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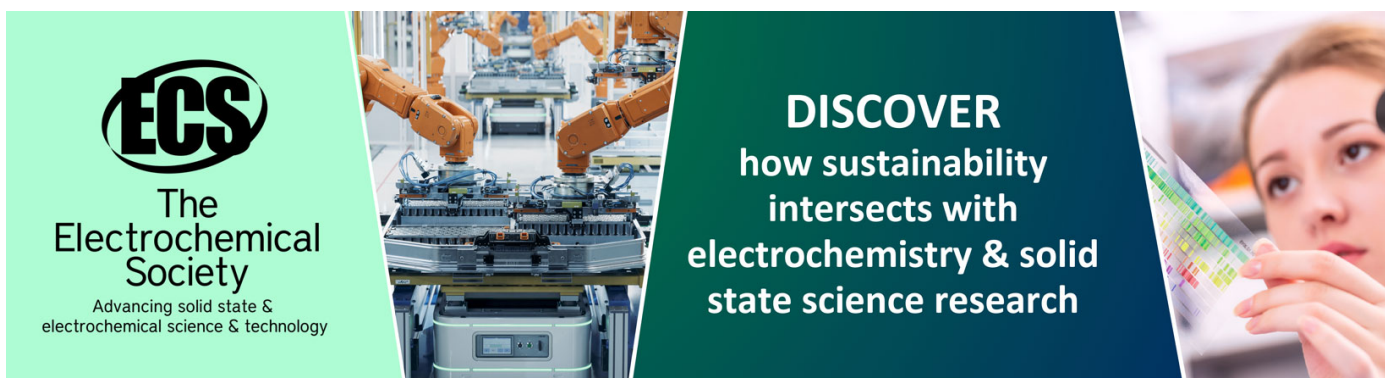
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Molecular dynamics simulation of water diffusion in mixed insulating oil at different temperatures

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Abstract. The effects of temperature and moisture on the mixed insulating oil micro-characteristics were investigated by molecular simulation. In order to analyse the mechanism of action between insulating oil and water molecule, the mixed insulating oil model consisting of mineral oil and natural ester with different mass ratio and different moisture content was established. Through the research of hydrogen bonding, radial distribution function (RDF) of oil molecules and the diffusion coefficient of water molecules, it shows that the higher the natural ester content in the model, the more the number of hydrogen bonds, the bigger the peak value of RDF, the smaller the diffusion coefficient of water molecules. At the same time, the increase of temperature weakened the binding effect of mixed insulating oil on water molecules, and the increase of water content enhanced the ability of mixed insulating oil and water molecules to form hydrogen bonds. The final results showed that different natural ester content enhanced the thermal stability and insulation characteristics of the mixed insulating oil.

1. Introduction

Transformer oil and insulating paper constitute the insulating structure of oil-paper. In the transformer working process, the aging of oil-paper insulation increases the water content. And water accelerates the aging process and shortens the service life of the transformer. In recent years, mixed insulation oil has become a research hotspot. Many scholars have conducted a series of studies on the types of crude oil, mass ratio and antioxidants used [1-6]. Moisture is always the main factor affecting the stable operation of transformer. Excessive moisture content will shorten the insulation life, and also affect the dielectric performance of the insulation system [7]. With the rapid development of computer technology, molecular simulation technology has been widely used in various fields. Many scholars used molecular simulation technology to explore the interaction energy between oil and water molecules as well as the anti-aging mechanism of insulating oil [8-10]. At present, the macroscopic and microscopic researches on mixed insulation oil are mostly concentrated at room temperature. However, there are few reports on the influence mechanism of water on mixed insulation oil under high temperature environment.

In this paper, molecular simulation method was adopted. 15 groups of compound models were built in Materials Studio software. The influence laws of high temperature and water on the micro-



characteristics of mixed insulation oil were analysed. Consequently, theoretical support for further research on the application of mixed insulation oil in high temperature environment was provided.

2. Simulation methods

2.1. Mineral oil model

Mineral insulating oil is mainly composed of three kinds of hydrocarbon mixtures: alkane (C_nH_{2n+2} , mass fraction about 60%), cycloalkanes (C_nH_{2n} , mass fraction about 10%~40%) and aromatic hydrocarbon (C_nH_{2n-6} , mass fraction about 5%~15%). In addition, there are a small amount of organic acids, sulfides, asphalt and other polymer and organic compounds. Three molecular structures of chain alkane $C_{20}H_{42}$, bicyclic alkane $C_{20}H_{38}$, and bicyclic aromatic hydrocarbons $C_{20}H_{26}$ are selected to build a mineral insulating oil model according to the reference [11]. Each mineral oil model consists of 10 hydrocarbons, including 1 chain alkane, 8 bicyclic alkane and 1 bicyclic aromatic hydrocarbons.

