REVIEW ARTICLE

VAN DER WAALS FORCE & HYDROPHOBIC EFFECT

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ARTICLE INFO	ABSTRACT
	Van der Waals forces are electrostatic forces. They operate not only between polar molecules but also between electrically neutral atoms and molecules. This is because the movement of electrons in the outer shell of the atoms temporarily leads to charge displacements – and to so-called polarization. Charged areas with different signs are then attracted to one another – and therefore ensure an attraction between two atoms, even if these are electrically neutral overall. The van der Waals force is an electromagnetic interaction between correlated fluctuating charges on two electrically neutral surfaces. As the surfaces approach more closely, the force increases as fluctuations of shorter and shorter length scale come into play, but ultimately the force will saturate when the surfaces are so close that the even shortest wavelength charge fluctuations are included.

INTRODUCTION

There are a strong and weak force in the world. Generally, a strong force is dominant. Most people prefer to strong force. In fact, weak force plays a very important role. The weakest force acting in the world of atoms and molecules is van der Waals force. This force is a force acting on any atom or molecule, but its force is too weak to be neglected. But there are creatures that use this force in a clever way in our world. A typical example is a geckos. Recent scientists have put to rest the age-old question of how geckos stick to walls. The answer is van der Waals forces, molecular attractions that operate over very small distances. The researchers are already trying to use their discovery to make wall-climbing robots and design materials that stick to dry surfaces[1,8]. Geckos stick because of the van der Waals force. This force comes from fluctuations in charge distributions between neighboring molecules, which need not be polar; their charge fluctuations naturally fall into synch, creating an attractive force[2]. It is true that geckos could stick to silicon dioxide, which is polar, and to gallium arsenide such as semiconductors, which is not. The lizards' feet were equally sticky on the two surfaces, proving that van der Waals forces are at work[8]. Van der Waals forces are the attractions/repulsions - the forces - between molecules or atoms, other than attractions like ionic attractions, and covalent attractions. These forces are Keesom Effect which caused by two polar atoms interacting with each other, Deybe Force Effect which caused between a molecule with is polar, and one that is not, and London Dispersal Effect that acts between two non-polar molecules/atoms[3]. Because the electrons around each molecule/atom repel each other, it creates a redistribution of charge, inducing an instantaneous dipole moment[3].

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Dispersion forces are caused by fluctuations in the electron distribution within molecules or atoms. Since all atoms and molecules have electrons, they all have dispersion forces. The electrons in an atom or molecule may, at any one instant, be unevenly distributed [4]. *The purpose of this study is to explore mechanisms of van der Waals forces forces and to identify the potential on the scientific field.*

Thermodynamics

Water has very strong hydrogen bonding, very strong dipole-dipole attractions, very weak London forces, But, Oil has very strong London forces [5]. London dispersion forces are weakest intermolecular force which induce attractive force between non-polar molecules, create from temporary fluctuations in electron density around atoms. The larger the molecule, the greater the dispersion force. When an alcohol dissolves in water, the interactions between the alcohol molecules are replaced by interactions between alcohol and water molecules - an interaction similar to that between water molecules. Like water molecules, alcohols have a dipole (unequal charge distribution), with a small negative charge on the oxygen(s) and small positive charges on the hydrogen (bonded to those oxygen atoms). It makes sense that molecules that have similar structures will interact in similar ways - and so small molecular weight alcohols can dissolve in water [6].

Let us explore the interactions that cause water and oil to separate from a mixture. When oil and water are mixed, the dipole-dipole interactions are disrupted, but constant molecular motion allows the stronger dipole-dipole attractions to partition the polar molecules from the mixture. Oil is a non-polar molecule, while water is a polar molecule. While all molecules are attracted to each other, some attractions are stronger than others. Non-polar molecules are attracted through a London dispersion attraction; polar molecules are

attracted through both the London dispersion force and the stronger dipole-dipole attraction[6]. The force of attractions between molecules has consequences for their interactions in physical, chemical and biological applications[6]. By considering entropy, it could be seen why water and oil are not mixed. Because entropy is not the only determining factor. It Should be included enthalpy [7].

