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Experimental and Theoretical Mechanism Study on Emulsification and Demulsification of Lubricating Oil

CHUNSHENG LI[1], JINLONG LI[1], JIANHUA WANG[1] and XIAOMIN SUN[2,*]

[1]92117 Unit of PLA, P.O. Box 7220, Beijing 100072, P.R. China
[2]Environment Research Institute, Shandong University, Jinan 250100, P.R. China

*Corresponding author: Email: sxmwch@sdu.edu.cn

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The system model is first established by simplification and idealization and then the average binding energies are calculated using AM1 semi-empirical method and applying periodic boundary condition to this study. The results show that the system added to antirusts binding energy is much larger than that of demulsifier, so that the formation of the interfacial film is relatively stable, which easily leads to emulsification. While the binding energy of interfacial film formed by demulsifier is weak and the strength of interfacial film is lower, which has a good ability of demulsification.

Keywords: Lubricating oil, Emulsification and demulsification, Semi-empirical method, Periodic boundary condition.

INTRODUCTION

In recent years, materials chemistry has enjoyed a rapid development in experimental research methods and several research methods are employed such as quantum chemical calculation and molecular simulation[1-5]. By quantum chemical calculation, the information about electronic structure and stereochemical structure of molecules can be obtained[6-9].

The nature of materials is determined by their structure and so the demulsification property of lubricants is finally determined by the structure of each component and the interaction between components in the system. In this work, proceeding from the structures of each component, *i.e.*, the molecules and atoms which constitute the system, the average binding energy between the components in the system was calculated with quantum chemical method. The intermolecular interaction of materials in the emulsion system and the effect of each lubricants' component on the emulsion stability were also explored. Models were first established by simplification and idealization and then the average binding energies between components of systems were calculated using the semi-empirical AM1 method and applying periodic boundary conditions. The greater the binding energy, the greater the intermolecular interaction of each component and the interfacial film strength and the emulsion is more stable.

In this experiment, the anti-rust agent CI (Fig. 1) was taken as the emulsifier and the demulsifier II (Fig. 2) as the demulsifier. Three typical systems including the base oil/water, base oil + CI/water and base oil + demulsifier/water were selected to calculate the average binding energy among components, in order to predict the force among components and then their effect on emulsion stability.

Establishment of the system model: For the convenience of computation, it needs to simplify and idealize for establishing the system model.

Base oils: The base oils are the 10 mPa.s hydrogenation refined mineral oils. According to their viscosity and preparation process, base oils are the alkanes which molecular weight for about 800. In addition, there are two extremes: one is straight-chain alkane with no side chain, denoted C_{57}; the other is maximum degree of branching of alkane and the main chain with 12 carbon, marked with C_{12}.

Antirust: The antirust is dodecene butyric acid and its structure is shown in Fig. 1.

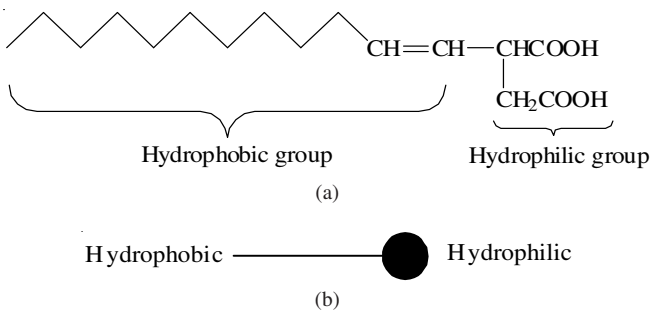
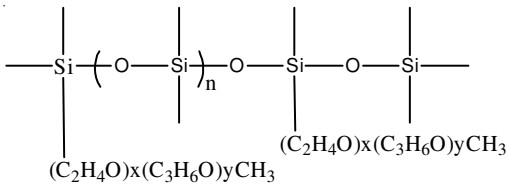
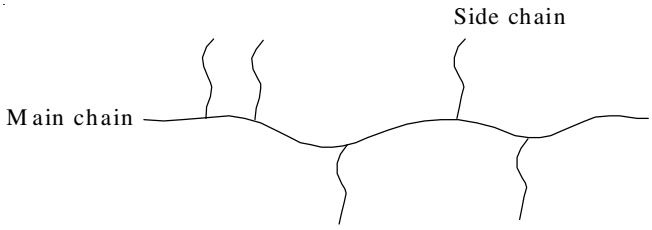


Fig. 1. The antirust's structure (a) and schematic (b)

Demulsifiers: The demulsifiers are the new synthesis of polyether silicone demulsifier, the structure shown in Fig. 2, main chain of siloxane and side chain of polyether.



