Surface Chemistry

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Long-Range Hydrophilic Attraction between Water and Polyelectrolyte Surfaces in Oil

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Abstract: *The outstanding water wettability and the capability of polyelectrolyte surfaces to spontaneously clean oil fouling are determined by their wetting mechanism in the surrounding medium. Here, we have quantified the nanomechanics between three types of polyelectrolyte surfaces (i.e. zwitterionic, cationic, and anionic) and water or oil drops using an atomic force microscope (AFM) drop probe technique, and elucidated the intrinsic wetting mechanisms of the polyelectrolyte surfaces in oil and water media. The measured forces between oil drops and polyelectrolyte surfaces in water can be described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Surprisingly, strong long-range attraction was discovered between polyelectrolyte surfaces and water drops in oil, and the strongest interaction was measured for the polyzwitterion. This unexpected long-range "hydrophilic" attraction in oil could be attributed to a strong dipolar interaction because of the large dipole moment of the polyelectrolytes. Our results provide new nanomechanical insights into the development of novel polyelectrolyte-based materials and coatings for a wide range of engineering, bioengineering, and environmental applications.*

Polyelectrolytes are an ubiquitous class of macromolecules found in living organisms and in nature in the form of proteins, DNA, and enzymes, and various polyelectrolytes have been synthesized recently for a multitude of applications in materials science and nanotechnology.[1] Since their ionic groups can superiorly bind water molecules by strong electrostatically induced hydration, polyelectrolytes can be easily wetted by water in air, exhibiting outstanding hydrophilicity.[1a,2] These tightly bound water molecules render the polyelectrolyte chains highly swelled in water,[2,3] and are believed to be the major mechanism for their promising applications such as underwater oil repellency,[4] antifouling,[1b,5] oil/water separation,[6] and lubrication.[7] Of all polyelectrolytes, the zwitterionic ones exhibit excellent hydrophilicity and hydration strength by integrating both positive and negative ionic groups.[1a,8]

Upon contact with hydrophobic oil, the polyelectrolyte surfaces, like most polar surfaces with high surface energy, will reorient their ionic groups inwards to lower the surface free energy, leading to evident loss of surface hydrophilicity and wettability alteration. Thereby the oil-wetted polyelectrolyte surfaces may not be easily re-wetted by water and the oil contamination adsorbed on many polyelectrolyte surfaces can be difficult to remove, which dramatically impacts the durability of their hydration-related performance.[5b,6b] To resolve the critical fouling issues caused by oil contamination and design novel materials and coatings with better performance and sustainability, knowledge on the water or oil (water/oil) wetting mechanisms of polyelectrolyte surfaces in oil or water (oil/water) medium is of both fundamental and practical importance.

Wettability of oil/water on a substrate surface in water/oil is essentially governed by their interaction forces in the surrounding liquid medium.[2,9] To take the oil wettability in water as an example, strong attraction (e.g. hydrophobic attraction) between an oil drop and a substrate surface across water will facilitate depletion of the confined water film and result in oil wetting on the surface, whereas repulsion will effectively prevent the surface from oil wetting and further oil fouling. Therefore, a systematic and quantitative understanding of the interaction forces of water/oil with polyelectrolyte surfaces in oil/water holds the key to elucidating the intrinsic oil/water wetting mechanisms of polyelectrolyte surfaces in water/oil. The development of drop/bubble probe AFM technique allows quantitative force measurements between solid surfaces and deformable drops or air bubbles in various liquid media,[10] which could help elucidate the wetting mechanism of solid surfaces of varying hydrophobicity.[11]

In this work, the drop probe AFM technique was applied for the first time to directly measure the interaction forces between three types of polyelectrolyte surfaces with permanently charged groups and water/oil drop in oil/water to explore their water/oil wetting mechanisms. The schematic of experiment setup using drop probe AFM is shown in Scheme 1. Toluene was used as a model oil throughout this study. The polyelectrolytes studied are zwitterionic poly-(3-[dimethyl(2-methacryloyloxyethyl) ammonium] propanesulfonate) (PMAPS), cationic poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC), and anionic poly(3-sulfopropyl acrylate potassium) (PSPAK). All three polyelectrolytes were synthesized using reversible addition–fragmentation chain-transfer (RAFT) polymerization and grafted onto gold surfaces by the thiol–gold bond. Details on the characterization of synthesized polyelectrolytes can be found in the Supporting Information.