Mixed and unmixed states of water and oil could be evaluated as Gibbs free energy. The lower the free energy, the more stable and tries to maintain that state. There are when it is mixed with water and oil (A), and when it is not mixed with water and oil (B), if it is left without any force, the state of B increases. Thus, assuming that the states of A and B are approached from a molecular point of view, the Gibbs free energy first consists of enthalpy (H) and entropy (S). The reaction formula is as follows.

$$G_{a,} = H - T S$$

Let G_a be the change in Gibbs free energy in the state where water and oil are mixed, and G_b be the change in Gibbs free energy in the state where water and oil are not mixed. Due to the strong polarity between the water molecules, they are strongly combined with each other. At this time, the enthalpy becomes smaller and it reaches a stable state. In other words, water is collected between water and oil is separated by oil. Entropy, on the other hand, means the degree of freedom of a substance. The more water and oil are mixed together, the greater the degree of freedom, or entropy. However, over time, the water molecules form a bond with each other, The oil molecules form a bond with each other, so that the water and the oil are not mixed and remain stable. In other words, the entropy becomes smaller and the enthalpy becomes smaller, so that Gibbs free energy becomes minus and water and oil are not mixed. Oils are slippery, and they do not mix with water. London forces holding the oil molecules together are large do to the large surface area of the oil, the hydrogen bonds holding water molecules together are large. The forces of attraction of between non-polar oil and polar water are weak at best, thus the overall process is highly endothermic and not allowed thermo chemically [11]. Water is held together by hydrogen bonds, oil isn't and it has to input energy to force the water molecules apart [12]. If you pour water and oil into a container and stir it with force, the water and oil will temporarily mix. This enthalpy also increases and the entropy also increases, resulting in Gibbs free energy (G) plus, resulting in unstable mixing of water and oil. Over time, the water form a bond with water, the oil form a bond with oil, so that they do not mix with each other. Again, Gibbs free energy turns negative and returns to stability. The Gibbs free energy is what determines if a reaction proceeds forward or not. Even though the entropy change would be positive, the enthalpy would be endothermic (H > 0) meaning the G >0 and they wouldn't mix [7,9].

For oil dissolving in water, entropy should be greater than zero, Free energy should be greater than zero, since the process is highly endothermic, Thus the overall process is non-spontaneous [11].

Hydrophobic Interactions

American chemist Walter Kauzmann discovered that nonpolar substances like fat molecules tend to clump up together rather that distributing itself in a water medium, because this allow the fat molecules to have minimal contact with water[13].

The mixing hydrophobes and water molecules is not spontaneous; however, hydrophobic interactions between hydrophobes are spontaneous. When hydropobes come together and interact with each other, enthalpy increases (is positive) because some of hydrogen bonds that form the clathrate cage will be broken. Tearing down a portion of the clathrate cage will cause the entropy to increase (is positive), since forming it decreases the entropy[13].

According to the formula:
  G= H-T S
  H=Small positive value,   S=Large positive value
Result :   G= Negative
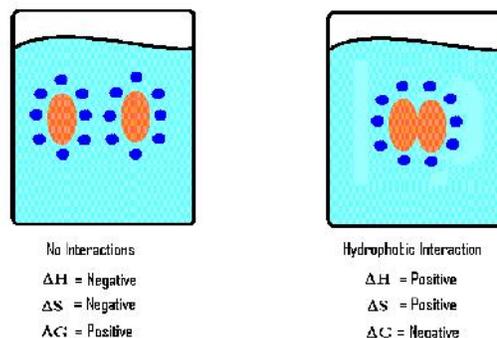A negative G indicates that hydrophobic interactions are spontaneous[13].

Figure 1 Formation of Hydrophobic Interactions

A drop of oil will spread out much more because a drop of oil is made out of hydrocarbons. Hydrocarbon chains are just carbons and hydrogens bonded together. These two atoms are similar in electronegative and therefore the overall molecule is not very polar at all. Polarity has to do with difference in charge within the molecule [14]. If there is a big difference in charge within the molecule than it will "stick" to itself just like magnets stick to each other. So the oil does not stick to itself well and spreads out. The water exhibits hydrogen bonding. Hydrogen bonding is the strongest among intermolecular forces. Water is made of oxygen and water. oxygen is very electronegative and "hogs" up electrons. This makes the oxygen hold a partial negative charge. The hydrogen is not very electronegative so a slight positive charge exists on the hydrogen. This difference is partial charge makes water very polar[15]. Because water has a negative and positive parts on itself it is able to stick to itself better. The water sticks to itself and does not spread out[15].