(a)



(b)

Fig. 2. The demulsifier's structure (a) and schematic (b)

In the ideal case, the surfacant should be closely packed in oil-water interface. There are three forces existed in the interface *i.e.*, the surfactants with oil phase, the surfactants with water phase and the closely packed force between surfactants.

Base oils/water system: For the absence of surfactants in oil-water interfacial, the interaction is relatively simple. Interface exists the intermolecular force of base oil, water and between oil and water (Fig. 3).

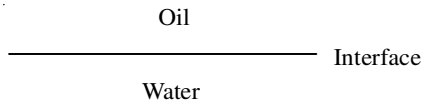


Fig. 3. Base oils/water system

Base oils + CI/water system: In the ideal case, the antirust oil molecules closely packed in the oil-water interface. There are existing intermolecular forces of base oil molecular with antirust, water molecular with antirust and antirust itself (Fig. 4).

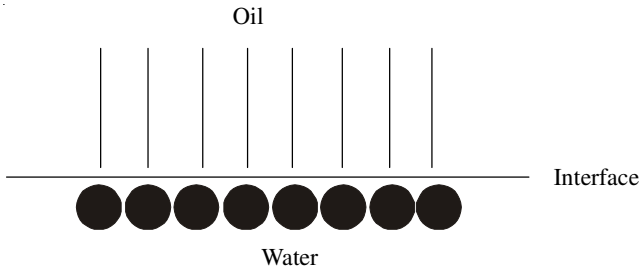


Fig. 4. Base oils + CI/water system

Base oils + demulsifiers/water system: The demulsifier molecules' main chain are siloxane, which can neither easily dissolve in water nor dissolve in oil; The side chain are polyether, it is easily dissolved in water. Ideally demulsifier's main chain should be closely packed on the oil-water interface, while the side chain douses into the water. For the impact of branching degree, there are far distance between the side chains, thus the interaction is negligible. There are demulsifier-base oil intermolecular force, demulsifier-water intermolecular and interactions among the demulsifier's main chain (Fig. 5).

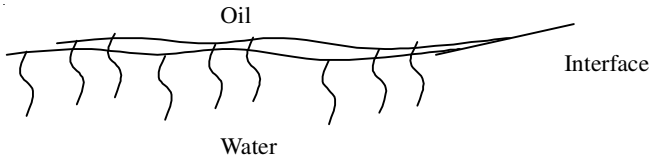


Fig. 5. Base oils + demulsifiers/water system

COMPUTATIONAL METHODS

Using quantum chemistry AM1 semi-empirical caculation method and applying periodic boundary conditions[10-12], the interface of the cluster configuration (n = 9) and average binding energy of the base oils, base oils + CI and base oils + demulsifiers three systems are calculated respectively.

RESULTS AND DISCUSSION

In order to simplify the system, the molecular weight 800 base oils are seperated into two extreme cases *i.e.*, straight-chain C_{57} and maximum branched-chain C_{12}. Firstly, the binding energy for base oil of straight-chain alkane in three systems are calculated. The greater the average binding energy, the greater the force is and the more closely combined, the formation emulsion is more stable. Cluster configuration of various system are shown in Fig. 6-10.

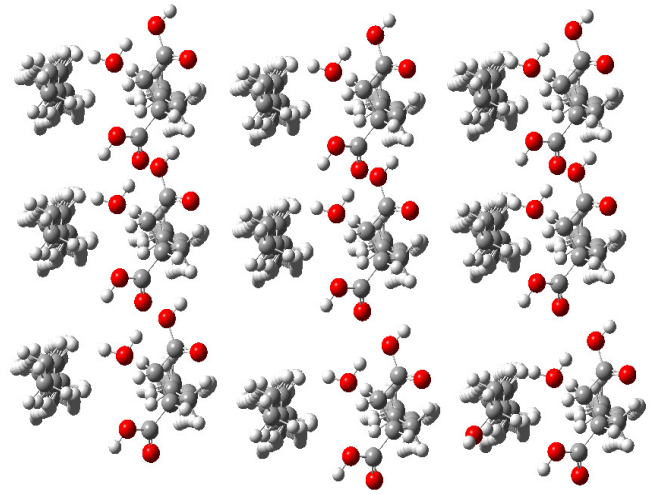


Fig. 6. Cluster configuration of (straight-chain base oils + $CI/H_2O)_n$ n = 9 system (vertical angle)

