

# Interfacial Water-Dictated Oil Adhesion Based on Ion Modulation

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Herein, we investigate the oil adhesion process on a carboxyl-terminated selfassembled monolayer surface (COOH-SAM) in ionic solutions and observe the interfacial water structure via surface-enhanced Raman scattering (SERS) in this system. It is found that the lower the tetracoordinated water content, the stronger the oil adhesion. Compared to monovalent ions, the strengthened binding of multivalent ions to the COOH-SAM surface makes the interfacial water more disordered, which eventually leads to a stronger oil adhesion. Notably, the amount of oil adhesion decreases with an increase in the thickness of the interfacial water region. The interfacial water-dictated oil adhesion has been demonstrated in capillary to simulate the water-driven oil recovery, providing a molecular-level explanation for enhanced oil recovery from low salinity water flooding and also indicating potential applications in intelligent microfluidic and seawater desalination.

## INTRODUCTION

Oil adhesion behavior has attracted much attention due to its potential applications in many fields, such as antifouling materials,<sup>1,2</sup> oil recovery,<sup>3,4</sup> and intelligent microfluidics.<sup>5,</sup> Most adhesion behavior in practical applications takes place in ionic solutions such as marine environment, cellular fluid, or underground rocks.<sup>7,8</sup> Ions play one of the most important and common roles in intracellular and extracellular fluids and in the natural environment, where they are thought to have a destructive effect on oil-repellent surfaces and exacerbate adhesion.<sup>9,10</sup> For example, for self-cleaning materials designed for ocean environments, the high ionic strength in seawater easily disrupts the surface hydration, thereby impairing its selfcleaning properties.<sup>11,12</sup> Moreover, for crude oil adhesion in rocks, ions are considered to transform surface wettability and changing oil recovery efficiency.<sup>13,14</sup> Thus, controlling the oil adhesion behavior in solution is indivisible from the effect of ions.

In general, oil adhesion is governed by surface energy, texture, and the interfacial tension of oil/water from the macroscopic perspective.<sup>15</sup> However, from the molecular level, it is inseparable from the perturbation of microscopic molecular interactions, such as electrostatic interactions brought by ions and charged surfaces, hydrogen bonding networks generated by water molecules, van der Waals forces between oil molecules and so forth. In the past decades, the effect of ions on oil adhesion was a direct electrostatic interaction between ions and charged interfaces. For example, Wang et al. modulated oil adhesion on polyelectrolyte film surfaces by introducing ions to alter interfacial electrostatic interactions.<sup>9</sup> However, perhaps the important and common

role of the water molecules at the solid-liquid interface dominated by hydrogen bonding is always overlooked.

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The interfacial water behaves differently from bulk water, plays key roles in various processes, such as heterogeneous catalytic reactions, biomacromolecules assembly, and lubrication.<sup>16-18</sup> Over the past decades, a wide variety of analytical techniques have been developed to elucidate the behavior of interfacial water.<sup>19-21</sup> For example, the sum-frequency generation (SFG) signal is generated at an asymmetric interface,<sup>22,23</sup> therefore the measured interfacial region is submolecular in extent, while the detection range of surfaceenhanced Raman scattering (SERS), determined by the local enhancement electromagnetic field induced by plasma resonance, is up to several nanometers.<sup>24,25</sup> It is found that the behavior of interfacial water detected previously does not always reflect the macroscopic functions of the materials because not only the water molecules at the submolecular level of the interface but those in the interfacial region that far beyond submolecular level, where the structure and behavior are different from those of bulk water, may play important roles in the functions.<sup>26</sup>

SAMs are 2D materials that are widely used in tuning the surface chemistry of materials. The structure and properties of SAMs have a subtle and investigable influence on macroscopic

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**Figure 1.** Probing interfacial water structure for oil adhesion in ionic solutions. (a) Schematic diagram for the preparation process of a carboxylterminated self-assembled monolayer surface (COOH-SAM), including vacuum evaporation of gold film and thioalcohol modification. (b) The interfacial water structures in oil nonadherent NaCl solution and oil adherent CaCl<sub>2</sub> solution. (c) The amount of oil adhesion in CaCl<sub>2</sub> solution is influenced by the pH-dependent thickness of interfacial water region.