Hydrophobic Effect

The "hydrophobic effect" refers to the poor solubility of nonpolar solutes in water. Thermodynamically, the hydrophobic effect is characterized by the positive free energy (G > 0) of transferring a nonpolar solute into water [17]. A very interesting aspect of the hydrophobic effect is its temperature dependence: the entropy (S) and the enthalpy (H) of the transfer process both increase quickly with temperature T[24]. A key component of the hydrophobic effect is thought to be water's hydrogen bonding to neighboring waters [24]. Because of enthalpy-entropy compensation, the free energy G is insensitive to the temperature. Hydrophobic forces are caused because molecules like ethane and other hydrocarbons - petrol etc. and oils like sunflower oil etc. are non-polar, and therefore don't "like" being dissolved in a polar solvent like water [16]. In water, there are hydrogen bonds between the individual molecules, which is why water is a liquid - the van der Waals forces are far too small in water to bind the water as a liquid at room temperature [15]. If we introduce non-polar substances into the water - polar solvent - it upsets these hydrogen bonds, and creates an increase in enthalpy because of this. Therefore the lowest energy state is for the hydrophobic hydrocarbons to separate themselves from the water [18]. The relationship between van der waals forces and hydrophobic interactions is that the van der waals act to bind the hydrophobe - non-polar substance - together, to separate from the polar solvent/water, and these contribute to the energy needed to separate the two substances [19]. The separation causes a decrease in the entropy of the system. To counter this decrease in entropy, there must be some decrease in enthalpy [19]. Because the hydrophobe disrupts the hydrogen bonding in water, when they separate, the hydrogen bonding then causes an decrease in enthalpy, because of the favorable interactions. This is also where the van der Waals forces come in. They are favourable interactions, so cause a decrease in enthalpy, and this helps the separation of the hydrophobe and the water into two separate phases, because it makes the separation more energetically favourable. They are not necessary, but make separation more favourable, because the enthalpy change is greater for the separation process [20]. This makes it more favourable. In liquid water, a single water molecule can form four hydrogen bonds with nearby water molecules. However, around an apolar solute such as hydrophobic molecules such as fats and oils interact with induced-dipole type of effects surrounding waters cannot form hydrogen bonds with it. Therefore the orientation of waters near the hydrophobic solute is more ordered and the entropy of the system is reduced [21].
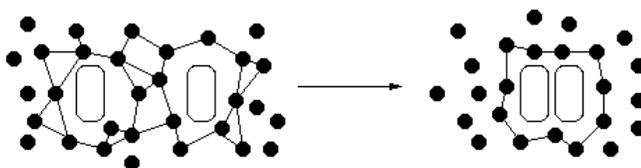

Figure 2 The hydrophobic effect

Source :https://image.slidesharecdn.com/supramolecularchemistry-121111042612-phpapp01/95/supramolecular-chemistry-28-638.jpg?cb=1352608096

For this reason, apolar solutes tend to be lumped together to minimize the number of waters affected by them. The area of the apolar interface is much larger in the unfolded state [Figure 2 left], and after hydrophobic association, the entropy is increased on the right hand side of [Figure 2 right].

Water molecules around a non-polar solute form a cage-like structure, which reduces the entropy. When two non-polar groups associate with each other, water molecules are liberated from the solvation shell, increasing the entropy[22]. Recent studies demonstrate that alcohol–water leads to incomplete mixing and infer that the negative entropy mixing of alcohol–water mixtures arises from the interplay between the relative strengths of the alcohol–alcohol, alcohol-water and water–water hydrogen bonds[41]. Water molecules and alcohol molecules are polar (has a negative and positive end) because of their O-H bond. The strong attractive forces between the molecules are known as hydrogen bonds. Hydrogen bonds are weaker than covalent bonds, but stronger than other attractive forces between covalent molecules (for example, van der waals forces). The hydrogen atoms within the O-H group are slightly positive, because the electrons are pulled away from them by the highly electronegative oxygen atoms. The oxygen atoms are slightly negative, because the electrons are closer to them. The positive hydrogen atoms and negative oxygen atoms in neighbouring molecules are attracted to each other forming a hydrogen bond approximately 5% as strong as a covalent bond [23]. When an alcohol is added to water, the hydrogen bonds in the water and alcohol have to be broken in order for them to mix. Breaking bonds requires energy; however (in smaller molecules) when the hydrogen bonds are reformed between the alcohol and water molecules energy is released, and this compensates for the initial energy needed to break the bonds. In larger molecules, the hydrocarbon tail of the molecule needs to fit in between the water molecules, and so it breaks more hydrogen bonds between the molecules. The tail cannot form hydrogen bonds, so the hydrogen bonds are replaced by van der waals forces [25]. These forces are much weaker, and so not as much energy is released when they form; not all of the energy needed to break the hydrogen bonds has been compensated for. So larger molecules do not dissolve as easily in water in comparison to smaller molecules. The carbon atoms (C) are black, the oxygen atom (O) is red and the hydrogen atoms (H) are grey. To the right of the ethanol molecule you can see a water molecule (H_2O). A closer examination reveals that, except for the oxygen atom, the ethanol molecule is symmetrical to a perpendicular plane between the carbon atoms. Only one hydrogen atom has been replaced by an oxygen-hydrogen group (-OH group). In the sum total, the ethanol molecule is electrically neutral, but the -OH group causes local differences in electro-negativity (so-called dipoles d+, d-)[26]. Normal water molecules have these dipoles, too, since they're also angled (109°). These dipoles on the ethanol and water molecules cause the formation of hydrogen bonds between the molecules.
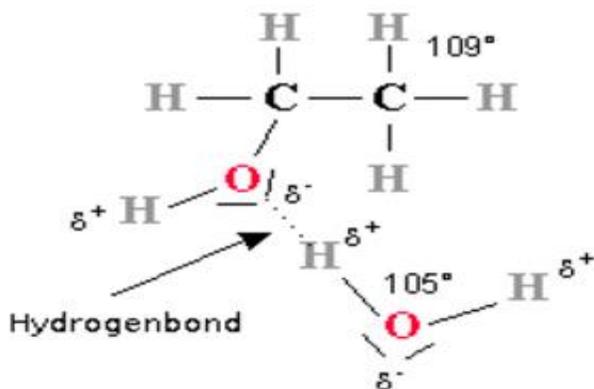
Figure 3 Hydrogen bonds between water and ethanol

