Influence of Dispersants on the Stability and Supercooling Degree of Gallium-Indium-Tin Alloy Nanofluids

Weijie Zhong [1, 2], Zhenyu Lv [1, 2], Jiayi Liu [1, 2], Chaobo Li [1, 2], Yudong Liu [1, 2, *]

[1] Key Laboratory of Low-grade Energy Utilization Technologies & Systems, Ministry of Education, Chongqing University, Chongqing 400044, China

[2] School of Energy and Power Engineering, Chongqing University, Chongqing 400044, China

* Corresponding Author Email: ydliu2000@cqu.edu.cn

Abstract. Against the backdrop of the growing demand for renewable energy, ice energy storage is of great significance for balancing the power grid and storing renewable energy. However, existing ice energy storage materials suffer from a large supercooling degree. When nanofluids are used to improve their performance, their stability is poor. This study focuses on gallium-indium-tin alloy nanofluids with different dispersants added. Through various characterizations and tests, it is found that xanthan gum has the best effect in enhancing stability. Adding gallium-indium-tin alloy nanoparticles to water can significantly reduce the supercooling degree, and it further decreases after adding xanthan gum, with an average reduction of 55.37% compared to water.

Keywords: Nanofluids; supercooling degree; Dispersants.

1. Introduction

Currently, the global demand for renewable energy is increasing day by day [1]. However, its intermittency and instability pose bottlenecks to the large-scale deployment of renewable energy [2]. Ice energy storage, as a large-scale latent heat energy storage method, can achieve peak shaving and valley filling of the power grid, consume unstable renewable energy on a large scale, and thus realize the large-scale storage and utilization of renewable energy. Existing ice energy storage materials have the defect of an excessively large supercooling degree. An overly large supercooling degree is not conducive to the nucleation and crystallization of ice energy storage materials and leads to high-energy consumption operation of refrigeration units. Nanofluids show potential in improving the performance of ice energy storage materials due to their higher thermal conductivity [3] and lower supercooling degree [4-6]. Nevertheless, nanofluids face the challenge of poor stability in practical applications. Nanoparticles are prone to aggregation and sedimentation [7-9], which greatly limits the performance and wide application of nanofluids.

Gallium-indium-tin alloy nanofluids, as a new type of liquid metal nanofluid, have potential application value in the field of ice energy storage. This paper focuses on gallium-indium-tin alloy nanofluids with different dispersants added, aiming to deeply analyze their stability and supercooling degree characteristics. By studying the influence of different dispersants on the stability and supercooling degree of gallium-indium-tin alloy nanofluids, it is expected to provide a theoretical basis and technical support for optimizing the performance of ice energy storage materials and promoting their practical applications.

2. Experiment

2.1. Preparation Scheme of Nanofluids

The gallium-indium-tin alloy nanofluids prepared in this project are dispersed by ultrasonic dispersion. The dispersed phase is oscillated and uniformly dispersed in water. The cavitation effect of ultrasonic waves is used to weaken the interaction force between droplets and the surface energy of a single droplet, thereby avoiding precipitation and preparing uniform and stable nanofluids [10]. Then, a dispersant is added during the preparation process to improve its dispersion stability.

To comprehensively study the influence of the addition of dispersants on the stability of liquid metal nanofluids, anionic dispersant sodium dodecyl sulfate (SDS), cationic dispersant dodecyltrimethylammonium bromide (DTAB), non-ionic dispersant Tween 20, organic polymer dispersant xanthan gum (XG), inorganic polymer dispersant sodium polyphosphate (SPP), organic amine dispersant triethanolamine (TEA), and chelating dispersant ammonium citrate (AC) were selected. The mass fraction of each dispersant is 0.05%, and the mass fraction of liquid metal is 0.2%. In addition, a liquid metal nanofluid sample without the addition of a dispersant was prepared as a control group.

2.2. Characterization of Nanofluid Stability

In this experiment, a nanoparticle size and zeta potential analyzer was used to measure the particle size distribution and zeta potential of nanoparticles. The Fourier transform infrared spectrometer was used to measure the infrared spectra of 7 different dispersants. The microstructures were observed by SEM and TEM.

2.3. Supercooling Degree Experiment

The steps to measure the temperature change curve of liquid metal nanofluids are as follows: Connect the power supply of the low-temperature constant-temperature circulating bath, set the target temperature to -10°C, and start refrigeration. When the temperature of the ethylene glycol working fluid is stable, start the computer and data acquisition instrument, and calibrate the T-type thermocouple. Install the calibrated thermocouple into a reagent bottle containing the sample, place it in a constant-temperature bath for cooling, and set the data acquisition time interval to 10s. After data acquisition, export the data in a table, take out and clean the thermocouple, and turn off the equipment and power supply. Each group of samples was repeated multiple times, and stable values were taken to draw curves and analyze.

