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Regulation Mechanism of Trivalent Cations on Friction Coefficient of a Poly(Vinylphosphonic Acid) (PVPA) Superlubricity System

Mengmeng Liu ¹, Caixia Zhang ^{1,*}, Lihui Wang ¹, Yanhong Cheng ¹, Ying Li ¹, Lianpeng Bai ¹ and Zhifeng Liu ^{1,2,*}

¹ Institute of Advanced Manufacturing and Intelligent Technology, Department of Materials and Manufacturing, Beijing University of Technology, Beijing 100124, China

² Key Laboratory of CNC Equipment Reliability, Ministry of Education, School of Mechanical and Aerospace Engineering, Jilin University, Changchun 130012, China

* Correspondence: zhang-cx15@bjut.edu.cn (C.Z.); lzjflu@jlu.edu.cn (Z.L.)

Abstract: The application range of superlubricity systems can be extended effectively by realizing an adjustable friction coefficient. In this study, a stable poly(vinylphosphonic acid) (PVPA) superlubricity system was developed using sodium chloride (NaCl) solution as the lubricant. A sudden increase in the friction coefficient occurred when a trivalent salt solution was introduced to the base lubricant during the friction process. The changes in surface microstructure and interfacial molecular behavior induced by trivalent cations were studied by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and molecular dynamics simulation. The regulation mechanism of trivalent cations with respect to the friction coefficient of the PVPA superlubricity system was explored. Although La^{3+} and Fe^{3+} in solutions exist in two forms (La^{3+} and $\text{Fe}(\text{OH})_3$), both can destroy the stable coating structure through a bridging effect, resulting in a sudden increase in the friction coefficient. The ability of various cations to attract the surrounding water molecules is an important reason for the varying degree of change of the friction coefficient. In addition, the degree of sudden increase in the friction coefficient is dependent on the concentration of trivalent cations. There is an extreme concentration at which the maximum sudden increase degree in friction coefficient can be obtained. This study provides insights into the realization of oil-based superlubricity through interface regulation.

Keywords: poly(vinylphosphonic acid) (PVPA) coating; La^{3+} ; $\text{Fe}(\text{OH})_3$; bridging effect; concentration-dependent



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1. Introduction

As a new subversive technology in the field of lubrication, water-based superlubricity has gradually shown its application advantages in industrial production and human daily life. Surface modification by polymer is a promising method to obtain superlubricity and has been widely reported [1–3]. Water-based, polymer-modified surfaces have good response characteristics to external stimuli, such as salt ions [4]. Such response characteristics are expected to be used to achieve adjustable friction, providing a new approach to intelligent operation.

Many applications are carried out in environments with multivalent ions. The structural changes of polymer-modified surfaces in response to multivalent ions in the environment can be harnessed to control friction [5]. Yu Jing et al. suggested that the microscale structural formation of polyelectrolyte brushes induced by multivalent ions strongly affect friction forces between coated surfaces [6]. Surface structural changes of polymer induced by multivalent ions have been widely studied [7–12]. Chen Wei et al. reported abrupt brush thickness shrinkage in the presence of trivalent Y^{3+} cations, which highlights the effect of multivalent counterions on the structure of polyelectrolyte brushes [7].

It is widely accepted that the electrostatic correlation effect represented by the bridging effect is the main cause of structural changes in polymer induced by multivalent ions. Tan Hong-Ge et al. studied the morphology of a polyelectrolyte brush grafted onto a surface with cubic geometry under optimal solvent conditions in the presence of trivalent counterions using molecular dynamics simulations. It was proposed that the trivalent-counterion-mediated bridging effect can induce lateral microphase separation of the cubic polyelectrolyte brush, resulting in the formation of pinned patches [8]. The presence of multivalent counterions can strongly affect the structure of polymer chains, even at relatively low concentrations [9]. However, the concentration of multivalent ions also plays an important role in the change in polymer surface structure. Studies by Blair Kathryn Brettmann et al. showed that there is a critical multivalent counterion concentration that enables the brush height to change from an extended state to a collapsed state [10]. The addition of multivalent counterions increases the complexity of the system. The change in polymer structure may be a result of the synergy of many effects. Yu Jing et al. concluded that poor solvent effects and multivalent ionic bridging combine to contribute to the strong phase separation of polyelectrolyte brushes [6]. Hao Qing Hai et al. found that, in addition to the bridging effect, the morphology of polymer-modified surfaces induced by trivalent ions is related to the grafting density of the polymer, the multivalent ion-induced lateral heterogeneities of the surface morphology at low grafting density and the vertical phase-separated structures at high grafting density [11]. The bridging effect of multivalent ions in polymer coatings can be divided into intrachain bridging and interchain bridging. Wang Lijuan et al. studied the collapse of polyelectrolyte brushes made of four-arm stars by trivalent salt counterions using Langevin dynamics (LD) simulations. The probability of intrachain bridging was found to be much greater than that of interchain bridging with respect to the collapse of fully charged star brushes due to the topological structure [12].

The reversibility of the multivalent electrostatic effect represented by the bridging effect is of considerable significance with respect to friction control [13]. Yu Jing et al. investigated the effect of monovalent, divalent and trivalent counterions on the structure of high-density polystyrene sulfonate (PSS) brushes, suggesting that the uptake of Y^{3+} counterions and the shrinkage of the brush are reversible by increasing the concentration of monovalent salt [9]. Robert Farina et al. showed that the chain structure of polyelectrolyte brushes can be regulated from extended and repulsive to collapsed and extremely adhesive by changing the concentration of lanthanum ions [14]. Multivalent ions in the environment can not only change the polymer structure but also combine with polymer molecular chains to form new complexes [15].

Although many studies have been conducted on structural changes in polymers induced by multivalent ions, there are still gaps in applications, such as friction. In the previous study, by exploring the coating structure and interface changes, we found that the sudden increase in the friction coefficient of the PVPA superlubricity system induced by Ca^{2+} and Mg^{2+} was closely related to the bridging effect of divalent ions and PVPA molecular chains [16]. In this study, based on the friction performance of a PVPA-modified Ti6Al4V surface in NaCl solution, the regulation mechanism of trivalent salt ions with respect to friction coefficient was studied in a PVPA superlubricity system. The results reveal differences between the regulating mechanisms of various trivalent cations. In addition, we found that the variation in the friction coefficient of the PVPA superlubricity system induced by trivalent cations was concentration-dependent. We expect that real-time autonomous control of friction can be realized by regulating interface properties and interactions by clarifying the behavior of polymer coatings in response to stimulation.

