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Abstract: Phase change material emulsions (PCMEs) are multifunctional fluids consisting of Phase Change Materials (PCMs) and carrier fluids. PCMEs could be potential candidates as heat transfer media in heating, ventilation and air conditioning (HVAC) systems. This is mainly because PCME could take advantage of its high heat capacity to reduce flow rate and thus saving pumping power whilst delivering the same amount of cooling effect. PCME can also simultaneously act as cold storage to shift peak-load to off-peak time and improve the COP of systems. However, the optimum design of the integrated system requires a good understanding of flow behaviour and heat transfer characteristics of PCMEs. In this paper, comprehensive reviews of their thermo-physical properties and potential applications as thermal energy storage and as alternative heat transfer fluids in air conditioning systems have been carried out to establish their limitations for future research.

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The Editor
Energy and Buildings

December 24th 2014

Dear Editor,
Please see attached a copy of a manuscript entitled "**Review of Phase change emulsions (PCMEs) and their applications in HVAC systems**" for consideration and publication in the journal.

The first author is Miss Jingjing Shao, who is the correspondence author, currently a Ph.D candidate in Department of Architecture and Built Environment, University of Nottingham.

The second author is Professor Jo Darkwa, professor at University of Nottingham. The third author is Dr Georgios Kokogiannakis.

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This manuscript has gone through major revision. Each change made has been highlighted in text according to reviewers' comments. Response letter to reviewers are attached as well.

Yours sincerely,
Jingjing Shao

Response letter to reviewers

Dear Reviewers,

Please see the attached manuscript entitled “**Review of Phase change emulsions (PCMEs) and their applications in HVAC systems**” for consideration.

This manuscript has been revised according to the reviewers' comments and each change has been highlighted in text.

Detailed responses to each reviewer's comments are attached.

Yours sincerely,

Jingjing Shao

To reviewer #1：

General Comments:

It is hard to tell whether the gaps in coverage are due to gaps in the review or gaps in the literature being reviewed.

Unnecessary gaps are eliminated.

Lack of understanding how PCMEs might be used in HVAC system

There are very limited published reports or studies regarding practical application of PCMEs in HVAC systems. Most current and past research investigations are focused on the enhancement of their heat transfer characteristics. The issues highlighted are therefore intended to provide good insights towards future studies as summarized in the conclusion.

Specific Comments:

Page 4 Figure 1: Without more explanation, the macro-emulsion graphic is not particularly helpful.

Figure 1 has been deleted.

2nd paragraph, lines 4-5: Why are O/W emulsions more favourable for HVAC systems?

Explanation is now given in the text. See Page 4, line 4-5.

2nd paragraph, general: In the absence of an integrated interpretation framework for these tests, this section adds little. Presumably there is some sort of logic tree one can follow through the tests? Can this be provided?

The whole paragraph has been revised to make it clear. More interpretation has been given. See Page 4, 1st paragraph.

Section 2.2.1 second line: "Paffins" is presumably meant to read "Paraffins"

It has been corrected. See Page 4, section 2.2.1, line 3

Page 5 2.2.2, second paragraph, 3rd line: Definition of "cream" not provided by this stage of the paper.

Definition has now been given in the text. See Page 5, 2.2.2, 2nd paragraph, line 3-4.

Page 6 Line 5: Definitions of "cream" and "flocculate" not provided by this stage of the paper.

Definitions to these terms have now been given in first appearance.

Page 6 Section 2.3, first paragraph, last line: The phrase "...and only the viscosity ratio between the dispersed and the continuous phase has limited effect on droplet size" needs rephrasing. It doesn't appear to make sense currently.

The sentence has been rephrased. See Page 6, section 2.3, 1st paragraph, last line.

Section 2.3, second paragraph, 6th line: Perhaps a comma rather than a full stop between "distributions" and "even"?

It has been corrected. See Page 7, section 2.3, line 1.

Page 9 2.4.2 first sentence: Higher thermal properties than what?

The sentence has been rephrased. See Page 9, section 2.4.2, 1st line.

Page 12 Section 2.4.4: These definitions need to be provided earlier to help readers understand the discussion in 2.2.2

Definitions have now been given in Section 2.2.2 at its first appearance.

Page 15/16 Bridging sentence: "Because the strength.....viscosity of emulsion" doesn't make sense as written and needs to be rephrased.

The sentence has been rephrased. See Page 16, 1st paragraph, line 3-5.

Page 16 Section 2.5 first sentence: Substantial improvement relative to what?

The sentence has been rephrased. See Page 16, section 2.5, 1st line.

Page 18 Third paragraph 4th line: 40W/cm-2. Firstly I assume that either the negative or the / is redundant; more generally this should be expressed in SI units with the cited paper's original figure and unit in brackets.