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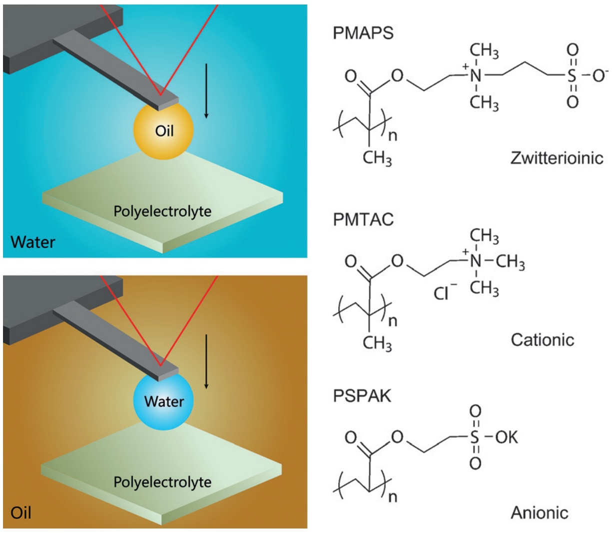

Scheme 1. Left: Experimental setup for measuring the interaction between a polyelectrolyte surface and an oil drop in water (top) and with a water drop in oil (bottom) using drop probe AFM. Right: Chemical structures of zwitterionic poly(3-[dimethyl(2-methacryloyloxyethyl)ammonium] propanesulfonate) (PMAPS), cationic poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMTAC), and anionic poly(3-sulfopropyl acrylate potassium) (PSPAK).

The water wettability of the polyelectrolyte surfaces was first evaluated by measuring their water contact angle in air ($\theta_{\mathrm{W/A}}$) and in oil ($\theta_{\mathrm{W/O}}$) (first two rows in Figure 1). The measured $\theta_{\mathrm{W/A}}$ shows that the zwitterionic PMAPS and anionic PSPAK can be readily wetted by water in air, showing $\theta_{\mathrm{W/A}}$ of $<5°$ and about 13°, respectively; while the cationic PMTAC shows a slightly larger $\theta_{\mathrm{W/A}} \approx 30°$. When the polyelectrolyte surfaces were immersed in oil, the measured water contact angle ($\theta_{\mathrm{W/O}}$) revealed that only the zwitterionic PMAPS surface could be still well wetted by water ($\theta_{\mathrm{W/O}} \approx 18°$), while both cationic PMTAC surface and anionic PSPAK surface showed much poorer water wettability, with $\theta_{\mathrm{W/O}}$ measured to be 75° and 57°, respectively. The difference in water wettability of the three polyelectrolyte surfaces is consistent with recent studies suggesting that the anionic sulfonate (SO_3^-) moieties of the PSPAK are more strongly hydrated than the cationic quaternary amine groups on PMTAC, and the relatively weak hydrophilicity of PMTAC may also be attributed to the presence of the three methyl groups on its quaternary amine group.[6a,12]

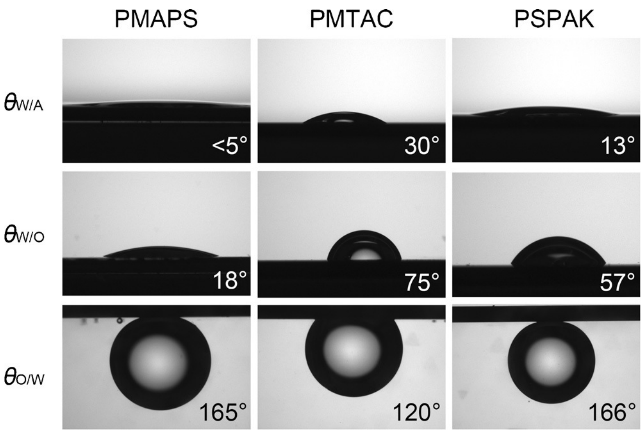

Figure 1. Images of water contact angle in air ($\theta_{\mathrm{W/A}}$), water contact angle in oil ($\theta_{\mathrm{W/O}}$), and oil contact angle in water ($\theta_{\mathrm{O/W}}$) of zwitterionic PMAPS, cationic PMTAC, and anionic PSPAK surfaces.