3. Results and Discussion

3.1. Results of Stability Characterization

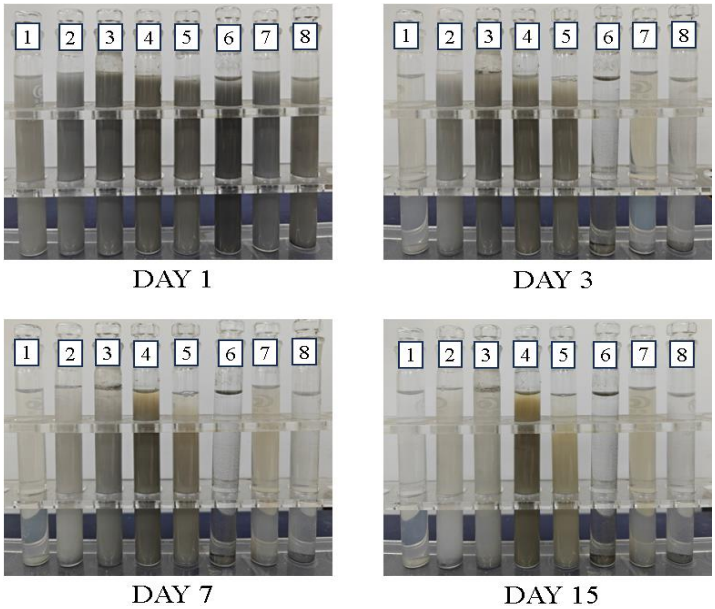
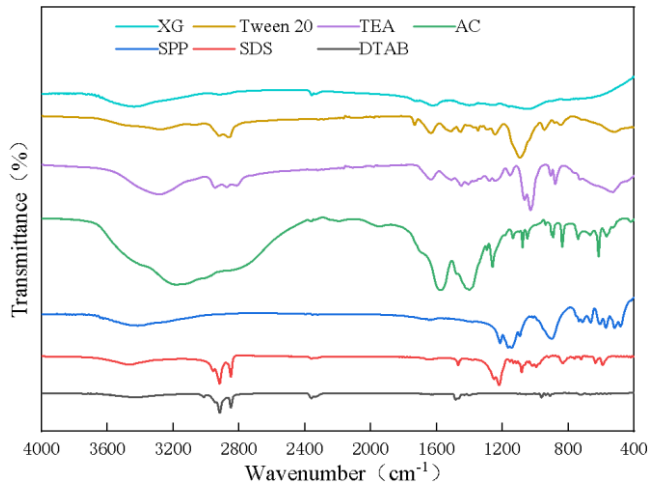


Fig 1. Comparison chart of nanofluids with different dispersants added.

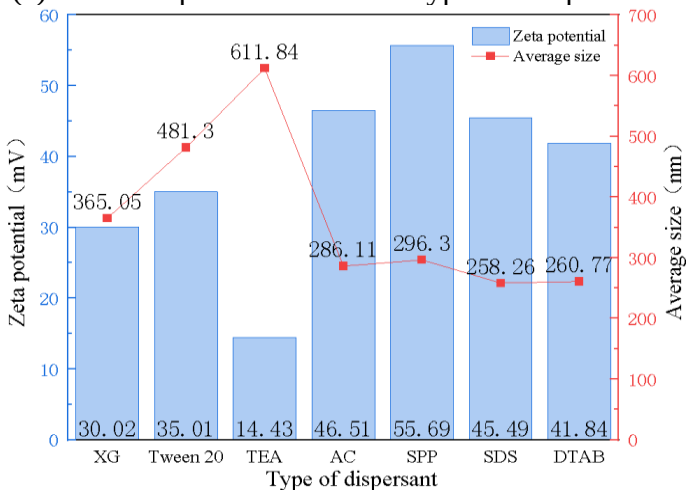
(1: Sodium polyphosphate; 2: DTAB; 3: Tween 20; 4: Xanthan gum; 5: SDS; 6: Triethanolamine; 7: Ammonium citrate; 8: Without dispersant)