Unit has been corrected. See Page 18, 3rd paragraph.

Page 19 Section 2.6 first line: Presumably PCMEs not "PCs"?

It has been corrected from PCS to PCME. See Page 19, Section 2.6, line 1.

Page 19 Section 2.6 second paragraph second line: Perhaps: "Conventional cold supply networks for air-conditioning operate over...."

It has been corrected now. See Page 19, Section 2.6, 2nd paragraph, 2nd line.

Page 20 First line: Is this all from ref 65 or are there other citations for these examples?

The statement has been rephrased and simplified.

Page 20 Third paragraph, second line: "Fictive"? Do not know what this is intended to mean

It has been corrected. See Page 20, 2nd paragraph.

Page 20 fourth paragraph, second line: Is there any particular reason that this has to be an electrical boiler?

Not necessary for electrical boilers, it has been corrected. See Page 20, last paragraph.

Page 21 Section 3, first sentence: This paper has reviewed development of PCMES for application in HVAC systems but I do not think it has really said a great deal about their application in HVAC systems.

Explanation has given in general comments.

Page 21 Section 3, third paragraph: This material is new and is not discussed in the body of the paper

Conclusion section has been revised. See Page 21-22.

To reviewer #2：

General Comments:

Suggested to give more insights regarding issues and future research

More insights are given in Conclusion

Specific Comments:

Page 4, paragraph 2:"W/O emulsions have higher viscosities but lower conductivities than W/O emulsions [19, 20]." Should it be "...lower conductivities than O/W emulsions"?

It has been corrected now. See Page 4, 1st paragraph, 4th line.

Page 5, paragraph 2:"Huang [24] tested different percentages of RT10 emulsion (15, 30, 50 and 75 wt%) and found that the latent heat capacity increased proportionally but there was no significant effect on the sizes of the droplets and their distribution." Does it mean that the density of the droplets changes with concentration?

The paragraph has now been modified to make it clear. See Page 5, 2nd paragraph.

Please explain the meaning of 'surfactant curvature' and its physical significance for emulsions.

More interpretation has been given in Page 7, 4th paragraph.

Page 8, paragraph 3: "….and compare the properties of three properties." Needs correction.

It has been corrected. See Page 8, 4th paragraph.

Please clearly define and explain all the terms in equation 1, to make it easier to understand how the expression on the right-most side was derived.

More interpretation has been given now in Page 7-8.

Page 9, paragraph 2: "PCMEs exhibit substantially higher thermal properties particularly thermal conductivity"; paragraph 3 - "PCMEs have relatively low thermal conductivities but could be improved with other materials". Seems contradictory.

Two sentences have been rephrased to make it clearer. See Page 9, Section 2.4.2, 1st and 2nd paragraphs.

Viscosity has been mentioned more than once. What impact does it have on the performance of the emulsion?

More explanation has been given now in Page 9, Section 2.4.2, 2nd paragraph.

Page 9: Both 'fibres' and 'fibers' have been used. Recommend consistency.

It has been corrected. See Page 10, 1st paragraph.

Page 11 last paragraph: "……that surfactant adsorption layer of surfactants could trigger nucleation." Repetition of 'surfactant'.

It has been corrected. See Page 12 line 3

Page 11, Effect of surfactants: SDS and Tween40 are said to drop the nucleation temperature. This

indicates that those two surfactants actually increase the degree of sub-cooling, not reduce it?
The paragraph has been rephrased to make it clear. See Page 11-12.

Page 18, line 3: 'Along heating test section…..' should be 'A long heating section…..'
It has been corrected. The paragraph has been rephrased. To make the paragraph clearer, a new figure has been attached. See Page 18 2nd paragraph.

A few terms have been used that may not readily be understood by the ENB audience. Examples are lipophilic, flocculate (this term has been defined well after its first usage), phase tension, etc.
Definitions to technical terms are now given in first appearance.

There are minor editorial corrections needed at several places in the manuscript.
Corrections have been made now.

Review of Phase change emulsions (PCMEs) and their applications in HVAC systems

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Review of Phase change emulsions (PCMEs) and their applications in HVAC systems

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Abstract

Phase change material emulsions (PCMEs) are multifunctional fluids consisting of Phase Change Materials (PCMs) and carrier fluids. PCMEs could be potential candidates as heat transfer media in heating, ventilation and air conditioning (HVAC) systems. This is mainly because PCME could take advantage of its high heat capacity to reduce flow rate and thus saving pumping power whilst delivering the same amount of cooling effect. PCME can also simultaneously act as cold storage to shift peak-load to off-peak time and improve the COP of systems. However, the optimum design of integrated system requires a good understanding of flow behaviour and heat transfer characteristics of PCMEs. In this paper, comprehensive reviews of their thermo-physical properties and potential applications as thermal energy storage and as alternative heat transfer fluids in air conditioning systems have been carried out to establish their limitations for future research.