The contact angle of an oil drop on the three polyelectrolyte surfaces in water ($\theta_{\mathrm{O/W}}$; last row of Figure 1) was also measured to evaluate their oil wettability in water. It was found that all the three polyelectrolyte surfaces could be readily wetted by oil in air with a contact angle less than 5°. However, when immersed in water, the polyelectrolyte surfaces showed distinct oil wetting behaviors. For zwitterionic PMAPS and anionic PSPAK, the oil drop was strongly repelled by the surface, exhibiting very large $\theta_{\mathrm{O/W}}$ of about 165°. Even when the oil drop was strongly compressed towards the PMAPS and PSPAK surfaces, the oil drop deformed significantly but the $\theta_{\mathrm{O/W}}$ remained almost unchanged during compression. After the oil drop was retracted from the surface, no oil residue was detected, demonstrating the excellent underwater oil repellency of PMAPS and PSPAK surfaces (see Figure S2 in the Supporting Information). Such oil repellency was not observed for the cationic PMTAC. In contrast, the oil drop was strongly attracted to the PMTAC surface, forming a relatively small $\theta_{\mathrm{O/W}}$ of about 120°. And the attached oil drop was also stably adhered to the PMTAC surface even when it was driven away from the surface (see Figure S2).

To elucidate the wetting mechanisms, drop probe AFM was applied to directly measure the interaction forces of the zwitterionic PMAPS, cationic PMTAC, and anionic PSPAK surfaces with a water drop in the oil medium and with an oil drop in the water medium. During a typical force measurement, a water/oil drop anchored on a force-sensing AFM cantilever was driven towards and then away from the surface when drop attachment occurred or a certain cantilever deflection was detected. Figure 2 A–C shows the measured interaction forces between a water drop and PMAPS, PMTAC, and PSPAK surfaces in oil medium at a driving velocity of 1 $\mu m\,s^{-1}$, under which the effects of hydrodynamic interaction could be minimized. For all the three cases, the water drops were found to readily attach onto the surfaces, indicated by the measured sudden jump-in behaviors on the force curves (indicated by the arrows in Figure 2 A–C). There is a strong attraction measured before water drop attachment. The zwitterionic PMAPS surface shows the strongest attraction to the water drop in oil with the force range measured to be up to about 1 μm, and such attraction is believed to be responsible for the high water wettability of the PMAPS surface in oil ($\theta_{\mathrm{W/O}} \approx 18°$). Force results between water droplets and another two types of zwitterionic polyelectrolyte surfaces, which are poly[2-(methacryloyloxy)ethyl phosphorylcholine] (PMPC) and poly[2-(*N*-2-methacryloyloxyethyl-*N*,*N*-dimethyl) ammonatoethanesulfonate)] (PMAES) surfaces, in oil also show similar strong long-range attraction (see Figures S3 and S4), suggesting that the measured long-range "hydrophilic" attraction forces in this work are general for interactions between water drops and polyelectrolyte surfaces