From Figure 1, it can be seen that for samples numbered 1 (sodium polyphosphate), 6 (triethanolamine), 7 (ammonium citrate), and 8 (without a dispersant), sedimentation is obvious over

time. By the 15th day, the upper liquid is clear, and there is a lot of sediment at the bottom, indicating poor dispersion stability. Sodium polyphosphate has a strong P - O stretching vibration absorption peak between 1200 - 1000 cm^{-1}. Although it contains a large number of phosphate structures, its molecular chain is short and simple. It is difficult to form a stable and thick adsorption layer on the surface of nanoparticles, and the space - steric hindrance it provides is insufficient. Moreover, the electrostatic effect is easily weakened by environmental factors, resulting in the easy sedimentation of nanoparticles. Triethanolamine has an overlapping peak of N - H and O - H stretching vibrations near 3300 cm^{-1} and a C - H stretching vibration peak at approximately 2900 cm^{-1}. The interaction between its hydroxyl and amino groups and the surface of nanoparticles is weak and unstable. The alkalinity of the amino group causes changes in the pH value of the solution, affecting the surface charge properties of the particles. The molecular spatial structure is loose, making it difficult to form an effective space - steric hindrance barrier, resulting in the easy sedimentation of particles. Ammonium citrate has a wide peak near 3400 cm^{-1} related to the N - H stretching of ammonium ions and the stretching vibration of hydroxyl groups, and an absorption peak at around 1600 cm^{-1} related to the bending of ammonium ions and the asymmetric stretching vibration of carboxylates. Although it contains functional groups such as carboxylates and ammonium ions, its interaction with nanoparticles is not strong and persistent. The negative charge of carboxylates is affected by the ions in the solution, making the electrostatic repulsion unstable, and the positive charge of ammonium ions affects the electrostatic interaction due to environmental changes. The overall structure cannot form an effective space - steric hindrance, making it difficult for nanoparticles to remain dispersed for a long time.



(a) Infrared spectra of different types of dispersants.

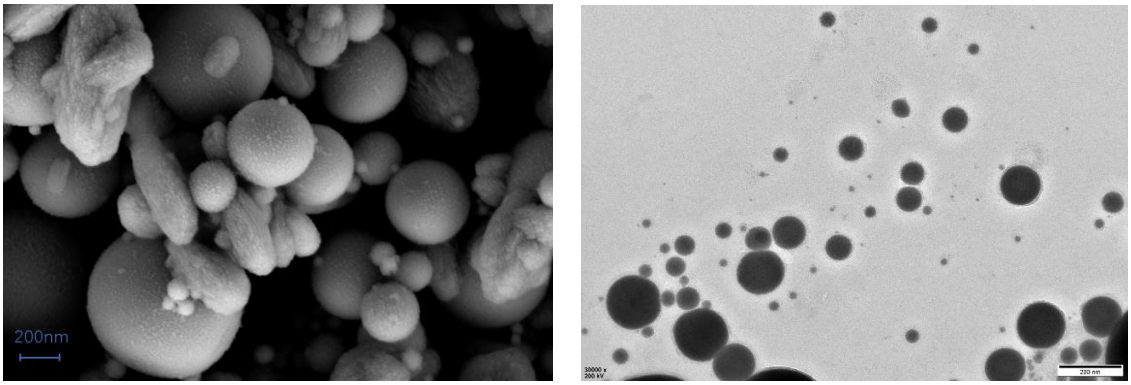


(b) Zeta potential and particle size of nanofluids with different types of dispersants added.

Fig 2. Characterization results of infrared spectra of dispersants/zeta potential and particle size of nanofluids.

However, for samples numbered 2 (DTAB), 3 (Tween 20), 4 (xanthan gum), and 5 (SDS), the turbidity is high and changes little during the observation period, indicating good dispersion stability. Among them, sample 4 (xanthan gum) has the most prominent stability. Xanthan gum has a wide absorption peak near 3400 cm^{-1} corresponding to the stretching vibration of hydroxyl groups. A large number of hydroxyl groups make it highly water - soluble and can form hydrogen bonds with nanoparticles to enhance affinity. The absorption peak at around 2900 cm^{-1} is related to the C - H stretching vibrations of methyl and methylene groups. The flexibility and bendability of the molecular chain help it form a network structure in the solution, increasing the space - steric hindrance and effectively preventing particle aggregation and sedimentation. DTAB has C - H stretching vibration absorption peaks of alkyl chains near 2900 cm^{-1} and 2800 cm^{-1}. It has a hydrophobic alkyl chain that can produce hydrophobic interactions with the surface of nanoparticles. There is an absorption peak related to C - N stretching vibration at around 1480 cm^{-1}. The trimethylammonium ion can be adsorbed on the surface of nanoparticles through electrostatic interaction to provide electrostatic repulsion, but the comprehensive effect is not as long - lasting and powerful as that of xanthan gum. Tween 20 may have a wide absorption peak related to hydroxyl groups near 3400 cm^{-1}. It has hydrophilicity and the ability to interact with the surface of nanoparticles. Strong absorption peaks near 2900 cm^{-1} and 2800 cm^{-1} indicate the presence of many methyl and methylene groups. Its polyoxyethylene ether structure and hydrophobic alkyl chain can form an adsorption layer on the surface of nanoparticles, maintaining particle dispersion through space - steric hindrance and partial hydrophobic interactions, but its long - term stability is slightly inferior to that of xanthan gum. SDS has C - H stretching vibration absorption peaks of alkyl chains near 2900 cm^{-1} and 2800 cm^{-1}. It has a long - chain alkyl structure that can produce hydrophobic interactions with the surface of nanoparticles. There is a strong absorption peak related to the S = O stretching vibration in the sulfate group at around 1200 cm^{-1}. The sulfate group can be adsorbed on the surface of nanoparticles through electrostatic interaction to provide electrostatic repulsion, but its molecular structure is simple, and it is not as good as xanthan gum in maintaining long - term dispersion stability.