2. Materials and Methods

2.1. Materials

PVPA (97%) was provided by Sigma Aldrich (St. Louis, MO, USA). Various kinds of salt (NaCl, $LaCl_3$ and $FeCl_3$) were purchased from J&K Chemicals (Beijing, China). Ti6Al4V (100 mm × 100 mm) foils with a thickness of 1 mm were supplied by Goodfellow, Inc.

(Cambridge, UK) and were cut into square samples of 10 mm × 10 mm. Ti6Al4V substrates used for modification were polished to smooth surfaces. Poly tetra fluorothylene (PTFE) balls (D ≈ 6 mm) with a roughness of approximately 280 nm and a shore hardness of 60 were purchased from Taobao, Inc (Hangzhou, China). All reagents mentioned above were used as received.

2.2. Preparation of PVPA Coatings on Ti6Al4V

PVPA coatings were prepared on Ti6Al4V substrates based on the method of horizontal evaporating self-assembly [17]. Briefly, Ti6Al4V foils with an oxide layer were obtained by heating in air at 140 °C for 8 h. The pretreated foils were then placed horizontally into a PTFE mold. An appropriate PVPA aqueous solution was injected into the mold, and the mold was heated at a temperature of 35 °C to accelerate the physical adsorption of PVPA molecules on Ti6Al4V. Finally, crosslinked networks were formed on Ti6Al4V after heating the samples at 260 °C for 6 h.

2.3. Evaluation of Tribological Properties

A universal micro-tribometer (UMT-3, Bruker Corporation, Capbell, CA, USA) was used to characterize the tribological properties of the PVPA-modified Ti6Al4V/PTFE interfaces. Briefly, a motor underneath the disk controlled the motor pattern of reciprocation and sliding speed. A precise two-dimensional sensor can simultaneously measure the normal load and frictional force generated during sliding contact. PVPA-modified Ti6Al4V and PTFE balls were sampled as tribopairs. The normal force was 2.5 N. The length of the reciprocating friction path and the frequency were 3 mm and 2 Hz, respectively, corresponding to a sliding speed of 12 mm/s. A volume of 6 mL NaCl solution with a concentration of 0.5 mol/L was used as the base lubricant for the friction experiment, ensuring the PVPA-modified surface was completely immersed. In the base lubrication system, the friction experiments were performed in the reciprocating mode at 25 °C. Another chlorine salt solution with a concentration of 0.5 mol/L was directly introduced into the base lubricant during the friction process. The volume of salt solution introduced at each time was 2 mL. All experimental results were obtained by averaging the values of at least three repetitions.

2.4. pH Detection and Surface Characterization

The pH of various solutions was measured by a pH meter (PB series, Sartorius Aktiengesellschaft, Gottingen, Germany). The pH meter should be calibrated with buffer solution before testing the pH of solutions. The surface morphologies of the PVPA coatings soaked in different solutions were observed by field-emission scanning electron microscopy (Gemini SEM 300, Carl Zeiss Aktiengesellschaft, Oberkochen, Germany). Energy-dispersive spectroscopy (EDS) and high-angle annular dark-field (HAADF) images were captured in an aberration-corrected scanning transmission electron microscope operated at 300 kV.

2.5. Molecular Dynamics Simulation

2.5.1. Geometry Optimization of Individual Molecules

Prior to molecular dynamics simulation, the individual molecular and ion models involved in the system, including the PVPA molecular chain, the PTFE molecular chain, water molecules, Na⁺, Cl[−], La³⁺ and Fe(OH)₃, should be established, and geometric optimization should be carried out. The minimum degree of polymerization was chosen for the PVPA and PTFE molecular chains to prevent non-convergence during geometric optimization. The models of PTFE and PVPA were composed of 1 and 2 monomers, respectively. The net charge of each molecular model was around 10^{−7}, which can be approximately regarded as electrically neutral. The Forcite module was used to optimize the geometry of individual molecules using the COMPASS II force field. The optimization accuracy was fine. The maximum number of iterations was set to 5000. Single atoms do not require geometric optimization, but the forcefield type needs to be calculated so that the atoms obtain the corresponding net charge.

2.5.2. Density Functional Theory (DFT) Study

Density functional theory (DFT) calculations were performed to calculate the interaction energy and to gain insight into the effect of mixing different salts on the PTFE–PVPA system. The simulation was performed using the DFT program DMol3 in Materials Studio (2019) [18]. The physical wave functions were expanded in terms of numerical basis sets, i.e., the Dmol3/GGA-PBE/DNP (3.5) basis set [19]. The core electrons were treated with DFT semicore pseudopotentials [20]. The exchange–correlation energy was calculated using the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) [21]. A Fermi smearing of 0.005 Ha (1 Ha = 27.211 eV) and a global orbital cutoff of 5.2 Å were employed. The convergence criteria for the geometric optimization and energy calculation were set as follows: (a) a self-consistent field tolerance of 1.0×10^{-6} Ha/atom, (b) an energy tolerance of 1.0×10^{-5} Ha/atom, (c) a maximum force tolerance of 0.002 Ha/Å and (d) a maximum displacement tolerance of 0.005 Å.

2.5.3. Model Building

In order to explore the disturbance of interface state caused by the introduction of new ions, the modeling process of the molecular dynamics simulation was divided into two steps. The origin system was built first. Geometrically optimized models of PVPA and PTFE were first placed together. The hydrogen atom of a hydroxyl group in the PVPA molecular chain and the fluorine atom in the PTFE molecular chain were fixed. One Na⁺, one Cl[−] and two water molecules were placed on the polymer model to form the original system. DFT calculations were performed with the Dmol3/GGA-PBE/DNP basis set to optimize the convergence of energy charge, displacement and force. The interaction of Na⁺ with the PVPA chain was then analyzed. The adsorption of salt ions on the PVPA molecular chain was approximately considered as their adsorption on the PVPA surface. After the original system attained stability, one Cl[−] molecule and one cation were added to build a new system. Compared to the complex lubricant mixture system, the molecular dynamics model established in this study was considerably simplified. Therefore, it does not reflect the actual state change of the PVPA interface, although the interface changes caused by the introduction of different cations can be qualitatively compared in this model to reflect the disturbance trend of various cations on the interface state.

