decreases to 0.12. This implies that it is the SDS surfactant rather than NaCl salt that plays the role of lubricious constituent in the solution. The following results measured by QCM will show that the competitive adsorption capacity of DS⁻ (the anion dissociated by SDS) is stronger than that of Cl⁻ at the Al₂O₃ surface. When the concentration of SDS is 1 mM, the COF does not respond to the change in the surface potential, although it keeps a low value. This is different from the results shown in Fig. 4 above, where 10 mM NaCl was added into the 1 mM SDS solution. As the concentration of SDS increases to 2 mM or greater, the electric response of COF becomes more and more evident. According to the knowledge of colloidal chemistry, both of the concentrations of the salts and surfactants affect the surfactant micellar state in the solutions. Hence, the electric response of COF is considered to depend on the micellar state of the SDS in solutions. Because the SDS used in the experiments was impure (approx. 95% as based on total alkyl sulfate content), the adsorption was a combination of SDS and other substances, and hence, the critical micelle concentration (CMC) is lower than that of the individual components (the CMC of pure SDS solution is about 8 mM at room temperature) [34].

![Fig. 8 Friction coefficient of Al₂O₃ plate vs. ZrO₂ ball over time in the mixed solutions with different contents of SDS and NaCl under different applied potentials of the working electrode near the contact area](image)

![Fig. 9 Friction coefficient and adsorption behaviors for the solutions with different SDS concentrations in the absence (a) and the presence of 10 mM NaCl (b)](image)
To further explore the influence of the mixture in the solutions on the behavior of the potential-controlled boundary lubrication systems, the mixture solutions with different molar ratios of SDS to NaCl, 1:1, 1:2, 1:5, 1:10, 1:20, and 1:50 were prepared and tested, and the results are shown in Fig. 8. For the mixtures with 1 mM SDS, when the concentration of NaCl is 1 mM or 2 mM, their lubrication behavior is similar to that of the 1 mM SDS solution without adding NaCl. The COFs in the above tests stabilize at about 0.12 after the running-in process, while the change of COF with time and surface potential is not obvious. However, when the concentration of NaCl increases to 5 mM in the 1 mM SDS solution, the COF increases from 0.12 to 0.20 when a negative surface potential of −0.6 V is applied and then decreases to 0.12~0.13 when a positive surface potential of +0.2 V is applied. According to the results in Figs. 4, 7, and 8, for the 1 mM SDS solutions, increasing the NaCl concentrations in a range of 0~10 mM cannot improve the lubrication performance of the system, but it plays an important role in improving the response of COF to electric field.

For the 0.5 mM SDS solutions with different contents of NaCl, the running-in time for the COF dropping from 0.3~0.4 to ~0.12 increases to about 800 s, which is much longer compared with the time of 200 s in the case of the 1 mM SDS solution. When the SDS concentration is further reduced to 0.2 mM, the running-in time further increases to more than 1800 s.

To further explore the effect of SDS concentration, friction the adsorption behaviors for the solutions with different SDS concentrations in the absence and the presence of 10 mM NaCl were investigated respectively, and the results are shown in Fig. 9. Here, the adsorption masses of the additives in the three different solutions were converted according to Eq. (1) from the QCM data. The results indicate when pure H2O was tested to be the base line, then the solution was injected at 180 s for the adsorption tests, and finally the pure H2O was injected at 900 s for the desorption testing. The test temperature was held at 25 °C.
that whether NaCl is present or not, the COF has a certain relationship with the adsorption amount of SDS. When the adsorbed mass is above 150 ng/cm², the COF decreases to 0.1 ~ 0.2 within the testing time of 600 ~ 900 s. However, when the adsorbed mass is below that value, the COF is about 0.35 ~ 0.45. For the pure SDS solutions, the critical concentration is about 0.4 ~ 0.5 mM, as shown by the blue dotted line in Fig. 9a. For the mixtures with 10 mM NaCl, the minimum SDS concentration for the lower COF is about 0.2 ~ 0.3 mM, as shown in Fig. 9b.

Combining the above results, it is evident that the SDS concentration affects the adsorption amount at the interface between the Al₂O₃ plate and the solution, and then changes the friction behavior of the system. Moreover, the presence of NaCl can also influence the adsorption amount at the solid–liquid interface and affect the friction behavior.