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wetting properties.<sup>27–29</sup> Herein, we investigate the oil adhesion process on a carboxyl-terminated self-assembled monolayer surface (COOH-SAM) in ionic solutions and observe the interfacial water structure via SERS in this oil-water-solid three-phase system. The results show that interfacial water plays a dominant role in the adhesion of oil droplets. The surface is prepared by vacuum-deposited gold film on Si substrate (with titanium film as an adhesion layer) and modification with a SAM of HS(CH<sub>2</sub>)<sub>11</sub>COOH (12mercaptododecanoic acid) (Figure 1a). The root means square roughness of the vaporized gold surface used in this work is 0.58 nm characterized by an atomic force microscope (AFM) (Figure S1). The COOH-SAM surface [isoelectric point (IEP) is about 2.9, Figure S2] exhibits different surface charge densities under different pH values.<sup>30</sup> It is reported that SAM-COOH has no significant molecular orientation since it can be both donor and acceptor for the hydrogen bonding to form dimeric species.<sup>31–33</sup> The results show that the introduction of ions increases the oil adhesion compared to pure water, which is attributed to disruption of the orderliness of the interfacial water. The efficiency of ions in regulating oil adhesion follows the Hofmeister series and is related to the ion valence. Compared to monovalent ions such as Na<sup>+</sup>, the stronger binding of multivalent ions like Ca2+ to the COOH-SAM surface makes the interfacial water more disordered, which eventually leads to stronger oil adhesion (Figure 1b). The lower the tetracoordinated water content, the stronger the oil adhesion. Furthermore, it is shown that with the increase of the surface charge density (which is pH dependent), the thickness of the interfacial water region gradually increases (Figure 1c). Our results present an in-depth insight for macroscopic oil adhesion from the perspective of microscopic interfacial water molecules, which can not only be applied to crude oil recovery but also provide a significant guidance for design of adhesion/ antiadhesion materials for biomedical or marine environments,

indicating potential applications in intelligent microfluidic and seawater desalination.

# RESULTS AND DISCUSSION

To study the influence of a series of ions on macroscopic properties, we investigated the oil adhesion and wettability on the COOH-SAM surface in different ion solutions. The type of oil used is *n*-decane (the same below). The oil adhesion force and contact angles increase with the cation sequence of NH4<sup>+</sup>  $< K^{+} < Na^{+} < Cs^{+} < Li^{+} < Mg^{2+} < Ca^{2+} < Ba^{2+}$ , which corresponds well to the Hofmeister series<sup>14,34</sup> (Figures 2a,b and S3). It is worth mentioning that the results of the oil adhesion force and contact angles show a dependence on the cation valence. The oil adhesion to negatively charged surfaces in divalent cation solutions (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>) is near 50  $\mu$ N, while in monovalent cation solutions  $(NH_4^+, K^+, Na^+, Cs^+, Li^+)$ is only about 10  $\mu$ N, and the adhesion force in pure water is close to 0. Considering the effect of oil polarity on the adhesion force, the results for other types of oils (silicone oil and octanoic acid) are also discussed (Figure S4). It is found that the adhesion force of silicone oil and octanoic acid in divalent ionic solutions is greater than that of monovalent ions, with results similar to those for *n*-decane. It can be concluded that the introduction of ions increases oil adhesion and macroscopic adhesion behavior and wettability properties exhibit specific ionic effects and valence dependence.