Figure 2 shows the zeta potential and particle size of nanofluids with different dispersants added. It can be seen that although the zeta potential of xanthan gum, which has the best stability, is not high, it can form multiple interactions such as hydrogen bonds and electrostatic interactions with the surface of nanoparticles through a large number of functional groups such as hydroxyl groups and carboxylates in its molecules. Thus, it can construct a stable adsorption layer on the particle surface. Moreover, the flexibility and entanglement of its molecular chain enable it to form a network structure in the solution, bringing strong space - steric hindrance. Even if the electrostatic repulsion is relatively limited, these synergistic effects are sufficient to ensure the good dispersion stability of nanoparticles. In addition, the addition of xanthan gum can also increase the thickness of the solution, enabling the metal nanodroplets to be more stably suspended. Sodium polyphosphate has the highest zeta potential because its large number of phosphate structures increase the surface charge density of particles. However, its molecular chain is short and the structure is simple. It is difficult to form a thick and stable adsorption layer on the surface of nanoparticles to provide effective space - steric hindrance, and it is easily affected by the charge shielding of ions in the solution and environmental factors on the dissociation degree of phosphate groups and the surface charge properties of particles, resulting in unstable electrostatic repulsion. Eventually, nanoparticles are prone to aggregation and sedimentation, and the dispersion stability is poor. Therefore, the dispersion effect of each dispersant is determined by multiple aspects such as zeta potential, particle size, molecular structure, the interaction between functional groups and nanoparticles, space - steric hindrance, and environmental factors. In practical applications, these factors need to be comprehensively considered to select the most suitable dispersant to achieve the ideal dispersion state of nanoparticles.



(a) SEM Image of Gallium-Indium-Tin Nanodroplets

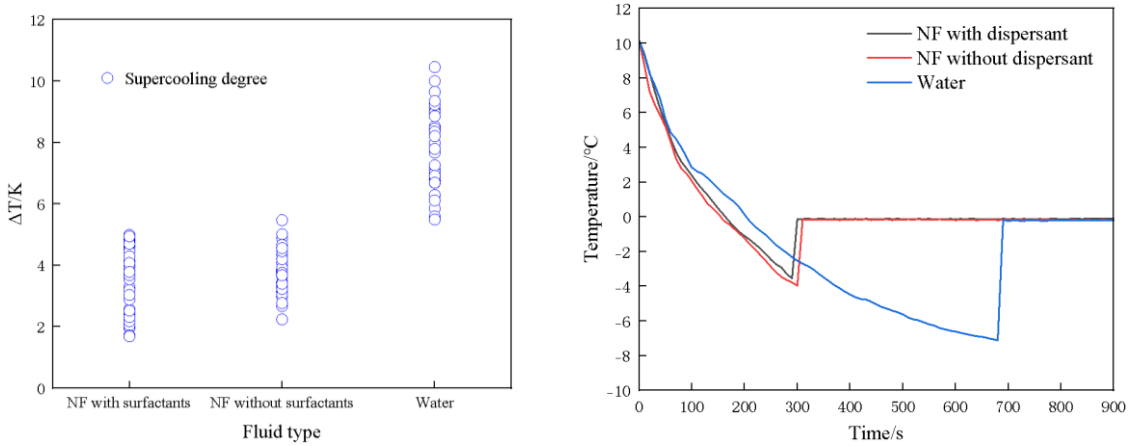
(b) TEM Image of Xanthan Gum-Gallium-Indium-Tin Nanofluid

Fig 3. Microstructure of Gallium-Indium-Tin Nanodroplets / Xanthan Gum-Gallium-Indium-Tin Nanofluids.