Keywords: PCM emulsion; thermal energy storage; thermo-physical properties; heat transfer; applications

Nomenclature

Δh_e	Total heat capacity	$\Delta\rho$	Density difference
$\Delta h_{f,e}$	Latent heat capacity of the emulsion	g	Gravity acceleration
Δh_w	Sensible heat capacity of water	δ_c	Viscosity of continue phase
Δh_{PCM}	Sensible heat capacity of paraffin	δ_{PCM}	Viscosity of PCM
$\Delta h_{f,PCM}$	Latent heat capacity of PCM	v	Separation speed
X_{PCM}	Weight fraction of PCM	$C_{p,w}$	Specific heat capacity of water
X_w	Weight fraction of water	$\overline{C_{p,PCM}}$	Average specific heat capacity of the paraffin in solid and liquid phase
V_{PCM}	Volume of PCM	AR	Aspect Ratio
V_w	Volume of water	G	Gibb's potential
Φ_w	Volume fraction of water	T	Temperature

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1. Introduction

According to the World Business Council for Sustainable Development (WBCSD), buildings represent more than 40% of final global energy consumption [1]. For instance, in China, buildings are responsible for about 25% of the country's total energy consumption and carbon emission [2], among which, at least 22% is attributed to commercial buildings [3]. Generally, Heating, Ventilation and Air Conditioning (HVAC) systems are responsible for 50% of whole building energy consumption with the consumption level reaching as high as 60% [4] in some large commercial buildings such as shopping malls.

Literature reviews have identified thermal energy storage (TES) technology based on phase change slurries (PCS) as a potential working fluid which could be used to reduce energy consumption in HVAC systems. They basically contain water and phase change materials (PCMs) such as paraffin and as such do possess much larger energy storage capacity than currently used chilled water based systems. Among the commonly produced types of PCS is phase change emulsion (PCME) which has over the past decade attracted interests from a number of researchers [5]. Inaba [6] was the first to investigate the cold heat release characteristics of PCME with different concentration levels of PCM. Inaba et al. [7] further studied the natural convection behaviour of PCME in rectangular cavities. Zhao et al. [8-10] mainly focused on the heat transfer properties of PCME. They theoretically analyzed the heat transfer characteristic of PCME and provided empirical formulas of rheological index and viscosity with temperature, and of heat transfer in ducts. Zhang et al. [5, 11-13] developed a tetradecane emulsion with a lower viscosity, and carried out a series of studies into heat transfer behaviour. Furthermore they analysed the factors affecting enhancement of laminar flow heat transfer.

However, the main barrier affecting the application of PCME is the difficulty in maintaining stability in the emulsions without experiencing any temperature stratification during phase change process [14]. Sub-cooling is another problem facing the application of PCME as it enlarges the operating temperature range of the systems and worsens the energy efficiency of air conditioning systems. Several studies on sub-cooling of PCME have been published including Huang et al. [15] who reported sub-cooling of 4.3 K and 14.7 K in tetradecane/water and hexadecane/water emulsions respectively. Royon and Guiffant [16] observed a 5.6Kof sub-cooling in aliphatic hydrocarbons-water emulsion.

This study therefore reviews the characteristics, challenges and advancement in the development and application of PCM emulsions in HVAC systems.

2. PHASE CHANGE EMULSIONS (PCMEs)

2.1 Classification of PCMEs

PCMEs are mixtures of two immiscible liquids and based on the sizes of droplets, they may be grouped into three main categories as follows: a micro-emulsion type, which is characterized by a thermodynamically stable behaviour with droplet diameters ranging from 10 to 100nm; mini-emulsion and macro-emulsion systems which are both thermo-dynamically unstable with droplet sizes ranging from 100 -1000nm and up to 1μm respectively [17].

Depending on the type of dispersed phase and carrier liquid, oil-in-water (O/W) direct emulsion or water-in-oil (W/O) inverse emulsion can be formed but more complex systems such as oil-in-oil (O/O) or multiple emulsions of different kinds (W/O/W, O/W/O, W/O/O) can also be obtained as shown in Fig. 1 [18]. W/O emulsions have higher viscosities but lower conductivities than O/W emulsions [19, 20]. Since PCMEs are to be circulated within air conditioning systems, lower viscosity is of vital importance to ensure a low pump power. Therefore, O/W emulsions are more favourable for application in air conditioning systems. The type of emulsion also depends on the method of preparation, properties of the stabilizing additive, and other various factors. If oil and water are emulsified with stabilizing additive, it is difficult to tell whether O/W or W/O emulsion is formed. In general, it is difficult to identify a particular type of emulsion by physical appearance especially when two types of emulsions are quite similar. The following five basic tests are therefore normally used in determining the type of emulsion [20, 21]. There is no order of priority in these tests but at least two tests are required to achieve a reasonable level of accuracy and conclusion.