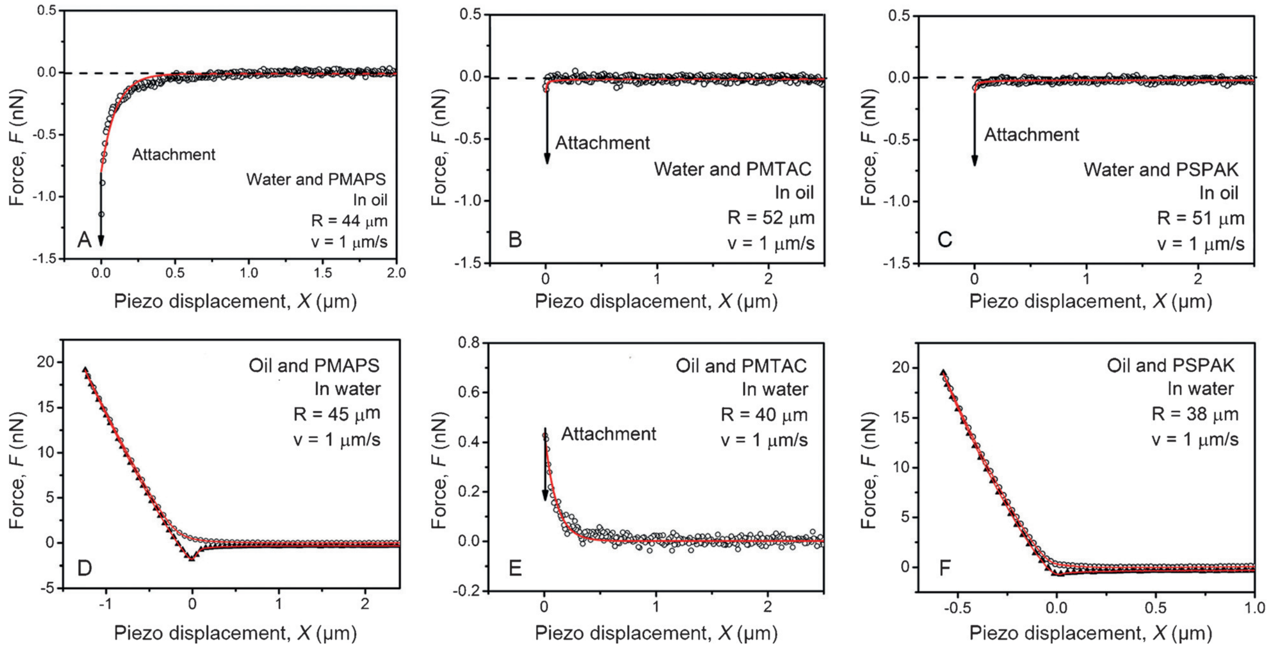

Figure 2. Measured (open symbols) and calculated (red curves) interaction forces of zwitterionic PMAPS (A and D), cationic PMTAC (B and E), and anionic PSPAK (C and F) with a water droplet in oil (i.e. toluene; A–C) and with an oil droplet in water (D–F). The arrows indicate attachment of a water/oil droplet on the polyelectrolyte surface. The pH of water is the natural pH (ca. 5.6). Open circles are force data measured during the approach, and solid triangles are force data measured during retraction.