Figure 3 shows the SEM image of gallium-indium-tin alloy nanodroplets. It can be seen that there are obvious gaps between gallium-indium-tin nanoparticles. In terms of particle morphology, most nanoparticles are approximately spherical, with a size of less than 200 nm. The formation of this spherical morphology is attributed to the isotropic growth mode, that is, during the growth process of nanoparticles, the growth rates in all directions are relatively close. Taking the gallium-indium-tin alloy nanofluid with xanthan gum added as a dispersant as an example, its TEM image is shown. It can be seen that the transparent xanthan gum is adsorbed on the surface of the liquid metal, wrapping the liquid metal to prevent it from aggregating with each other and achieving the effect of dispersion and stability.

3.2. Results of the Supercooling Degree Experiment

In the study of material phase transformation, nucleation is the key initial step in the transformation of a liquid to a solid. Due to the disorderly thermal motion of atoms or molecules, it is a random event based on probability. However, under the collective behavior of a large number of atoms or molecules, the nucleation process follows specific statistical laws. The phase transformation supercooling degree, as an important external manifestation of nucleation, provides a thermodynamic driving force for nucleation and is closely related to nucleation. Therefore, it should also conform to the corresponding statistical laws. To explore this law and ensure reliable results, this paper conducted 30 repeated tests on each sample, laying a data foundation for subsequent analysis. Figure 4 (a) shows the supercooling degrees of 30 repeated experiments for each sample, and Figure 4 (b) shows the cooling curves of each sample selected to be close to its average supercooling degree.



(a) Supercooling degree data of samples.

(b) Cooling curves of samples.

Fig 4. Effect of Dispersants on the Supercooling Degree of Nanofluids.

From Figure 4, it can be seen that when nanoparticles are added to the base fluid, the supercooling degree of the liquid metal nanofluid is significantly reduced. The average supercooling degree of 30 measurements is 3.84°C, with the best inhibition effect. Compared with the average supercooling degree of water of 7.82°C under the same working conditions, it is reduced by 50.90%. Gallium-indium-tin alloy provides a large number of heterogeneous nucleation sites in water. According to the classical nucleation theory, during the process of water condensing into ice, a high energy barrier needs to be overcome, which requires a high supercooling degree to accumulate sufficient energy. The presence of gallium-indium-tin alloy provides a surface for water molecules to preferentially attach to. The atomic arrangement characteristics of the alloy surface have a certain adaptability to water molecules, making it easier for water molecules to arrange regularly on its surface, thereby reducing the energy barrier that needs to be overcome for nucleation.

At the same time, after adding the dispersant xanthan gum to the nanofluid, the average supercooling degree is further reduced to 3.49°C, a reduction of 55.37% compared to water. As a dispersant, xanthan gum can make gallium-indium-tin alloy particles more uniformly dispersed in water and prevent the aggregation of alloy particles. Uniformly dispersed alloy particles provide more effective heterogeneous nucleation sites for water molecules. More nucleation sites mean that water molecules have more opportunities to contact suitable nucleation surfaces during the cooling process, making it easier to form ice nuclei.

4. Conclusion

Different types of dispersants have significantly different effects on the stability of gallium-indium-tin alloy nanofluids. Xanthan gum, DTAB, Tween 20, and SDS can effectively improve the stability of nanofluids, with xanthan gum performing the best. Its large number of hydroxyl groups enhance the affinity with nanoparticles, and the network structure formed by its molecular chain provides strong space - steric hindrance. Even if the zeta potential is not high, it can still ensure the good dispersion stability of nanoparticles. However, sodium polyphosphate, triethanolamine, and ammonium citrate have poor dispersion effects, and nanoparticles are prone to sedimentation. This is because they have deficiencies in forming stable adsorption layers, providing effective space - steric hindrance, and maintaining the stability of electrostatic repulsion.

Adding gallium-indium-tin alloy nanoparticles can significantly reduce the supercooling degree of the fluid. The average supercooling degree is reduced from 7.82°C of water to 3.84°C, with an obvious inhibition effect. After further adding xanthan gum, the average supercooling degree can be reduced to 3.49°C. This is because gallium-indium-tin alloy provides heterogeneous nucleation sites, reducing the energy barrier for nucleation, and xanthan gum makes the alloy particles uniformly dispersed, providing more effective nucleation sites and promoting the formation of ice nuclei.

Acknowledgements

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