The ions act on the interfacial water structure and eventually lead to differences in macroscopic properties.<sup>35,36</sup> Therefore, to directly characterize the structure of interfacial water in the presence of ions, SERS is used to detect the interfacial water signal, which effectively reduces the interference of bulk water due to the surface plasmon resonance effect of Au atoms.<sup>24,25</sup> It is reported that the Raman spectrum of the interfacial water can be divided into three Gaussian peaks according to the stretching vibration mode of the OH bond:<sup>24,37</sup> (a) the



**Figure 2.** Connection between macroscopic oil adhesion and microscopic interfacial water. (a) Cation adsorptions on negatively charged COOH-SAM follow the Hofmeister series. (b) Distinct efficiency of cations in modulating the adhesion force and contact angles of COOH-SAM surface follows the Hofmeister series. (c) Raman spectra of interfacial water in the presence of a series of cations on COOH-SAM surface at pH = 7, and the peak is fitted into three Gaussian subpeaks, representing tetracoordinated water (3200 cm<sup>-1</sup>), weakly hydrogen-bonded water (3400 cm<sup>-1</sup>), and free water (3600 cm<sup>-1</sup>), respectively. (d) The relationship between the adhesion force and the proportion of the three types of water is measured, and the result indicates that oil adhesion increases with the decrease of the tetracoordinated water content.

tetracoordinated water formed by tetrahedrally coordinated hydrogen bond (3200  $\text{cm}^{-1}$ ); (b) the weakly hydrogen-bonded water built up by partial hydrogen bond ( $3400 \text{ cm}^{-1}$ ); as well as (c) the free water formed by dangling hydrogen bond (3600 cm<sup>-1</sup>). In this context, the Raman spectra of the interfacial water on the COOH-SAM surface in the presence of different cations are demonstrated (Figure 2c). The peak area ratios at 3200, 3400, and 3600 cm<sup>-1</sup> correspond to the ratios of tetracoordinated water (orange), weakly hydrogen-bonded water (green), and free water (purple) at the interface, respectively. It is reported that the O-H stretching signal from COOH-SAM does not contribute to the Raman signal.<sup>38</sup> From water to monovalent ions and then to divalent ions, it is obvious that there is a decrease in the content of tetracoordinated water, a slight decrease in free water, and an increase in weakly hydrogen-bonded water. In order to further investigate the relationship between adhesion force and tetracoordinated water content, the peak area of each subpeak is compared with the adhesion forces (Figure 2d). We can notice that as the tetracoordinated water decreases, the oil adhesion gradually increases. Furthermore, the tetracoordinated water content varies with ions in accordance with the Hofmeister series and is dependent on ion valence, similar to the oil adhesion and wettability results. Given the complex properties of self-assembled monolayers,<sup>39-44</sup> we investigate

the effect of carbon chain length of COOH-SAM on the oil adhesion and interfacial water structure (Figure S5). As a result, there is little difference in oil adhesion and interfacial water structure between COOH-SAM surfaces with different carbon chain lengths, suggesting that terminal COOH groups may play a dominant role in the macroscopic properties. Considering the effect of substrate roughness on the properties of SAM,<sup>41,45</sup> we, therefore, introduce plasma treated Si(100)-Au surface (Figure S6) and rough silicon nanowire surfaces (SiNWs, Figure S7) to investigate the oil adhesion behavior and interfacial water structure. The SiNW surfaces exhibit significantly lower adhesion than the other two surfaces due to the reduced contact area and the conclusion that the lower the interfacial tetracoordinated water content, the stronger the oil adhesion remains (Figure S8). In brief, the enhanced interaction between the cation and the negatively charged surface reduces the ordering of the interfacial water, leading to the stronger oil adhesion.

The specific ion effects are also influenced by the ion concentration (Figures 3a and S9). Na<sup>+</sup> and Ca<sup>2+</sup> are chosen as the representatives of monovalent ions and multivalent ions, respectively. As shown in Figure 3a, the adhesion force of oil droplets in different concentrations of NaCl and CaCl<sub>2</sub> solution is tested. Initially, when the cation concentration is smaller than  $1 \times 10^{-2}$  M, the surface shows no oil adhesion.

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Figure 3. Effect of cation concentration on oil adhesion. (a) Adhesion force of oil droplets vary with cation concentration in NaCl,  $CaCl_2$  solution on COOH-SAM. (b,c) Raman spectra of interfacial water vary with cation concentration in NaCl and  $CaCl_2$  solution. (d,e) The schematic shows the transformation of an oil-free adherent surface to an oil adhering surface based on the interfacial water structure as the concentration of Na<sup>+</sup> and Ca<sup>2+</sup> increase.