2.5.4. Interaction Energy Calculation

The interaction energy (E_{int}), indicating the intensity of the interaction between the components in the system, was derived according to the following equation:

$$E_{\text{int}} = E_{\text{tot}} - \sum E_{\text{com}} \quad (1)$$

where E_{tot} and E_{com} represent the total energy of the system and the energy of each of its components, respectively. A negative E_{int} value corresponds to stable adsorption of the components. A more negative value of E_{int} indicates a stronger interaction in the system.

3. Results and Discussion

3.1. Regulation Mechanism of Trivalent Cations with respect to the Friction Coefficient of a PVPA Superlubricity System

Our previous study showed that the surface of PVPA-modified Ti6Al4V can maintain stable superlubricity properties in monovalent salt solutions [22]. In this study, 0.5 mol/L NaCl solution (6 mL) was used as the base lubricant to obtain a stable, ultra-low-friction coefficient (0.006–0.007), as shown by the square curve in Figure 1. Following stable operation of the PVPA superlubricity system for 500–600 s, 0.5 mol/L LaCl₃ solution (2 mL) was added to the base lubricant. The friction coefficient of the system suddenly increased when LaCl₃ solution was added, as shown by the diamond curve in Figure 1. The sudden increase in the degree of the friction coefficient was $285.24 \pm 62\%$. When FeCl₃ solution (2 mL) with a concentration of 0.5 mol/L was added into the basic lubricant, the friction

coefficient of the PVPA superlubricity system also increased suddenly, with a degree of $1825.86 \pm 70\%$, as shown by the triangle curve in Figure 1.

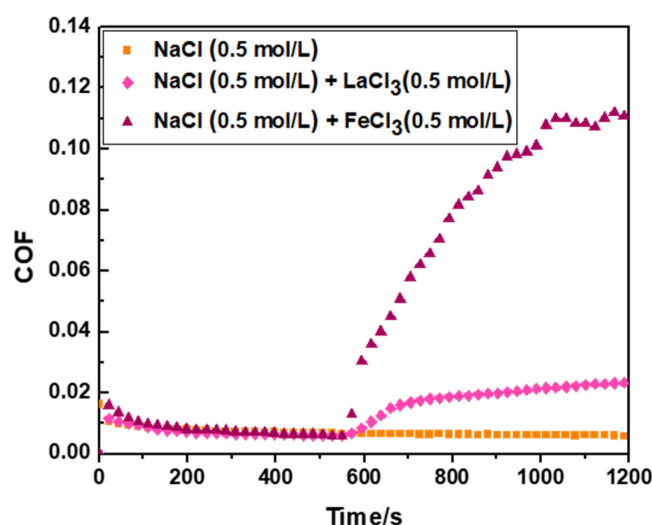


Figure 1. Variations in the friction coefficient of PVPA-modified Ti6Al4V in an NaCl solution sliding against PTFE balls and variations in the COF induced by the introduction of LaCl₃ and FeCl₃ solutions.

Based on the volume ratio of trivalent salt solution and basic lubricant in the addition process, a mixture solution of basic lubricant and trivalent salt solution was prepared in a ratio of 3:1 (basic lubricant: trivalent salt solution). SEM and EDS were used to detect the morphology and element distribution of PVPA-modified surfaces after soaking in NaCl/LaCl₃ and NaCl/FeCl₃ mixed solutions, respectively, to establish the relationship between the change in surface structure and element distribution and the change in friction coefficient.

The morphologies of PVPA-modified surfaces after soaking in NaCl/LaCl₃ and NaCl/FeCl₃ mixed solutions are shown in Figure 2(a₁) and (b₁), respectively. PVPA coatings soaked in the two mixed solutions both exhibited cracking phenomena, with sharp edges appearing on the coated surface. Such sharp edges aggravate the wear of PTFE [23], as shown in Figure S1 in the Supplementary Materials Section S1. This could be the main reason for the sudden increase in friction coefficient. The distributions of elements on the PVPA-modified surfaces after soaking in NaCl/LaCl₃ and NaCl/FeCl₃ mixed solutions are shown in Figure 2(a₂–a₁₀) and (b₂–b₁₀), respectively. The atomic percentages of elements on the two sample surfaces are shown in Table 1.

The atomic percentages of Ti, Al and V on the PVPA-modified surface after soaking in NaCl/LaCl₃ mixed solution were significantly higher than those after soaking in an NaCl/FeCl₃ mixed solution. The degree of damage of trivalent lanthanum ions on the PVPA coating was greater than that of trivalent iron ions on the PVPA coating, as also proven by the difference in P element on the surface of the two samples. Compared to the PVPA coating surface, the trivalent lanthanum ion tends to adsorb on the exposed Ti6Al4V surface after the coating cracks, as shown in Figure 2(a₁₀). However, the trivalent iron tends to adsorb on PVPA surface, as shown in Figure 2(b₁₀).