### 3.3 Effect of Inorganic Salt

According to the above analysis, the adsorption and desorption behavior of the SDS in liquid are the key path for controlling the electric response as well as the boundary lubrication of the tribo-systems. Meanwhile, the presence of inorganic salts can affect the state of the SDS in aqueous solution, thereby affecting the tribological behavior as well as the adsorption and desorption behavior as shown in Fig. 9. To understand the effect of the added NaCl salt on the SDS structures at the solid–liquid interface, the QCM characterization was carried out. The measurement procedure is as described above. As shown in Fig. 10a, the adsorption films in the three cases of different NaCl concentrations can all be regarded as rigid films, and all of the obtained three adsorption isotherms yield the Langmuir type adsorption.

Figure 10b shows the adsorption and desorption behaviors at the interface between the Al₂O₃-coated quartz crystal sensor and 10 mM NaCl solution. A baseline tested in pure H₂O was obtained in the first 180 s. Then 10 mM NaCl solution was injected with the same pumping speed. After 40 ~ 50 s, the solution entered the module through an inlet tube. During the period of the solution into the module, the NaCl concentration of the liquid in the module can be regarded as from 0 to 10 mM. It takes about 180 s for the adsorption equilibrium. Comparing with the baseline in pure H₂O, the equilibrium adsorption capacity of NaCl is about 33 ng/cm². Pure H₂O is then injected into the module instead of the 10 mM NaCl solution at 900 s. Due to the diffusion and competitive adsorption of the adsorbents at the interface, the adsorption capacity starts to decrease until it reaches to the desorption equilibrium in pure H₂O after about 180 s.

Figure 10c and d presents the adsorption and desorption behavior of the 1 mM SDS solution and the mixtures of 1 mM SDS and 10 mM NaCl, respectively. The equilibrium adsorption capacity in Fig. 10c is about 220 ng/cm², indicating that adsorption capacity of SDS on Al₂O₃ solid is greater than that of the Na⁺ and Cl⁻ shown in Fig. 10b. Moreover, it takes about 520 s to reach the adsorption equilibrium from pure H₂O to 1 mM SDS solution and takes about 500 s for the desorption process.

However, for the mixtures of 1 mM SDS and 10 mM NaCl, the time required for adsorption and desorption equilibrium is about 60 s and 120 s, respectively, as shown in Fig. 10d, which are significantly shorter than the time required for the 1 mM SDS without NaCl in Fig. 10c. In addition, the equilibrium adsorption capacity is about 193 ng/cm² in the mixture solution. Comparing with the adsorption isotherm in Fig. 10c, the relative low adsorption capacity is considered to be caused by the Cl⁻ ions in the mixture, which occupies the positions of DS⁻ in the condition of 1 mM SDS solution. In this work, it is assumed that there is no overlap and interaction between different kinds of ions (Cl⁻ and DS⁻) adsorbed on the surface of the sensor. When the area percentage that Cl⁻ ions occupied is α, then that of the DS⁻ occupied is 1-α. The adsorption of the NaCl and SDS anions on solid surface can be expressed by

\[
\Gamma_{\text{mix}} = \alpha \cdot \Gamma_{\text{NaCl}} + (1 - \alpha) \cdot \Gamma_{\text{SDS}},
\]

where \(\Gamma_{\text{mix}}\) is the total adsorption capacity in the mixtures, \(\Gamma_{\text{NaCl}}\) and \(\Gamma_{\text{SDS}}\) are the adsorptions of the NaCl and SDS anions, respectively. Substituting the equilibrium adsorption capacities of the NaCl and SDS anions into the Eq. (2), the value of \(\alpha\) is estimated to be 1/7. That is so say, if there is no overlap among the different ions or molecules, the area occupied by Cl⁻ ions is about 14% and the area occupied by DS⁻ is about 86% at the interface of the solid and liquid.