When the concentration increases from  $1 \times 10^{-2}$  to 1 M, the adhesion force in NaCl solution remains at a low value, while the adhesion force in CaCl<sub>2</sub> solution starts to increase and reaches a maximum value of about 54  $\mu$ N at 1 M. The concentration continues to increase from 1 M, and the adhesion force in CaCl<sub>2</sub> solution remains at a high value, while the adhesion force in NaCl solution begins to rise and reaches a maximum value of about 10  $\mu$ N at 4 M. The adhesion of oil droplets in divalent ion solution is significantly higher compared to monovalent ions based on interfacial water dominance. The effect of ion concentration on interfacial water is also measured in NaCl and CaCl<sub>2</sub> solution (Figure 3b,c). The tetracoordinated water remains basically unchanged with the addition of small amounts of ions until the concentration is  $1 \times 10^{-6}$  M. When the ion concentration range is  $1 \times 10^{-6}$  to 1  $\times$  10<sup>-2</sup> M, although the percentage area of tetracoordinated water gradually decreases with the addition of ions, there is no change in the oil adhesion behavior currently. After the ion concentration increases from  $1 \times 10^{-2}$  M, Ca<sup>2+</sup> and Na<sup>+</sup> begin to appear different. The percentage area of tetracoordinated water in  $Ca^{2+}$  decreases from 0.17 to lower, and the macroscopic manifestation of adhesion starts to rise sharply. In contrast, the percentage area of the tetracoordinated water in Na<sup>+</sup> decreases from 0.25 to near 0.2, and the adhesion force does not change significantly. The ion concentration continues to increase from 1 M, the interfacial water structure in the CaCl<sub>2</sub> solution remains basically unchanged, and at the same time the adhesion force is smoothly maintained at a high value of about 54  $\mu$ N, while the content of tetracoordinated water in the NaCl solution starts to decrease significantly with

increasing ion concentration, leading to a sudden increase in adhesion force. Combining the microscopic interfacial water structure and macroscopic adhesion results, a simplified model is proposed to explain the concentration-induced changes (Figure 3d,e). According to above results, it can be concluded that low concentrations of ions are not sufficient to produce changes in microscopic interfacial water structure and macroscopic adhesion. Once the concentration increases, divalent ions begin to cause changes in microscopic interfacial water and macroscopic adhesion first. After the concentration continues to increase, the changes induced by monovalent ions start to appear.

In addition to ionic specificity in solution, we also focus on the effect of surface charge density on the structure and thickness of interfacial water.<sup>26,36</sup> A gradient confined spatial approach is developed to compare the thickness of interfacial perturbed water at different pH values in ion solutions (Figure 4a). A quartz slide is placed on the COOH-SAM surface, and dispersed silicon spheres with a diameter of 1  $\mu$ m are clamped at the end of the substrate to form a trapping water layer with increasing thickness (Figures S10 and S11). Since the angle formed by the quartz slide and substrate is small enough, the laser parallelly moves 100  $\mu$ m to the right, and the vertical detection thickness of water layer can be increased by 5 nm. At tip area far away from the silicon sphere, the water layer detected by the laser are mainly interfacial signals; when close to the silicon sphere, with the thickness of solution increases, the proportion of interfacial signals decreases, and the water layer detected is mainly from bulk (Figure 4b). It is reported that the evolution of the water structure on the solid surface

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**Figure 4.** Measurement of the thickness of the interfacial perturbed water. (a) Schematic diagram of gradient confined spatial approach for comparing the thickness of interfacial perturbed water at different pH values. (b) At the position far away from the silicon sphere, the water molecules detected by the laser are mainly interfacial water; when close to the micron sphere, the water detected are mainly bulk water. (c) The evolution of the interfacial water structure with thickness can be basically divided into three zones, which are interfacial water ( $d_1$ ), transitional water ( $d_2$ ), and disordered bulk water. The interfacial perturbed water, also called the interfacial water region, is defined as the sum of the interfacial water and the transitional water ( $d_1 + d_2$ ), referring to the region where interfacial water exists, which plays an important role in the function of the materials. (d) The tetracoordinated water content decreases first and then tends to be stable with the increase in the measured water thickness. It can be found that the thickness of the interfacial perturbed water for pure water is about 20–30 nm. (e) Schematic illustration of the structural evolution of the CaCl<sub>2</sub> solution at the COOH-SAM interface. Pink spheres represent Ca<sup>2+</sup> and blue spheres represent Cl<sup>-</sup>. (f) Variation of the tetracoordinated water content with measured CaCl<sub>2</sub> solution thickness at pH 2, 7, 12. It can be observed that the thickness of interfacial perturbed water in 1 M CaCl<sub>2</sub> varies with pH: ~50 nm (pH = 12) > ~30 nm (pH = 7) > ~20 nm (pH = 2).