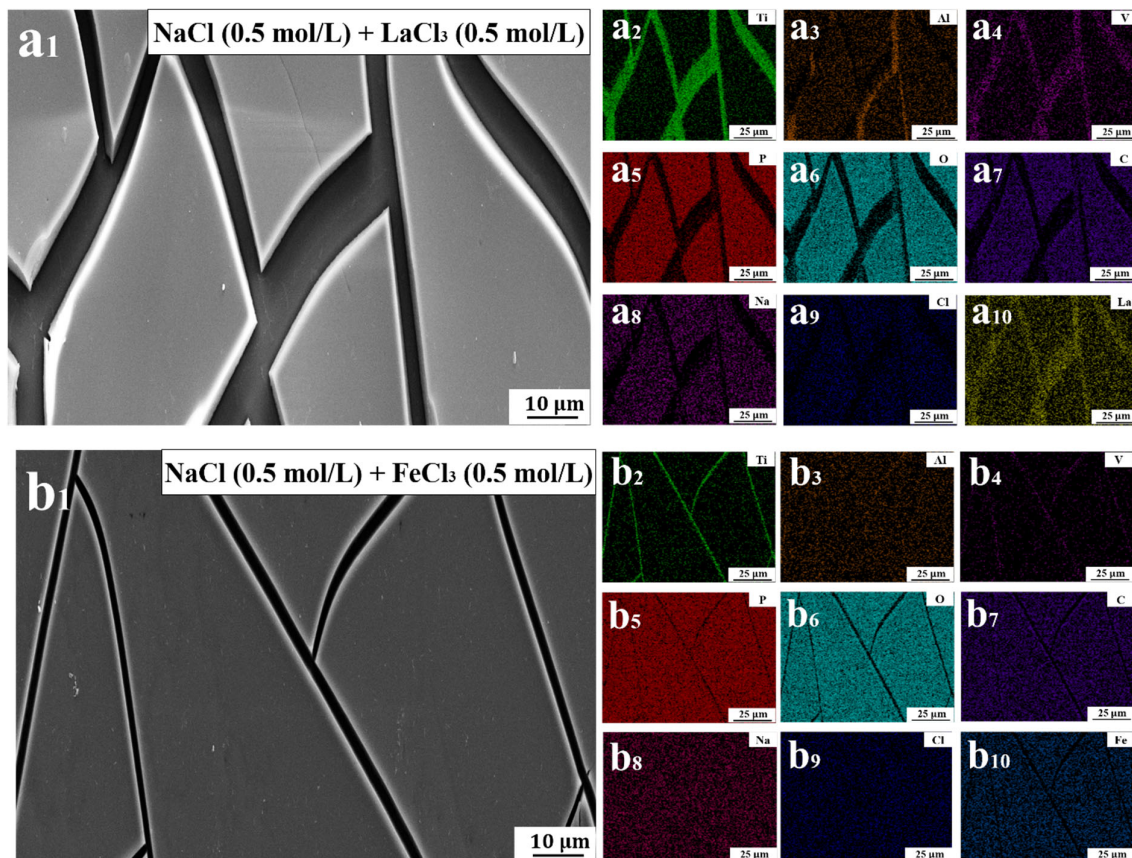
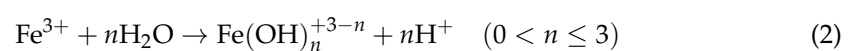


Figure 2. (a₁) Microstructure of a PVPA-modified surface after soaking in an NaCl/LaCl₃ mixed solution; (a₂–a₁₀) EDS mapping in the region of a₁. (b₁) Microstructure of a PVPA-modified surface after soaking in an NaCl/FeCl₃ mixed solution; (b₂–b₁₀) EDS mapping in the region of (b₁).

Table 1. The atomic percentages of elements on PVPA-modified surfaces after soaking in different mixture solutions.

Elements	Ti	Al	V	P	O
NaCl/LaCl ₃	19.58 ± 0.44	0.27 ± 0.05	0.86 ± 0.27	9.77 ± 0.21	22.40 ± 0.58
NaCl/FeCl ₃	5 ± 0.21	0 ± 0.05	0 ± 0.18	17.1 ± 0.37	35.55 ± 0.81
	C	Na	Cl	La	Fe
NaCl/LaCl ₃	11.76 ± 1.24	5.99 ± 0.14	8.81 ± 0.19	20.56 ± 0.71	0
NaCl/FeCl ₃	20.40 ± 1.45	2.71 ± 0.09	3.43 ± 0.12	0	15.81 ± 0.60

The presence of salt ions in solutions may be the main reason for the adsorption difference. Sung et al. reported that after LaCl₃ was dissolved in neutral water (pH 5.7–7), the trivalent lanthanum ion mainly existed in the form of La³⁺. However, when FeCl₃ was dissolved in neutral water, the trivalent iron mainly existed in the form of Fe(OH)_n^{+3−n}, and the pH value of the water reduced as a result of the subsequent reaction [24]:



The pH values of deionized water, basic lubricant (0.5 mol/L NaCl solution) and mixed solutions were measured. NaCl solution and trivalent salt solution were mixed in a volume ratio of 3:1 (NaCl solution: trivalent salt solution). The results are presented in Table 2.

Table 2. pH values of different solutions.

Solution	Deionized Water	NaCl	NaCl/LaCl ₃	NaCl/FeCl ₃
PH	6.2	6.2	5.8	2.2

As shown by detection results in Table 2, compared to deionized water, the pH value of NaCl solution does not change. After mixing the NaCl solution and the LaCl₃ solution, the pH value of the mixed solution did not obviously change. When the NaCl solution was mixed with FeCl₃ solution, the pH value of the solution decreased to 2.2. We speculate that the change shown in Equation (2) took place in the NaCl/FeCl₃ mixed solution, and the value of n is generally identified as 3 [24].

Molecular dynamics simulation was used to study the interface change of PVPA induced by La³⁺ and Fe(OH)₃. The effect of interface change on the sudden change in friction coefficient was analyzed. The interaction energy between PVPA chains and ions can effectively reflect the change in the PVPA interface. When studying the role of introduced cations, the role of anions can be ignored. To more clearly reflect the interactions between the introduced cations and PVPA chains, as well as those between Na⁺ and the PVPA chains before and after the introduction, Cl[−] and water molecules were removed from the new system, as shown in Figure 3. Notably, the removal behavior did not affect the specific value of the interaction energy.

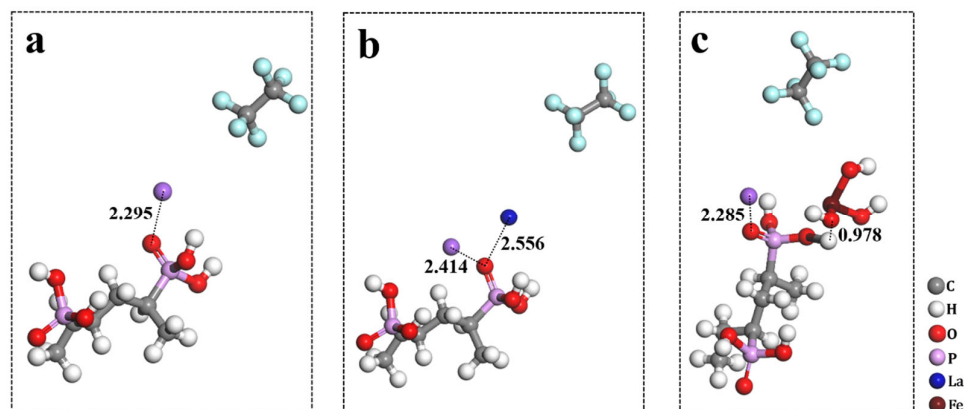


Figure 3. Intermolecular distance between the introduced ions and the PVPA chain and that between Na⁺ and the PVPA chain before and after the introduction of the ion: (a) Na⁺-PVPA, (b) Na⁺-PVPA and La³⁺-PVPA, and (c) Na⁺-PVPA and Fe(OH)₃-PVPA.