The adsorption process shown in Fig. 10 can be fit with the classical Langmuir adsorption isotherm model [35, 36]:

\[
\Gamma = \Gamma_{\infty} \frac{Kc}{1 + Kc},
\]

where \(\Gamma\) is the adsorption at a certain concentration, \(\Gamma_{\infty}\) is the maximum adsorption at high solution concentration, \(c\) is the concentration of the surfactant in the bulk solution, \(K\) is a function of \(c\), and the adsorbed molecules at the interface, which can be expressed by

\[
K = \frac{\theta}{c(1 - \theta)},
\]

where \(\theta\) means the fraction of the surface area occupied by the adsorbed molecules.

In this experiment, owing that the solution was injected by an external pump with a constant rate, the relationship between the concentration of the surfactant in the QCM testing module and the time (\(t\)) could be expressed in Eq. (5):

\[
c = At,
\]
where $A$ is a constant depended on the pumping rate of the liquid.

Substituting Equation and (5) into Eq. (3), we get

$$\Gamma = \Gamma_\infty \frac{KAt}{1 + KAt}$$

Equation (6) is used to fit the adsorption process from the start to equilibrium in Fig. 10c and d, and the fitting curves are plotted in Fig. 11a and b, respectively. The blue lines are the testing results of QCM, and the red lines are the fitting curves. The parameters and related factors of the fitting curves are listed in Table 1. The correlation coefficient ($R^2$) indicates that the model fits the experimental data well. From Table 1, we can see that the saturated adsorption capacity at the Al$_2$O$_3$ surface is 223 ng/cm$^2$ in 1 mM SDS solution and 211 ng/cm$^2$ in the mixture of 1 mM SDS and 10 mM NaCl. These results also indicate that Cl$^-$ can occupy a part of the space on the Al$_2$O$_3$ surface and decrease the adsorption capacity in the mixture, comparing with 1 mM SDS solution, which is consistent with the results in Fig. 10.

Since $A$ can be regarded as a constant, $KA$ directly relates with the fraction of the surface area occupied by the adsorbed molecules ($\theta$), according to Eq. (4). Comparing the values of $KA$ for the two solutions, it can be concluded that the adsorption rate of the additives in the mixture is 2.03 times faster than that in the SDS single solution at the same pumping time.

From the experiment results described above, adsorption of the DS$^-$ anions on the rubbing surfaces of the ceramic tribo-pairs results in formation of lubricious boundary films and, thus, reduction in friction coefficient, while the desorption of the DS$^-$ anions from the surfaces gives rise to rebound in friction. For the SDS surfactant solutions with relative low concentrations (lower than the CMC), the adsorption of DS$^-$ anions on solid surfaces can be expressed by

$$\Gamma = l c \exp\left(\frac{-\Delta G_{ads}}{kT}\right),$$

where $l$ is the characteristic thickness of the adsorption layer, $c$ is the bulk concentration of the anions, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\Delta G_{ads}$ is the standard free energy of adsorption [36, 37].

In general, $\Delta G_{ads}$ includes the contributions from electrostatic interactions ($\Delta G_{elec}$), chemical interactions, hydrophobic lateral interactions, hydrophobic interaction between the hydrocarbon chains and hydrophobic sites on the solid, hydrogen bonding, and desolvation energy. For the tribosystem shown in Fig. 1, $\Delta G_{elec}$ is negligible, because Al$_2$O$_3$ and ZrO$_2$ surfaces in aqueous solutions with pH value of 6–8 are electrically neutral [38, 39]. It is not affected by the presence of an electric field on the working and counter electrodes neither. However, the local concentration of DS$^-$ anions, $c$, around the contact point depends on the charging state of the steel holder (i.e., working electrode). For dilute SDS solutions (<0.2 mM in the presence of 10 mM NaCl, <0.4 mM in the absence of NaCl as shown in Fig. 9), when the working electrode is positively charged, more DS$^-$ anions are attracted towards the contact area as shown in Fig. 12a and vice versa as shown in Fig. 12b, comparing to the uncharged state. This makes the adsorption amount of DS$^-$ anions, $\Gamma$,
tunable by the electric field applied on the steel ball holder. Therefore, it can be regarded as an indirect tunable adsorption approach. For concentrated SDS solutions such as 1 mM SDS + 10 mM NaCl, on the other hand, spontaneous adsorption of SDS is strong enough to form a good adsorption film, and the applied potential plays a minor role in boundary film formation. If one part of a tribo-pair is conductive and serves as the working electrode, the electrostatic interaction predominates the standard free energy of adsorption, as shown in Eq. (8).