with thickness can be basically divided into three zones, which are interfacial water  $(d_1)$ , transitional water  $(d_2)$ , and disordered bulk water  $^{4\delta,47'}$  (Figure 4c). The water layers closest to the interface is the interfacial water  $(d_1)$ , which is strongly bonded to the surface; when beyond the interfacial water, the bulk water is gradually introduced, and the interfacial water and bulk water coexist, which is called the transitional water  $(d_2)$ ; until the measured water layer increases to the point where the interfacial water can be neglected, this refers to the bulk water. Here, we define the interfacial perturbed water, also called the interfacial water region, as the sum of the interfacial and transitional water  $(d_1 + d_2)$ , referring to the region where interfacial water exists. For convenience, the proportional area of the tetracoordinated water is still used to characterize the interfacial water structure. For pure water, the variation of the tetracoordinated water content with the thickness of the water layer is measured (Figure 4d). Mathematically, the data points are fitted to a logistic function for further analysis. At first, the content of tetracoordinated water decreases steadily with the increase of water layer; when the thickness of water layer approaches near 20-30 nm, it gradually flattens out. When the water molecules detected change from the interface dominated to the bulk dominated, the tetracoordinated water content drops from the high value to the equilibrium value and remains unchanged. It can be found that the thickness of the interfacial perturbed water for pure water is about 20-30 nm.

As for the 1 M  $CaCl_2$  solution at pH 2, 7, and 12, the trend of tetracoordinated water content is different from that of pure water. Due to the existence of electric double layer (EDL), the cations are always adsorbed on the surface as a tight layer

(Figure 4e). At the position with the thinnest water film, the concentration of cations is the highest, thus the hydrogen bond network of the interface is destroyed mostly, leading to the result that the tetracoordinated water content is at the lowest point. With the increase of the thickness of the measured water, the influence of cations weakens and the content of tetracoordinated water increases. Until the thickness threshold reaches, the curve tends to be flat. We measure the changes in interfacial water thickness at three pH values (Figure S12), which represent the three states of surface negative charge density (Figure S13). At pH 2, the surface is very weakly positively charged, and only a few anions are arranged in the dense layer; therefore, the tetracoordinated water with four hydrogen bonds on the interface is destroyed to a lesser extent. Nearly 14% of tetracoordinated water still exists at the interface. As for pH 12, the strongly negatively charged surface causes a lot of cations to accumulate in the EDL, and the tetracoordinated water on the interface is destroyed to a great extent. As a result, only  $\sim 8\%$  of the tetracoordinated water is present. The interfacial tetracoordinated water content of pH 7 is about 10%, which is between pH 2 and pH 12. Further, it can be concluded that the thickness of the interfacial perturbed water in 1 M CaCl<sub>2</sub> varies with pH:  $\sim$ 50 nm (pH = 12) >  $\sim$ 30 nm (pH = 7) >  $\sim$ 20 nm (pH = 2) (Figure 4f). Similarly, the interfacial perturbed water thickness in NaCl solution varies with pH and is also measured (Figure S14).