The minimum distances of La³⁺ and Fe(OH)₃ from the PVPA molecular chain were 2.556 Å and 0.978 Å, respectively, as shown in Figure 3b,c. The interaction energies of La³⁺ and Fe(OH)₃ with the PVPA molecular chain were −30.89 Kcal/mol and −155.3 Kcal/mol, respectively, as shown in Table 3. The calculation method is described in the Supplementary Materials Section S2. Fe(OH)₃ exhibited a greater degree of adsorption on the PVPA surface than La³⁺. It is believed that La³⁺ binds to the oxygen atoms in the phosphate radical group on the PVPA molecular chain through electrostatic interaction. Furthermore, oxygen atoms in Fe(OH)₃ can form hydrogen bonds with the hydrogen atoms in the phosphate radical groups on the PVPA molecular chain. Bonding to PVPA chains by hydrogen bonding is stronger than that of by electrostatic effect. Both La³⁺ and Fe(OH)₃ can bind to one to three phosphate groups, although with differences in binding methods. These phosphate groups may come from the same PVPA molecular chain or from adjacent PVPA molecular chains. Such a bridging effect can directly damage the stability of the PVPA coating and even cause cracking of the coating, as shown in Figure 2(a₁,b₁). This may be the main reason for the increase in friction coefficient.

Table 3. Calculated interaction energies of introduced cations with the PVPA chain and with H₂O.

Solution	Form	Interaction Energy (Kcal/mol)
Introduce LaCl ₃ to NaCl	PVPA-La ³⁺	−30.89
	H ₂ O-La ³⁺	−61.44
Introduce FeCl ₃ to NaCl	PVPA-Fe(OH) ₃	−155.30
	H ₂ O-Fe(OH) ₃	−24.78

The friction coefficients of the PVPA superlubricity system both increased suddenly due to the bridging effect of La³⁺ and Fe(OH)₃ with the PVPA molecular chain, but the degree of the sudden increase in friction coefficient varied. We speculate that the degree of sudden increase in friction coefficient is closely related to the degree of hydration of introduced ions. Highly hydrated ions adsorbed on the surface can contribute a certain degree of lubrication and reduce the degree of sudden increase in friction coefficient.

In this study, the degree of hydration of introduced ions in the PVPA superlubricity system are reflected by the interaction energy between the introduced ion and surrounding water molecules. The greater the interaction energy between the introduced ion and surrounding water molecules, the stronger the degree of attraction of the introduced ion to surrounding water molecules and the higher the degree of hydration of the introduced ion. The interaction energies of La³⁺ and Fe(OH)₃ with surrounding water molecules are −61.44 Kcal/mol and −24.78 kcal/mol, respectively, as shown in Table 3. Compared with Fe(OH)₃, La³⁺ adsorbed on the surface has a stronger attraction to surrounding water molecules. In other words, La³⁺ adsorbed on the surface can result in an improved lubrication effect. In addition, EDS results showed that part of the La³⁺ can adsorb on the Ti6Al4V surface exposed after PVPA coating cracking. These La³⁺ ions can play the role of avoiding direct contact between the two friction pairs to a certain extent after attracting water molecules. Although the degree of damage of La³⁺ to the PVPA coating is greater than that of Fe(OH)₃, combination of the stronger attraction of La³⁺ to surrounding water molecules and the stable adsorption of La³⁺ on exposed the Ti6AlV surface lead to a sudden increase in the degree of friction coefficient induced by La³⁺ less than that of Fe(OH)₃.

In our previous study [16], we found that the introduction of new monovalent cations during the friction process disturbed the state of the monovalent cations in the base lubricant to a certain extent and that this disturbance could affect the change in the friction coefficient. In this study, the introduction of La³⁺ and Fe(OH)₃ also disturbed the state of Na⁺ to a certain extent. In the original system, the minimum distance of Na⁺ to the PVPA molecular chain was 2.295 Å, as shown in Figure 3a. With the introduction of La³⁺ and Fe(OH)₃, the minimum distance of Na⁺ to the PVPA chain changed to 2.414 Å and 2.285 Å, respectively, as shown in Figure 3b,c. This change was influenced by both the adsorption degree of Na⁺ on PVPA and the repulsion of Na⁺ by introduced ions. Before the introduction of new ions, the interaction energy between the PVPA molecular chain and Na⁺ was −6.68 Kcal/mol. After the introduction of La³⁺ and Fe(OH)₃, the interaction energies between the PVPA molecular chain and Na⁺ were −7.59 Kcal/mol and −7.45 Kcal/mol, respectively, as shown in Figure 4. Both La³⁺ and Fe(OH)₃ can enhance the adsorption degree of Na⁺ on the PVPA molecular chain. The interaction energies of Na⁺ with La³⁺ and Fe(OH)₃ were 26.38 Kcal/mol and 2.37 Kcal/mol, respectively. Compared with La³⁺, the repulsion effect of Fe(OH)₃ on Na⁺ can be ignored. Therefore, after the introduction of Fe(OH)₃, the adsorption degree of Na⁺ on the PVPA molecular chain was enhanced, resulting in a decrease in the minimum distance between Na⁺ and the PVPA molecular chain. The introduced La³⁺ had a significant repulsion effect on Na⁺. The minimum distance from Na⁺ to the PVPA increased under the combined effect of the attraction effect of PVPA on Na⁺ and Na⁺ repulsion by La³⁺.

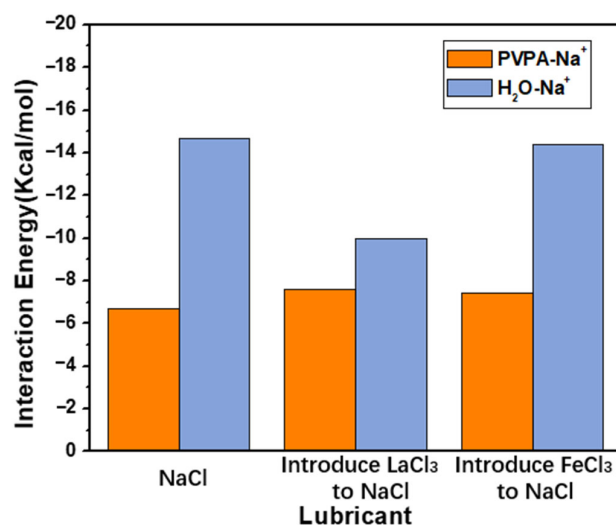


Figure 4. The interaction energies of Na⁺ with PVPA molecular chains and surrounding water molecules before and after the introduction of La³⁺ and Fe(OH)₃.