Source:https://www.whisky.com/information/knowledge/production/background-knowledge/alcohol-and-water.html

Therefore the -OH group is hydrophilic (water-loving), while the rest of the ethanol, the C_2H_5 group, is lipophilic (fat-loving). Of course hydrogen bonds are always formed. Therefore to each dipole in the drawing above another dipole with the opposite electric charge is attached, be it a dipole of a water molecule or of an alcohol molecule [27].

Molecular Surface Area(MSA) and Van der Waals

A larger molecule with more surface area will have more van der Waals forces than a smaller molecule and, as a result, the larger molecule will have a higher boiling point [28]. Van der Waals forces are weak compared to dipole-dipole interactions and hydrogen bonding, and they are much weaker than covalent and ionic bonds. Van der Waals forces are caused due to the number of electrons present and size of the molecule [29]. Take a molecule like neon gas. One would think there is no attraction between the noble gas molecules, but there is. The electrons surrounding the molecule are present at random positions. So, if they happen to instantaneously all go to one side of the molecule, that side becomes partially negative, and the other end becomes partially positive, for that instantaneous moment[30]. The negative side pushes the electrons in an adjacent molecule, which pushes the electrons in another, etc. This causes an attraction between instantabeous positive and negative sides of molecules. These are very weak forces between temporary dipoles. The electrons around a molecule aren't always symmetrical. If at a particular moment, more electrons are around the left side of a molecule than the right, then the left side carries a partial negative charge and the right side carries a partial positive charge [31]. These partial positive and negative charges will be attracted toward partial negative and positive charges on other molecules. These forces are relatively very weak, but as the surface area between two molecules increases, the van der Waals forces increase because there is more room for interaction. Dipole-dipole interactions are similar to van der Waals, but these forces are between permanent dipoles while van der Waals forces are between temporary dipoles. Dipole-dipole interactions are a lot stronger than van der Waals forces. The more electrons present, the weaker their outer orbitals are, so they become more random in nature, and become more

subject to Van der Walls forces[32]. Larger molecules have a larger "surface area" of its electron cloud, this also becoming subject to stronger Van der Walls forces[32].
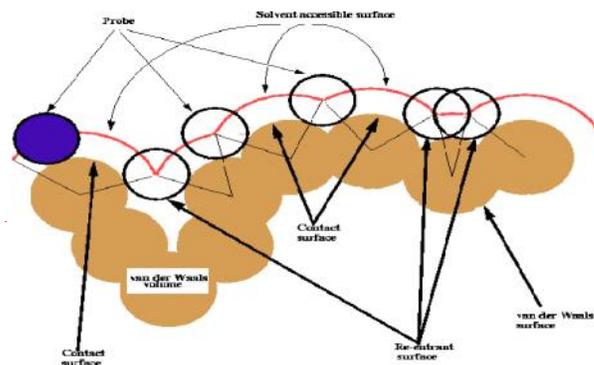