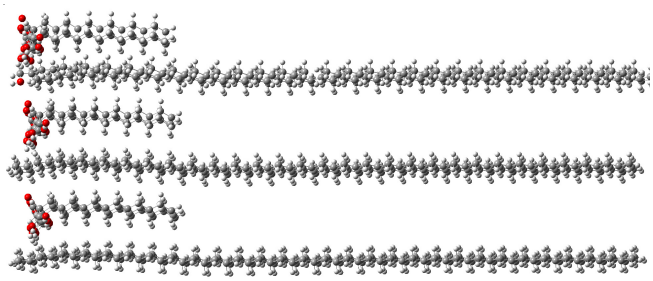


Fig. 7. Cluster configuration of (straight-chain base oils + $CI/H_2O)_n$ n = 9 system (side of the angle)

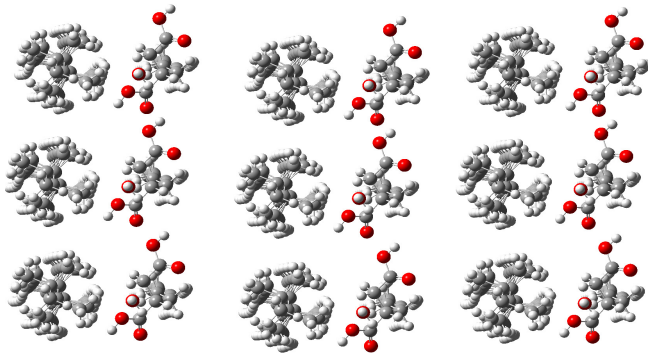


Fig. 8. Cluster configuration of (branched-chain base oils + $CI/H_2O)_n$ n = 9 system (vertical angle)

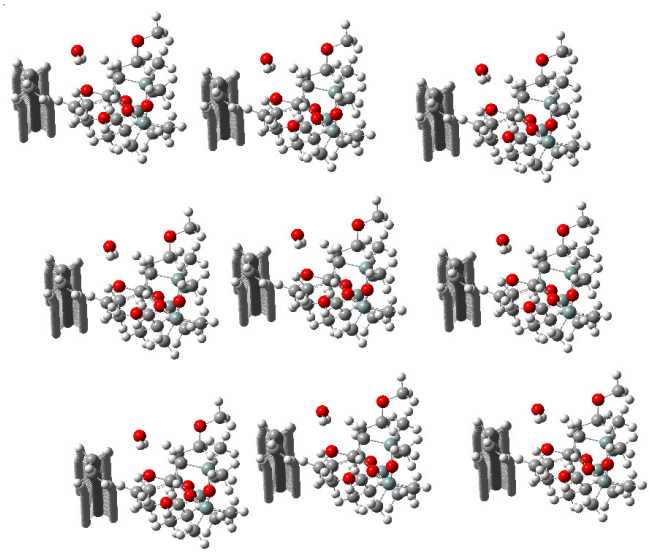


Fig. 9. Cluster configuration of (straight-chain base oils + demulsifiers/ $H_2O)_n$ n = 9 system (vertical angle)

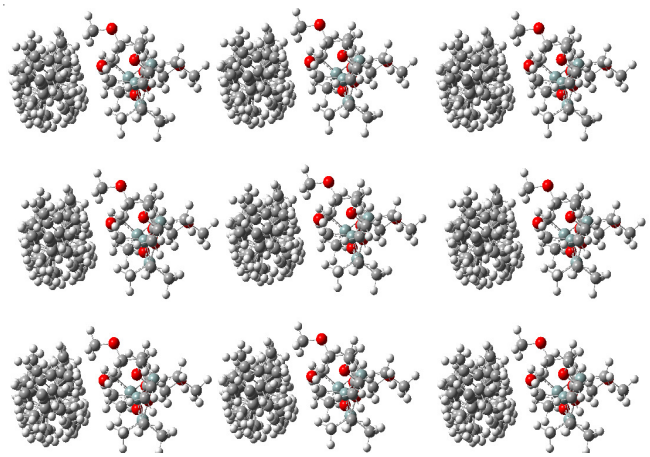


Fig. 10. Cluster configuration of (branched-chain base oils + demulsifiers/ $H_2O)_n$ n = 9 system (vertical angle)