in oil. Zwitterionic polyelectrolytes can form intermolecular or intramolecular zwitterionic complexes depending on the thickness and grafting density, which may affect the ion distribution inside the polymer surface.[13] Zwitterionic PMAPS surfaces with intermolecular or intramolecular zwitterion complexes were synthesized by varying thickness and grafting density based on a procedure reported previously (see the Supporting Information).[13] The interaction forces between these PMAPS surfaces and water droplets in oil were also measured. All the force results show very strong long-range attraction (Figure S5), which suggests that the measured long-range attraction might not be so sensitive to the parameters like film thickness and grafting density. In addition, such long-range "hydrophilic" attraction was not observed between a water drop and simple hydrophilic surfaces like bare hydrophilic silica. These findings suggest that the long-range "hydrophilic" attraction is most likely an intrinsic characteristic of the zwitterionic polyelectrolyte surfaces. On the other hand, the cationic PMTAC and anionic PSPAK surfaces only weakly attract a water drop within less than 200 nm, and thereby they show much larger $\theta_{W/O}$ values of 75° and 57°, respectively. Such long-range "hydrophilic" attraction in oil has never been reported previously, and cannot be described by the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. According to the DLVO theory, the only effective surface interaction in oil is the van der Waals (VDW) interaction, and there is no electrical double layer (EDL) interaction because of the absence of free ions in oil. Taking a refractive index of 1.450, 1.333, and 1.497 for the polyelectrolyte, water, and toluene, respectively,[2,14] the Hamaker constant for the water/oil/polyelectrolyte system can be estimated to be 1.84×10^{-21} J on the basis of Lifshitz theory,[2] indicating that the VDW interaction is relatively weak and only becomes relatively significant at very short distance (< 10 nm). The calculated force curve (Figure S6) using a theoretical model based on Reynolds lubrication theory and augmented Young–Laplace equation including the effect of disjoining pressure shows a slight repulsion because of hydrodynamic interaction before water drop attachment (i.e. jump-in behavior), demonstrating the invalidity of the classic DLVO theory in describing the forces measured in oil medium (Figure 2 a–c).[10a,15] This unexpected long-range "hydrophilic" attraction between water droplet and hydrophilic polyelectrolyte surfaces in oil resembles the long-range hydrophobic attraction between hydrophobic objects in water, and it might be attributed to the strong electrically induced ion–dipole and dipole–dipole interactions between polyelectrolyte molecules and water across oil,[16] which are generally believed to have a longer range and larger magnitude than VDW interaction.[2,14] Theoretically, the total interaction energy between two polar molecules consists of three contributions, including the Debye induction force, the Keesom orientation force, and the London dispersion force, and the interation potential can be given by $\omega_{total} = -(C_{ind} + C_{orient} + C_{disp})/r^6$, where r is the separation between two molecules.[2] For highly polar molecules, the interaction energy is mainly dominated by the dipolar term with $C_{orient} = -u_1^2u_2^2/3(4\pi\varepsilon_0\varepsilon)^2kT$, where u is the dipole moment, ε_0 is the vacuum permitivity, ε is the dielectric constant of medium, k is the Boltzmann constant, and T is the temperature. For the zwitterionic groups on PMAPS, the dipole moment can be estimated to be about 25 Debye,[17] which is more than 10 times larger than that of a small polar molecule (e.g. water molecule with a dipole moment of

1.85 Debye). Therefore, the interaction energy between PMAPS and water in non-polar oil with small ε (2.38 for toluene) is extremely strong, which can be 100 times stronger than normal VDW interaction energy between two small molecules. Therefore, the Hamaker constants of the VDW interaction between water droplets and the three polyelectrolytes can be roughly estimated to be 10^{-18} J, 0.4×10^{-18} J, and 0.4×10^{-18} J for PMAPS, PMTAC, and PSPAK, respectively. The theoretically calculated results using these modified Hamaker constants are shown in Figure 2A–C (red curves), which, interestingly, are in coincidence with the measured interaction forces (symbols). Such long-range attraction may also arise from electrically induced ion–dipole interaction because the zwitterion group on PMAPS can be treated as two individual charges for the large dipole moment.[6b,14] Other factors like ion-hopping and reorientation of solvent molecules may also contribute to the measured long-range attraction. The interaction forces were also measured at a higher velocity (e.g., 10 and 30 $\mu m\,s^{-1}$), which showed very weak repulsion of several nanonewtons before the water drop attachment because of repulsive hydrodynamic interaction (Figure S7).