2.2. Natural ester model

In natural esters, more than 95% of the components are triglycerides. And the rest are lipids, water and other impurities. In the refining of natural esters, lipids are often removed by alkali, decolorization and distillation to improve physical and chemical properties of natural esters. In this paper, according to literature [12], each natural ester model was set to consist of 10 triglycerides, including 1 glycerol tristearate, 1 tripalmitin, 5 glycerol trioleates, 2 triglycerides and 1 stearic acid linolenic acid triglyceride.

2.3. Simulation method

In this paper, the mass ratio of mineral oil and natural ester is 9:1, 8:2 and 7:3. The water content is 1%, 3% and 5%. 15 groups of compound models are set up to carry out molecular dynamics simulation respectively, as shown in the figure 1. In molecular dynamics simulation and model optimization, COMPASS force field is selected, which is suitable for processing systems composed of organic and inorganic molecules. In order to get the model with lower energy, geometry optimization and anneal processing are performed on 15 sets of models. Smart method is adopted for structure Optimization. Five annealing cycles are set in the annealing process to obtain stable state with lower energy. According to the normal operating temperature and possible local temperature rise in the transformer, in order to explore the high-temperature micro-characteristics of the mixed insulation oil, the temperature is set at 90°C, 120°C and 150°C. NVT canonical ensemble is used for molecular dynamics simulation, with time of 50ps, integral step length of 1FS, and kinetic information collection interval of 500FS.

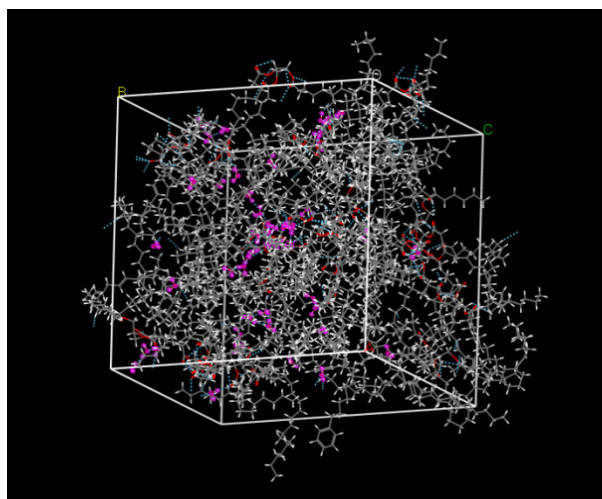


Figure 1. Mixed oil structure model.

3. Simulation results and analysis

3.1. Number of hydrogen bonds

Hydrogen bonding is an important intermolecular force, which refers to a strong non-bonding interaction between the hydrogen atoms that bond with the more electronegative atoms and more electronegative atoms. Hydrogen bonds is the electrostatic attraction between the hydrogen nuclei on strong polar bonds and the atoms with high electronegativity and unshared electron pairs [13]. The formation of hydrogen bond between adjacent molecules can significantly improve the melting and boiling point of the polymer to promote the thermal stability of the polymer. Currently, the determination methods of hydrogen bond include geometric methods and energy methods. This paper adopts the default geometric method in Materials Studio. The angle formed by the donor and acceptor of hydrogen bond is greater than 90° , and the distance between hydrogen bond and acceptor is no more than $2.5\text{\AA}$.

Table 1 and 2 calculate the number and average length of hydrogen bonds in different mixed oil mass ratio models (mineral oil: M, natural ester: N) at different simulated temperatures. It can be seen that the higher the natural ester content, the more hydrogen bonds, the smaller the average bond length. The higher the temperature, the fewer hydrogen bonds, the larger the average bond length. Figure 2 shows the hydrogen bonds around the insulating oil, with the hydrogen bonds represents by a blue dotted line. It can be seen that the ester group oxygen atoms of the natural ester can form hydrogen bonds with H in the water molecule, leading to increase the number of hydrogen bonds with a high content of natural ester. And the smaller the hydrogen bond length, the greater the bond energy.

Table 1. Number and average length of hydrogen bonds in different mixed oil mass ratio models.(120°C)

Mass ratio (M: N)	Number	Length($\text{\AA}$)
9:1	70	2.22297774
8:2	140	2.20073916
7:3	226	2.14803774

Table 2. Number and average length of hydrogen bonds in different temperature models. (Mass ratio 8:2)

Temperature ($^\circ\text{C}$)	Number	Length($\text{\AA}$)
90	152	2.16398453
120	140	2.20073916
150	126	2.23978672