The introduction of new ions also interfered with the attraction of Na⁺ to surrounding water molecules. Before the introduction of new ions, the interaction energy between Na⁺ and surrounding water molecules was −14.67 Kcal/mol. After the introduction of La³⁺ and Fe(OH)₃, the interaction energies of Na⁺ and surrounding water molecules were −10 Kcal/mol and −14.37 Kcal/mol, respectively, as shown in Figure 4. Compared to Fe(OH)₃, the introduction of La³⁺ led to a greater decrease in the attraction of Na⁺ to surrounding water molecules. The state change of Na⁺ can be ignored compared with the change in the interface state caused by the introduction of ions. In other words, the perturbation of the cations in the base lubricant resulting from the introduction of multivalent cations had a negligible influence on the change in friction coefficient.

The above study shows that the friction coefficient of a PVPA superlubricity system can increase suddenly when adding LaCl₃ or FeCl₃ solution into the basic lubricant during the friction process. The increase in friction coefficient could be caused by the tearing off of microbands of PTFE from the ball surface, as a sharpened profile of the PVPA coating was generated by the bridge effect between introduced ions and the PVPA molecular chains. Trivalent lanthanum ions in the solution mainly exist in the form of La³⁺, which is adsorbed on the surface through an electrostatic effect. These trivalent cations can enhance the hydration degree of the surface by attracting surrounding water molecules, playing a lubrication role. However, trivalent iron ions mainly exist in the form of Fe(OH)₃, which can be connected to PVPA surface by hydrogen bonds. However, their attraction to surrounding water molecules is less than that of La³⁺, resulting in a sudden increase in friction coefficient greater than that of La³⁺.

3.2. Regulation of Ion Concentration with respect to the Friction Coefficient of PVPA Superlubricity Systems

A related study showed that the bridging effect between salt ions and polymers is concentration-dependent [25], which may lead to changes in friction results. Concentrations of 0.01 mol/L, 0.1 mol/L and 1 mol/L were selected for LaCl₃ and FeCl₃ to add to basic lubricant during the friction process in this study. Combined with the result obtained with a concentration of 0.5 mol/L reported in Section 3.1, the influence of ion concentration on the sudden change in friction coefficient was investigated.

The pH values 0.5 mol/L NaCl solution mixed with different concentrations of trivalent salt solution were detected. The volume ratio of NaCl solution and trivalent salt solution in the mixed solution was 3:1. The results are presented in Table 4. The concentration of LaCl₃ in the mixed solution had no obvious effect on the pH value of the mixed solution. Trivalent lanthanum ions in the mixed solution are always presented as La³⁺.

According to Equation (2), the more Fe^{3+} reacts with water molecules, the lower the pH value of the solution. With increased FeCl_3 concentration, the pH value of the $\text{NaCl}/\text{FeCl}_3$ mixed solution decreased continuously. Almost all the trivalent iron ions in mixed solutions with varying FeCl_3 concentrations appear in the form of $\text{Fe}(\text{OH})_3$ [24].

Table 4. pH values of mixed solutions with different concentrations of trivalent salt solutions.

Trivalent Salt Solution Concentration (mol/L)	0.01	0.1	1
pH ($\text{NaCl}/\text{LaCl}_3$)	5.8	5.8	5.7
pH ($\text{NaCl}/\text{FeCl}_3$)	3.3	2.6	2

The introduction of LaCl_3 solutions with different concentrations in the friction process can cause the friction coefficient to suddenly increase, as shown in Figure 5. For concentrations of 0.01 mol/L, 0.1 mol/L and 1 mol/L, the friction coefficient of the PVPA superlubricity system increased by $518.46 \pm 92\%$, $574.24 \pm 88\%$ and $360.90 \pm 65\%$, respectively. Combined with the increase in the friction coefficient at a concentration of 0.5 mol/L in reported Section 3.1 ($285.24 \pm 62\%$), it can be concluded that a higher concentration of LaCl_3 does not result in a greater degree of sudden increase in friction coefficient. Instead, there is an extreme value of concentration at which the maximum of the sudden increase degree of friction coefficient can be obtained.

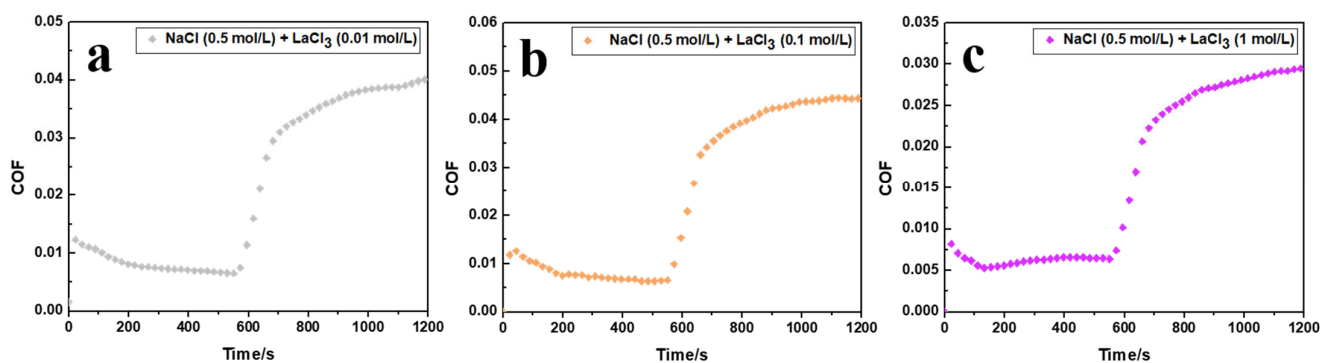


Figure 5. Variations in the COF of PVPA-modified Ti6Al4V in an NaCl solution sliding against PTFE balls induced by the introduction of LaCl_3 solutions with varying concentrations: (a) 0.01 mol/L, (b) 0.1 mol/L and (c) 1 mol/L.