\[
\Delta G_{\text{ads}} \approx \Delta G_{\text{elec}} = -zF\psi_b,
\]

where \( z \) is the valency of the adsorbate species, \( F \) is the Faraday constant and \( \psi_b \) is the electric potential [36]. Thereby, tuning \( \psi_b \) can directly change the adsorption capacity of
ions at the solid–liquid interface. This can be referred as direct tuning adsorption approach, which has been reported previously. Comparing between the two approaches, the advantage of the indirect approach is no requirement for the conductivity of friction pairs and hence applicable to both conductors and insulators, while the direct approach has a quicker response.

According to colloid science, when an inorganic salt is added to the SDS solution, the increase of counterions reduces the electrostatic repulsion between the DS− ions and compresses the double electric layer, tending the formation of SDS micelles [40]. The schematic diagrams of the ions in SDS solutions without or with NaCl are shown in Fig. 13. When SDS concentration is lower than the CMC, isolated ions distribute in the solution (Fig. 13a). Figure 13b presents the state of ions in the mixture solution of 1 mM SDS and 10 mM NaCl. Due to the presence of NaCl, the concentration of Na+ in the solution increases from 1 mM (by the dissociation of SDS) to 11 mM (by the dissociation of SDS and NaCl). Therefore, more counterions can adsorb on the surface of DS− ions as well as their aggregations by the electrostatic interaction, causing the formation of micelles in relatively lower concentration of the SDS. Zhang et al. had researched the effect of concentration and addition of ions on the adsorption of SDS on stainless steel surface in aqueous solutions in 2015 [31]. The result in this work agrees well with the conclusion that adsorption isotherm shifts to lower SDS concentration regime with added Na+ salts.

From the adsorption isotherm shown in Fig. 10c and d, we can see that the process of the solitary DS− ions from starting adsorption to adsorption equilibrium on the solid surface is relatively slower in SDS solution than that of the SDS micelles in the mixture solution. The phenomenon can be explained with the schematic diagram of the DS− and Na+ in the above two solutions shown in Fig. 13c and d, respectively. Although the transport of micelles is generally slower than single ions or molecules, the transport rate of material is faster due to the fact that more material is transported in a micelle. This is also true for the desorption process. Therefore, addition of NaCl salt improves the response of adsorption/desorption as well as friction to the changes in surface potentials.

Moreover, in Fig. 10d, the maximal adsorption capacity in the SDS and NaCl-mixed solution reaches 193 ng/cm² at about 270 s and then decreases to a relatively stable value of 180 ng/cm² after 360 s. A similar process occurs during the desorption process. This phenomenon is considered to be caused by the phase transition process after the first adsorption equilibrium [41, 42]. That is to say, when micelles just arrive at the interface, the entirety adsorption is carried out firstly, which increases the adsorption capacity rapidly. Then, it takes tens of seconds for the micelles to be self-assembled at the interface under the electrostatic and hydrophobic interactions. During the process, the desorption factor also shows a relatively significant changes, as shown in Fig. 10a. This result also indicates that in the mixture solution of 1 mM SDS and 10 mM NaCl, the state of adsorbents at the solid–liquid interface is micelle, rather than solitary DS− ions or SDS molecules.

### 4 Conclusions

Through a proper design of electrode cell, active control of the friction between ZrO₂ ball and the Al₂O₃ plate in water-based lubrication has been realized by applying an external electric field. The COF can be varied reversely with the applied electric field in the range of 0.12 to 0.35. The addition of inorganic salts containing counterions to the surfactant solution can shorten the response time by facilitating the formation of SDS anions into micelles. Moreover, an indirect adsorption model has been proposed that when one of the electrodes is near the contact area of the friction pairs, the applied electric field can change the distribution of the concentration of the surfactant SDS. As a result, the adsorption and desorption behavior of the SDS at the interface between the friction pairs can be controlled indirectly, which can influence the tribological behaviors of the system significantly. This work indicates a novel method to realize the active control of friction for the water-based lubricants with ceramics working as friction pairs and also improve the understanding of boundary lubrication processes.

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**Declarations**

**Conflict of interest** There are no conflicts to declare.

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