Figure 2D–F shows the measured interaction forces between an oil drop and polyelectrolyte surfaces in water. Although the chains of three polyelectrolytes can all be well hydrated in water, they show distinct interaction forces and behaviors with oil drops. For zwitterionic PMAPS and anionic PSPAK surfaces, no jump-in behavior was observed on the force curves, and the oil drop could not attach onto the surface under a maximum force load of 20 nN. Even at higher force load, no attachment of oil drop was observed and the force curves showed no jump-in behaviors (Figure S8), corresponding to very strong underwater oil repellency and large $\theta_{O/W}$ (165°). Such oil repellency in water can be attributed to repulsive EDL interaction between oil drop and PMAPS or PSPAK surfaces in water. Using reported zeta potential of -40 mV, -60 mV, and -35 mV for PMAPS, PSPAK surfaces and oil,[11a,18] respectively, the aforementioned theoretical model incorporating the effects of EDL interaction was applied to calculate the interaction force curves between oil drop and PMAPS or PSPAK surfaces (red curves in Figure 2D and F), which show good agreement with the measured interaction forces (open symbols in Figure 2D and F). The steric repulsion induced by the extended polyelectrolyte chains may also inhibit oil droplet attachment. In contrast, the force profile between cationic PMTAC surface and an oil drop in water shows a sudden jump-in behavior when the repulsion reaches about 0.5 nN (Figure 2E), suggesting attachment of oil drop on the PMTAC surface. The measured slightly repulsive force is due to the weak hydrodynamic repulsion when the oil drop approached close to the PMTAC surface. With reported zeta potentials of $+85$ mV and -35 mV for PMTAC and oil,[11a,18b] respectively, the theoretically calculated force curve (red curve in Figure 2E) agrees well with the measured data (open symbols in Figure 2E), indicating that the attractive EDL interaction between positively charged PMTAC and negatively charged oil drop results in oil drop attachment. This attraction further leads to the relative low $\theta_{O/W}\approx120°$ of PMTAC. Moreover, bridging interaction of the extended PMTAC chains may also play a role in droplet attachment. A certain amount of water could be trapped in the PMTAC chains (e.g. as hydration layer of the polyelectrolyte chains) after oil drop attachment.

Oil de-wetting test in water of the three polyelectrolyte surfaces was conducted to test their spontaneous cleaning performance of oil fouling. As shown in Movie S1, the zwitterionic PMAPS surface could be readily wetted by oil in air, but when the oil-wetted PMAPS surface was immersed in water, the flat oil layer rapidly shrank into a single small drop and detached from the surface. However, the oil layer on cationic PMTAC and anionic PSPAK surfaces only partially shrank into small oil drops, and the oil drops were stably pinned on the surfaces without detachment (Movies S2 and S3). This oil cleaning performance of the polyelectrolyte surfaces can be well explained by the aforementioned interaction forces of polyelectrolytes in oil and water measured using the drop probe AFM. When an oil-wetted zwitterionic PMAPS surface is immersed in water, the long-range "hydrophilic" attraction between PMAPS surface and water across the oil layer (Figure 2A) strongly attracts the water towards the PMAPS surface, leading to depletion of the oil layer and thereby cleaning of the oil fouling. The PMAPS chains are then highly hydrated and regain their oil repellency. In comparison, the attraction of cationic PMTAC and anionic PSPAK surfaces towards water droplets is relatively weak and short-ranged (Figure 2B and C), which is not strong enough to attract the water to the surface and deplete the oil layer. Therefore, the oil fouling cannot be completely cleaned by immersing in water, leaving a considerate amount of oil on the surface.

In summary, for the first time and through direct force measurements we have quantified the nanomechanics of zwitterionic, cationic, and anionic polyelectrolyte surfaces with water or oil drops to elucidate their intrinsic wetting mechanisms. The zwitterionic PMAPS surface was found to be readily wetted by water both in air and oil and exhibit strong oil repellency in water. The anionic PSPAK surface can be well wetted by water in air and also repel oil in water, but cannot be fully wetted by water in oil. The cationic PMTAC surface cannot be well wetted by water in oil, and also strongly attract oil drops in water. The measured interaction forces between polyelectrolyte surfaces and oil drop in water can be well described by DLVO theory, showing that the PMAPS and PSPAK surfaces repel oil drops due to EDL repulsion, while the PMTAC surface attracts oil drops resulted from opposite charges of PMTAC and surfaces of oil drops. In contrast, the interaction forces measured in oil show strong long-range "hydrophilic" attraction between the polyelectrolyte surfaces and water drops, with the strongest interaction measured for the zwitterionic PMAPS surface. Such unexpected strong and long-range "hydrophilic" attraction may be attributed to the strong dipolar interactions arising from the large dipole moment of the polyelectrolytes and other factors like ion hopping. Our results provide nanomechanical insights into the mechanisms of wetting and spontaneous oil cleaning properties of polyelectrolyte surfaces, which provide valuable guidance for the design and development of polyelectrolyte-based materials and coatings with various engineering, bioengineering, and environmental applications.

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