SEM was used to observe the surface microstructures of PVPA-modified surfaces soaked in $\text{NaCl}/\text{LaCl}_3$ mixed solutions with varying concentrations of LaCl_3 . The influence of the concentration of La^{3+} on the PVPA surface morphology was investigated. After soaking the PVPA coating in a mixed solution containing 0.01 mol/L LaCl_3 , no cracks appeared on the coating surface, as shown in Figure 6a. When the concentration of LaCl_3 was increased to 0.1 mol/L, obvious cracks appeared on the coating surface, as shown in Figure 6b. When the concentration of LaCl_3 was 0.5 mol/L and 1 mol/L, obvious exposed Ti6Al4V appeared on the surface, as shown in Figure 2(a1) and Figure 6c, respectively.

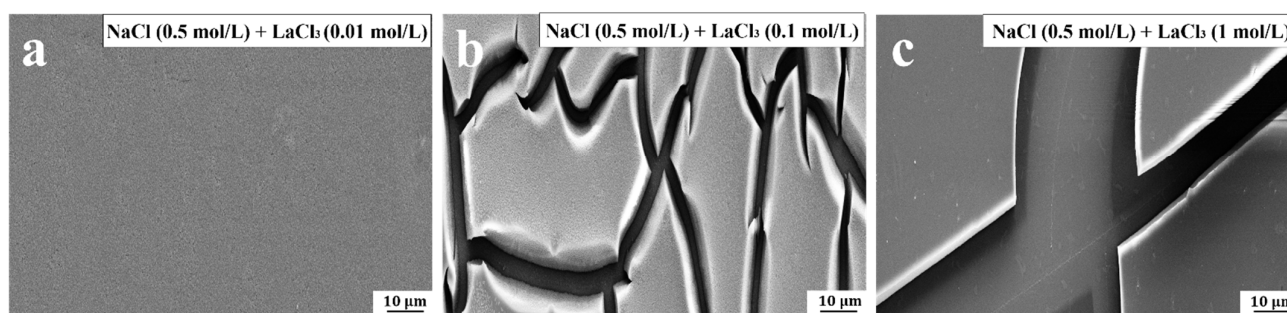


Figure 6. Surface microstructures of PVPA-modified surfaces soaked in NaCl/LaCl₃ mixed solutions with varying concentrations of LaCl₃: (a) 0.01 mol/L, (b) 0.1 mol/L and (c) 1 mol/L.

The bridge effect between La³⁺ and the PVPA molecular chain is the main reason for the sudden increase in the friction coefficient. The degree of bridging effect can be reflected by the degree of PVPA cracking, which is related to the concentration of LaCl₃ in the mixed solution. The higher the concentration of LaCl₃ in the mixed solution, the more obvious the cracks on the PVPA coating. However, the coating did not peel off completely. We speculate that the main role of La³⁺ is to bridge the PVPA molecular chain and destroy the coating structure before the appearance of surface exposure of Ti6Al4V due to coating cracks. In this process, the higher the concentration of LaCl₃, the more La³⁺ is involved in the bridging effect and the greater the degree of sudden increase in friction coefficient. La³⁺ tends to adsorb on exposed Ti6Al4V surfaces when the surface exposure of Ti6Al4V occurs due to coating cracks. At this point, the main role of La³⁺ is to play a lubrication role by attracting surrounding water molecules, which can inhibit the sudden increase in friction coefficient to a certain extent. Therefore, the sudden increase in friction coefficient at concentrations of 0.5 mol/L and 1 mol/L is less than that at 0.01 mol/L and 0.1 mol/L, respectively. When surface exposure of Ti6Al4V occurs due to coating cracks, as the concentration of LaCl₃ continues to increase, it can continue to damage the coating structure. Therefore, the sudden increase in friction coefficient caused by the introduction of LaCl₃ solution with a concentration of 1 mol/L is greater than that of 0.5 mol/L.

The introduction of FeCl₃ solution with varying concentrations in the friction process can cause the friction coefficient of the PVPA superlubricity system increase suddenly, as shown in Figure 7. When the concentrations of FeCl₃ are 0.01 mol/L, 0.1 mol/L and 1 mol/L, the degree of sudden increase in the friction coefficient are $825.37 \pm 95\%$, $2648.14 \pm 102\%$ and $2000 \pm 77\%$, respectively. Compared to trivalent lanthanum ions, trivalent iron ions almost always exist in the form of Fe(OH)₃ in mixed solutions with varying concentrations of FeCl₃. Combined with the degree of sudden increase in the friction coefficient ($1825.86 \pm 70\%$) with a concentration of 0.5 mol/L reported in Section 3.1, it can be concluded that the dependence of Fe(OH)₃ on the degree of induction of the sudden increase in friction coefficient with respect to concentration is similar to that of La³⁺. There is an extreme concentration value at which the maximum degree of sudden increase in friction coefficient can be obtained.

Figure 8 shows the microstructures of PVPA-modified surfaces soaked in NaCl/FeCl₃ mixed solutions with varying concentrations of FeCl₃. Fe(OH)₃ binds to more than one hydroxyl group from the same or an adjacent molecular chain by hydrogen bonding, and the degree of this special bridging effect is also dependent on the concentration of FeCl₃. When the concentration of FeCl₃ in the mixed solution increases from 0.01 M to 0.1 M, cracks begin to appear on the surface of the PVPA coating, as shown in Figure 8a,b. When the concentration of FeCl₃ is 1M, an obvious Ti6Al4V bare part appears on the surface, as shown in Figure 8c. We speculate that when the concentration of FeCl₃ is low, one Fe(OH)₃ molecule will be hydrogen-bonded to three hydroxyl groups. When the concentration increases, some Fe(OH)₃ molecules can only bind to one hydroxyl group, so the Fe(OH)₃ will not cause further damage to the coating and can attract the surrounding

water molecules for lubrication. This may be an important reason for the existence of extreme degree of the sudden increase in friction coefficient.