As it can be seen from Table-1, in the a, b, c three systems composition by the straight-chain base oil, the binding energy of demulsifier-demulsifier, demulsifier-H_2O, C_{57}-demulsifier all less than CI-CI, CI-H_2O, C_{57}-CI. The binding energy of CI-CI is -15.90 kcal/mol while demulsifier- demulsifier is only -3.78 kcal/mol, the force between demulsifiers is much smaller than the force between antirusts, so when the demulsifier closely packed at the interface, the force between demulsifier much smaller than the force between emulsifier and the formation of interfacial film strength is lower than the interfacial film formed by emulsifier. The binding energy of CI-H_2O is -7.38 kcal/mol while demulsifier-H_2O is only -0.99 kcal/mol, the force between antirust and water is much higher than the force between demulsifier and water. The binding energy of C_{57}-CI is -4.65 kcal/mol while C_{57}- demulsifier is -2.20 kcal/mol.

TABLE-1
AVERAGE BINDING ENERGY BETWEEN VARIOUS COMPONENTS OF STRAIGHT-CHAIN BASE OILS SYSTEM

(a) Average binding energy between various components of straight-chain base oils/water system	
	Average binding energy (kcal/mol)
H_2O-H_2O	-5.36
C_{57}-C_{57}	-0.14
C_{57}-H_2O	-1.52
(b) Average binding energy between various components of straight-chain base oils + CI/water system	
	Average binding energy (kcal/mol)
CI-CI	-15.90
CI-H_2O	-7.38
C_{57}-CI	-4.65
(c) Average binding energy between various components of straight -chain base oils + demulsifiers/water system	
	Average binding energy (kcal/mol)
Demulsifier-demulsifier	-3.78
Demulsifier-H_2O	-0.99
C_{57}-demulsifier	-2.20

Table-2 shows the average binding energy in branched-chain base oils system. Similarly, it can be seen that in a, b, c these three system, the binding energy of demulsifier-demulsifier, demulsifier-H_2O, C_{12}-demulsifier all less than CI-CI, CI-H_2O, C_{12}-CI.

TABLE-2
AVERAGE BINDING ENERGY BETWEEN VARIOUS COMPONENTS OF BRANCHED-CHAIN BASE OILS SYSTEM

(a) Average binding energy between various components of branched-chain base oils/water system	
	Average binding energy (kcal/mol)
H_2O- H_2O	-5.35
C_{12}-H_2O	-1.84
C_{12}- C_{12}	-0.14
(b) Average binding energy between various components of branched-chain base oils + CI/water system	
	Average binding energy (kcal/mol)
CI-CI	-15.90
CI-H_2O	-7.38
C_{12}-CI	-3.40
(c) Average binding energy between various components of branched-chain base oils + demulsifiers/water system	
	Average binding energy (kcal/mol)
Demulsifier-demulsifier	-3.78
Demulsifier-H_2O	-0.99
C_{12}-demulsifier	-1.96

The above data suggest that whether straight-chain or branched-chain base oils, the binding energy in the system which added the antirusts is much higher than the system with

demulsifiers. So the antirusts are easy to cause emulsion, after adding the demulsifiers, the demulsifiers adsorption to the interface, replace the antirusts, the new formation of interfacial film with low strength then emulsion is damaged.

Conclusion

In this study, the system model is first established by simplifying and idealizing and then the average binding energies are calculated using AM1 semi-empirical method and applying periodic boundary condition. The results show that the system added antirusts binding energy is much larger than the system of demulsifier, so the formation of the interfacial film is relatively stable, which easily leads to emulsification. While the binding energy of interfacial film formed by demulsifier is weak and the strength of interfacial film is lower, which has a good ability of demulsification.

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