With the increasing pH, the thickness of interfacial perturbed water increases, which would lead to differences in oil adhesion. Based on the device schemed in Figure 4a, the 1 M  $CaCl_2$  solution is injected into the confined space first, followed by oil, after which the advancement of oil droplets in

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**Figure 5.** Application of interfacial water-dictated oil adhesion in water driven oil recovery. (a) Schematic diagram of water driven oil recovery. (b) Capillaries used to simulate subsurface rock channels are first prewetted with 1 M NaCl solution (pH = 2, 7, 12), filled with oil, and then rinsed with corresponding NaCl solution, and the results shows that no residue is displayed on the capillaries. (c) When the capillaries are first prewetted with 1 M CaCl<sub>2</sub> solution (pH = 2, 7, 12), filled with oil, and then rinsed with corresponding CaCl<sub>2</sub> solution, there are residues on the capillaries, and the residual amount decreases with the increase of pH. The scale bar is 100  $\mu$ m.

the confinement space is observed by fluorescence microscopy (Figure S15). The results show that the advancing distance of oil droplets in the confined space follows the order pH 2 > pH 7 > pH 12, revealing that the thicker the interfacial perturbed water, the less it will be replaced by oil, which confirms the effect of interfacial water thickness on oil adhesion.

It is considered that the adhesion of subsurface crude oil is related to ions and the recovery of crude oil could be improved by low salinity water flooding,48,49 but molecular-level explanation is still not well-known. Based on the above phenomena and conclusions, taking molecular interaction into account, we propose that the presence of divalent ions reduces the content of interfacial tetracoordinated water, further leading to an increase in oil adhesion. As a proof of concept, we use capillary tubes to simulate subsurface rock channels and *n*-decane to simulate crude oil (Figure 5a). The inner diameter of the capillary is 0.3-0.4 mm. Practically, we rinse the capillary with 1 M NaCl and CaCl<sub>2</sub>, followed by dyed oil droplets and then with corresponding NaCl and CaCl<sub>2</sub>. Fluorescence microscopy images show that when rinsed with CaCl<sub>2</sub> solution, there is obvious residual *n*-decane on the capillary, while there is no residual when rinsed with NaCl solution (Figure 5b). In addition, no oil residues are found in the capillaries rinsed with NaCl solutions of different pH values, while oil droplets are found in all rinses with CaCl<sub>2</sub> solutions of different pH values. As shown in Figure 5c, the larger the pH, the less the oil residue. In addition, the effects of pure water and groundwater in the capillary are also considered (Figure S16). Combined with the above conclusion, it can be revealed that the increase in pH brings about an increase in the thickness of interfacial water, resulting in less oil adhesion. As a brief summary, the strong binding of multivalent ions to the surface reduces the interfacial tetracoordinated water content and enhances the adhesion of oil droplets. On the contrary, low salinity water flooding can improve oil recovery because its

interfacial tetracoordinated water content is sufficient to block the adhesion of crude oil to the subsurface minerals.

## CONCLUSIONS

In summary, the oil adhesion behavior and wettability are adjusted by modulating the structure of interfacial water based on ion introduction from the microscopic perspective. It is found that compared to monovalent ions, stronger binding of multivalent ions to the negatively charged COOH-SAM surface destroys the ordering of interfacial water, leading to enhanced adhesion of oil droplets. The macroscopic adhesion force is inversely proportional to the microscopic tetracoordinated water content. Importantly, the difference in the amount of oil adhesion caused by divalent ions demonstrates a correlation with the pH-induced thickness of interfacial perturbed water; the greater the thickness, the less the adhesion. Our research will contribute to the explanation of the principle of superwetting and adhesion behavior at the molecular level and provides ideas for the mechanism of oil recovery by water flooding

## ASSOCIATED CONTENT

## **3** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c07975.

Materials and methods; the root-mean-square roughness of the Si(100)-Au and plasma-treated Si(100)-Au surfaces; isoelectric point of COOH-SAM; the measurement of oil adhesion process; variation of contact angles with ion concentration; the effect of carbon chain length of COOH-SAM and substrate roughness on oil adhesion and interfacial water structure; detailed information on the wedge setup; the thickness of the interfacial water region in NaCl, and CaCl<sub>2</sub> solutions; zeta potential of COOH-SAM; demonstration of oil adhesion in confined space; and demonstration of oil recovery by water drive with pure water and groundwater (PDF)

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#### Author Contributions

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#### Notes

The authors declare no competing financial interest.

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