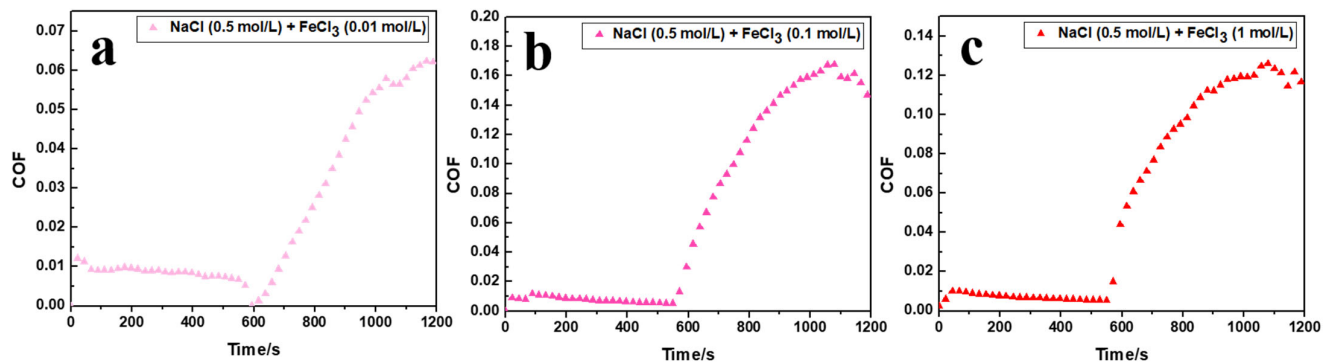


Figure 7. Variations in the COF of PVPA-modified Ti6Al4V in a NaCl solution sliding against PTFE balls induced by the introduction of FeCl₃ solutions with varying concentrations: (a) 0.01 mol/L, (b) 0.1 mol/L and (c) 1 mol/L.

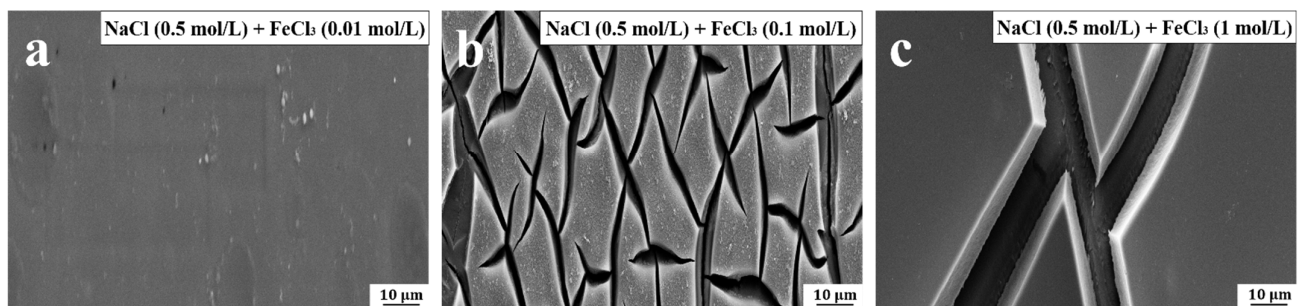


Figure 8. Surface microstructures of PVPA-modified surfaces soaked in NaCl/FeCl₃ mixed solutions with varying concentrations of FeCl₃: (a) 0.01 mol/L, (b) 0.1 mol/L and (c) 1 mol/L.

The above analysis indicates that a PVPA coating can respond to the presence of trivalent ions, even at low concentrations. In addition, the degree of the sudden increase in friction coefficient caused by the introduction of trivalent ions in the friction process is concentration-dependent. There is an extreme concentration at which the maximum degree of increase in the friction coefficient can be obtained.

4. Conclusions

In this study, trivalent salt solutions (LaCl₃ and FeCl₃) were added to the base lubricant (NaCl solution) during the friction process, achieving real-time control of the friction coefficient of a PVPA superlubricity system. The friction coefficient of the PVPA superlubricity system increased suddenly in response to the addition of trivalent salt ions in real time. The degree of the sudden increase in friction coefficient was affected by the type and concentration of cations.

Even for cations with the same valence state, the degree of the sudden increase in friction coefficient obviously differs. One important reason is the difference in the form of trivalent cations in the solution. Trivalent lanthanum ions exist in the form of La³⁺ in salt solution. An La³⁺ ion can bind to more than one oxygen atom from the same PVPA chain or adjacent PVPA chains by electrostatic effects. This type of binding is called a bridging effect, which can destroy the internal structure of the PVPA coating and cause obvious cracks in the coating. Before the cracking of the coating exposes the Ti6Al4V substrate, the main role of La³⁺ is to destroy the coating structure through the bridging effect. In this process, the higher the concentration of LaCl₃ solution, the greater the sudden increase in friction coefficient. When the Ti6Al4V substrate is exposed by coating cracking, La³⁺ is

more likely to adsorb on the exposed Ti6Al4V surface, which enhances the hydration degree of the friction interface by attracting surrounding water molecules. This change can inhibit the sudden increase in the degree of friction coefficient. Therefore, there is an extreme concentration at which the sudden increase in the friction coefficient can be maximized.

Trivalent iron ions in salt solution mainly exist in the form of $\text{Fe}(\text{OH})_3$ and bind to the hydroxyl group on the PVPA molecular chain by hydrogen bond. A bridging effect similar to that of La^{3+} also occurs, resulting in the destruction of the PVPA coating structure. The ability of $\text{Fe}(\text{OH})_3$ to attract surrounding water molecules is less than that of La^{3+} . As a result, the degree of sudden increase in friction coefficient caused by the FeCl_3 solution is greater than that caused by LaCl_3 at the same concentration. However, the degree of sudden increase in the friction coefficient induced by $\text{Fe}(\text{OH})_3$ has a similar concentration dependence as that of La^{3+} . This study provides a theoretical basis for the intelligent regulation of water-based superlubricity of polymer coatings by expanding the application of the response of polymer coatings to multivalent ions under friction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants10080191/s1>, Section S1. Microscopic observation of surface morphology of PTFE balls after sliding. Figure S1: Wear morphologies of PTFE balls lubricated by (a) NaCl solution, (b) NaCl/ LaCl_3 mixed solution and (c) NaCl/ FeCl_3 mixed solution; Section S2. Calculation of the interaction energy.

Author Contributions: M.L. and L.W. conceived and designed the experiments; M.L. and L.B. conducted the experiments; C.Z. and M.L. analyzed the data; Y.C. and Y.L. contributed reagents/materials/analysis tools; and C.Z. and Z.L. compiled the manuscript. All authors have read and agreed to the published version of the manuscript.

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