Figure 4 **The solvent accessible surface of a molecule**

Source:http://www.ccl.net/cca/documents/molecular/modeling/node5.html

The van der Waals surface cannot enter into contact with a solvent, therefore is not truly an accessible surface[33]. To ``smooth" the roughness of the van der Waals surface, it is called the concept of a contact surface and a solvent accessible surface [34]. These surfaces are obtained by rolling a spherical probe of a diameter corresponding to the size of a solvent molecule (usually water) on the original van der Walls surface as above [Figure 5]. As a result, the area where the probe touches the van der Waals surface is called the contact surface, the center of the spherical probe traces a surface called the *solvent* accessible surface and the patches over narrow gaps and clefts traced by the surface of the probe are called re-entrant surfaces [34]. The exploration of molecular volume and surface is essential for the understanding of drug action since short range dispersion forces play a major role in the binding of drug molecules to receptors [15]. For efficient and specific binding, the receptor cavity, in most cases, must be tightly filled with the interacting ligand[6]. On the other hand, when walls of the receptor cavity are rigid, even a small extra volume in the ligand prevents efficient binding and renders the molecule inactive. The surfaces of interacting molecules also need to be of complementary character, i.e., they should both be hydrophobic or hydrophilic which will in practice represent their ability to form hydrogen bonds. The net charge on the interacting surfaces also needs to be complementary for strong bonding. The exploration of molecular volume and surface is frequently the first and most important step on the path to understanding the molecular basis of drug-receptor interactions [15]. At the nanoscale, the entire world is bumpy. Even smooth objects like glass have bumps and ridges when viewed with a powerful microscope. For an animal, like the gecko, to stick and make maximum contact, its feet have evolved specific nanoscale features. An average gecko has about 6.5 million setae (or tiny hairs) on its feet [8]. Each setae branches out (like split ends on a hair) into approximately 100–1000 spatulae, which are about 200 nanometers wide. It is the contact of these near billion spatulae with the surface that creates enough interactions (van

der Waals) to keep the gecko on the wall [33]. In the case of a gecko, the small hairs (setae) on their feet have nanosized "split-ends" (spatulae)[8]. The millions of hairs on each foot make intimate contact with the surface of a wall or glass. The atoms of each are so close that a normally very weak force (van der Waals) becomes very strong. At the nanoscale, this force becomes dominant over gravity, which is fighting to pull the lizard toward the Earth. Two molecules can interact by Van der Waals forces when they are at a certain distance apart [35]. The molecules are stabilized by Van der Waals interaction at the Van der Waals contact distance because the potential energy of the system at this distance is at its lowest [36]. The minimum potential energy point corresponds to the Van der Waals contact distance [37]. As the distance between the molecules increase, the weakly bonded molecules lose their stability and are no longer affected by the Van der Waals forces due to their large distance apart[38]. When the distance between the two molecules decrease, however, the stabilization is decreased as well due to the electrostatic repulsion between the molecules [39]. Let's look at the mechanism of the stabilization energy. The Figure 6 as below shows the combination of two hydrophobic molecules and a number of water molecules. [Figure 6-A] shows that the two hydrophobic molecules are very well intertwined. [Figure 6-B] has some gaps. [Figure 6-C] contains a number of water molecules between the two hydrophobic molecules, so there is a significant gap. Therefore, [Figure 6-C] shows fewer hydrogen bonds than [Figure 6-A] and [6-B]. [Figure 6-A] and [6-B] show the same number of hydrogen bonds, but, [Figure 6-A] shows a larger van der Waals force due to the narrow distance between the contact surfaces as compared with [Figure 6-B][40].
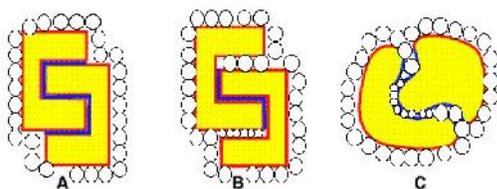

Figure 5 The combination of two hydrophobic molecules

White: water molecules , **Yellow:** hydrophobic molecules

CONCLUSION

Nature, as in the case of geckoes, is utilising Van-der-Waals forces in scaling walls of various inclinations, even including inverted planes. The van der Waals force is weaker than chemical bonding effects, but plays an important role in abroad range of areas, such as surface and colloidal science, nano electromechanical systems, and nano technology. Material scientists, process designers and even drug researchers will one day benefit from the better understanding of van der Waals forces. It could, for example, then be possible to systematically modulate the forces.

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