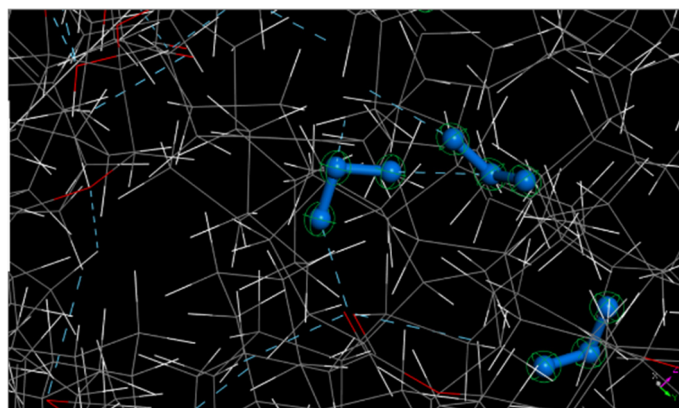


Figure 2. The hydrogen bond between the ester group oxygen atoms of natural esters and water molecule.

3.2. Radial distribution function

The radial distribution function (RDF) is used to describe the physical quantity of the distribution of other particles around a studied particle, and to characterize the law that the density of other particles changes with the distance from the studied particle. Its physical meaning is the probability of the occurrence of another molecule at the distance from a molecule “r”. The formula is shown in Equation 1.

$$g(r)=4\pi r^2\rho^2(r) \quad (1)$$

Intermolecular interactions can be divided into hydrogen bond interactions and van der Waals interactions, with the former generally considered to be 0.2~0.3nm and the latter 0.3~0.5nm [14]. Figure 3 shows the RDF of mineral oil and natural ester in the mixed insulating oil at different temperatures. It can be seen from the figure 3 that the RDF variation trend of the three model oil molecules is basically the same, with spikes appearing at 0.217nm and 0.257nm, confirming the presence of a large number of hydrogen bonds in the oil molecules. At different temperatures, the RDF peak value of natural esters is higher than that of mineral oils, indicating that natural esters are more likely to form hydrogen bonds than mineral oils. And the higher the natural ester content, the shorter the hydrogen bond length, the higher the bond energy. Therefore, the presence of natural ester in mixed insulation can enhance the interaction between oil and water molecules, which is beneficial to improve the thermal stability.

Figure 4 shows the RDF of the natural ester in the mixed insulating oil at different temperatures. It can be seen that the peak value of RDF decreases as temperatures rise. This indicates that the increase of temperature leads to the decrease of intermolecular force and weakens the binding effect of oil molecules on water molecules.

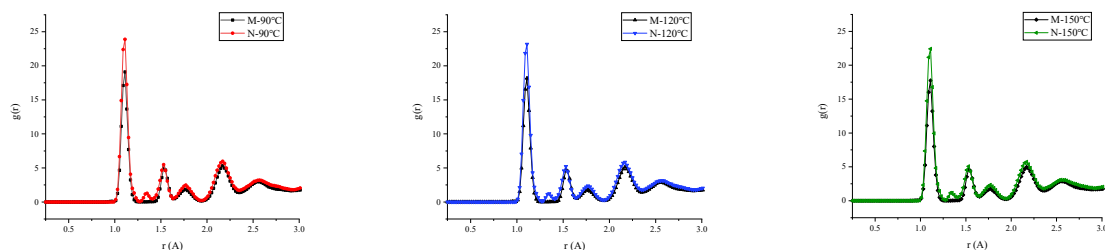


Figure 3. RDF of mineral oil and natural ester in mixed insulating oil at different temperatures.

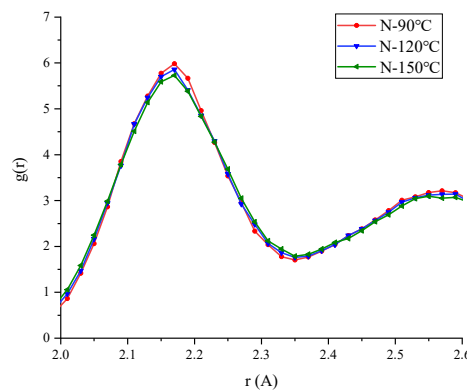


Figure 4. RDF of natural ester in mixed insulating oil at different temperatures.

3.3. Diffusion coefficient

The mean square displacement (MSD) describes the change rule of the mass of water molecules with time, and its definition is shown in Equation 2.

$$\text{MSD} = \langle |r(t) - r(0)|^2 \rangle \quad (2)$$

In the equation, $r(t)$ and $r(0)$ are the particle position vector of the time “ t ” and the initial moments respectively. The $\langle \rangle$ is the average of all molecules within the system. When the molecular diffusion time is long enough, it can be seen from Einstein's relations that the diffusion coefficient is 1/6 of the MSD slope, and its expression equation is shown in Equation 3.

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle \quad (3)$$

By MATLAB software, the curve of MSD over time is fitted to form $y=ax+b$ through linear fitness. Writing down and calculating diffusion coefficient. Figure 5 and 6 respectively show the MSD curves of water molecules with different mass ratios and different temperatures. Table 3 shows the water molecular diffusion coefficients of the model at different mass ratios and temperatures.

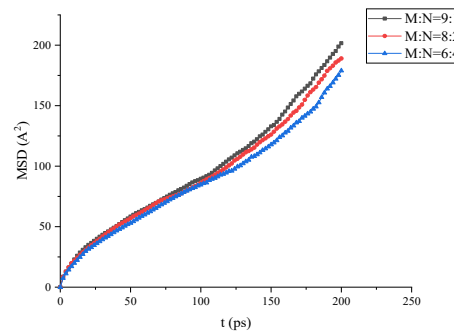


Figure 5. MSD of water molecules in the mixed insulating oil with different mass ratio.

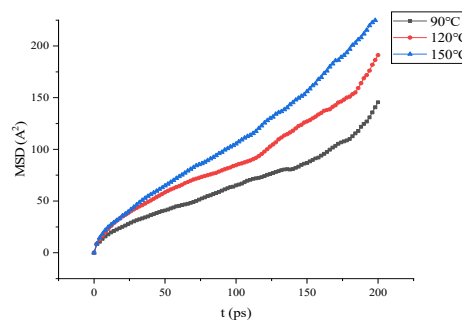


Figure 6. MSD of water molecules in the mixed insulating oil at different temperatures.

Table 3. Diffusion coefficients of water molecules at different mass ratios and temperatures.

Mass ratios	9:1	8:2	7:3
Temperature			
90°C	0.1092	0.0897	0.0699
120°C	0.1691	0.1521	0.1344
150°C	0.2007	0.1931	0.1862

It can be seen from figure 5 that the variation trend of MSD curve of water molecules in mixed insulating oil with different mass ratios is basically the same. As natural esters have hydrophilic polar

groups, whose saturated water content is higher than mineral oil, they have a binding effect on water. Therefore, as the content of natural esters increases, the MSD of water molecules decreases continuously. As can be seen from figure 6, with the continuous rise of temperature, the MSD of water molecules increases, which conforms to the classical diffusion theory. The result proves that the rise of temperature weakens the binding effect of natural ester on water molecules.

It can be seen from table 3 that the diffusion coefficient of water molecules at 150°C is less affected by the change of natural ester content than that at 90°C. This indicates that as the temperature rises, the kinetic energy of molecules including oil and water increases, and the irregular motion of the system becomes more intense. Natural esters have a saturated water content 20~30 times higher than that of mineral oils. Therefore, even though temperature rise will increase the saturated water content of insulating oil, mineral oils cannot strongly restrain the diffusion of water molecules due to its weaker water-holding capacity. Thus, the diffusion coefficient of water molecules is more affected by temperature.

3.4. Initial moisture content

The initial moisture content in insulating oil directly affects the interaction between moisture and insulating oil at high temperature. In this paper, molecular dynamics simulation of mixed insulating oil with initial moisture content of 1%, 3% and 5% was carried out at 120°C. Table 4 and 5 records the number and length of hydrogen bonds between molecules in the mixed insulating oil model under different initial conditions.

Table 4. The average number of hydrogen bonds in the model with different initial water content.

Moisture content \ Temperature	90°C	120°C	150°C
1%	1.30	1.06	0.80
3%	2.96	2.80	2.56
5%	3.28	3.20	3.08

Table 5. The average length of hydrogen bonds in the model with different initial water content (Å) .

Moisture content \ Temperature	90°C	120°C	150°C
1%	2.29117346	2.34336478	2.39539322
3%	2.16398453	2.20073916	2.23978672
5%	2.11824736	2.14594938	2.16270231

It can be seen from the table that with the increase of initial water content, the average number of hydrogen bonds in the model molecules is larger, the average bond length is smaller, and the bond energy is larger. This reflects that the increase in water content enables natural esters to interact more with water molecules to form hydrogen bonds. At the same time, the intensity of molecular motion increases with the increase of temperature, and the number of inter-molecular hydrogen bonds decreases. But as water content rose, the trend waned.

4. Conclusion

Based on the molecular dynamics simulation, the conclusion is as follows:

With the increase of the natural ester content in the mixed insulating oil, the number of hydrogen bonds increases. And the bond energy increases, improving the thermal stability and insulating properties of the insulating oil mixture model. With the proportional increase of the content of natural ester at high temperature, the degree of decrease in the diffusion coefficient of water molecules decreases. With the increase of water content, the ability of natural ester to form hydrogen bond with

water molecule is enhanced. When the moisture content exceeds a certain value, the influence of temperature on the number and average bond length of hydrogen bonds are weakened. The research provides reference for the operation and maintenance of mixed insulating oil at high temperature.

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