1) Dilution test: The dilution test is based on the solubility of the continuous phase. O/W emulsions can be diluted with water and W/O emulsions with oil. If the emulsion is O/W type and it is diluted with water, it will remain stable, but if it is diluted with oil, the emulsion will break as oil and water are not miscible with each other.

2) Dye-solubility: In the dye-solubility test, either a water-soluble or oil-soluble dye can be used and then observe the colour pattern of emulsion under a microscope. Oil-soluble dye will dissolve and dye the dispersed phase in an O/W emulsion, and the continuous phase in a W/O emulsion.

3) Filter paper: The filter paper test involves impregnating filter paper with Carbonyl Chloride ($CoCl_2$). O/W emulsion will then change the colour of the filter paper from blue to pink.

4) Fluorescence: The fluorescence test is based on the idea that some oils are fluorescent under UV light. When using UV light to test the emulsions, O/W type will show a potty pattern, on the other hand, the main body of W/O emulsion will be fluorescent.

5) Conductivity: The conductivity test needs a light bulb to be attached to two electrodes. If the electrode is immersed into an O/W emulsion, the bulb glows as the O/W emulsions have a very high specific conductance.

Figure1

2.2 Components of PCME

2.2.1 Paraffin

Paraffin wax consists of a mixture of mostly straight chain n-alkanes $CH3\text{-}(CH2)_n\text{-}CH3$. The crystallization of (CH_3)-chain releases a large amount of latent heat. Both the melting point and latent heat of fusion increase with chain length. Paraffins are safe, reliable and non-corrosive. They are chemically inert and stable, and show little volume changes on melting [22]. Various types of paraffin are available for HVAC applications. For instance, when a paraffin is used for comfort cooling application, it should melt within the temperature range of 0 and 20°C [23]. There are three types of paraffin that have melting points fits this range; tetradecane CH_3-$(CH2)_{12}$-CH_3 (T_m=5.9°C, h_f=227kJ/kg), pentadecane CH_3-$(CH2)_{13}$-CH_3 (T_m=10°C, h_f=206kJ/kg) and hexadecane CH_3-$(CH2)_{14}$-CH_3 (T_m=18°C, h_f=236kJ/kg). Due to cost considerations, commercial products with polymers blends such as RT6, RT10 and RT18 from Rubitherm Technologies GmbH, which have similar properties as pure paraffins, are preferred. Despite of the favourable characteristics of paraffin, they have some undesirable properties such as low thermal conductivity and flammability. All these undesirable effects can be minimized by modifying the wax and the storage unit [22].

Higher concentration of paraffin tends to increase the heat capacity of the emulsion. In contrast, increasing concentration level has little or no effect on the size of dispersed droplets. For instance as shown in Fig. 2, Huang [24] tested different percentages of RT10 emulsion (15, 30, 50 and 75 wt%) and found that their latent heat capacities increased proportionally. However, all the samples were of similar sizes ranging from 1–10 mm and of mean diameter d50 of 3–5 mm, which suggested that the paraffin fraction had no significant effect on the droplets size distribution.

Figure 2

2.2.2 Surfactants

Surfactants are indispensable components of PCME. They are chemical compounds that stabilize mixtures of oil and water by reducing the surface tension at the interface between oil and water molecules. They have strong influence on the stability and sub-cooling degree of emulsions. Surfactants improve stability by lowering the interfacial tension. The lower the interfacial tension is the less energy required to form the emulsion [25]. Surfactants consist of hydrophobic and hydrophilic portions, which attract both oil and water droplets as shown in Fig. 3[24]. Surfactant between the droplet phase and the continuous phase serves as a protective layer which prevents the droplets from being broken [26].

Figure 3

Phase change emulsions that have been stabilized by surfactants have several advantages as compared with microencapsulated or shape-stabilized phase change slurries [27, 28]. Micrometre-sized droplets can easily be obtained by emulsification procedure. Such small particles do not cream rapidly, i.e. the process of droplets migrating to form a concentrated layer at the top of the emulsions. This layer normally exhibits high efficiency in heat transfer due to enlarged surface-to-volume ratio. Another advantage of using surfactant is the negligible thermal resistance of protective surfactant layer. Furthermore, surfactants prevent deposition of paraffin particles onto the surface of cooling system and thus reduce the risk of obstruction.

Surfactants can be classified into several different groups as shown in Fig. 4: non-ionic, ionic, amphoteric surfactant and polymer emulsifier [29, 30]. Ionic types are most commonly used surfactants, but the non-ionic types are more effective. Non-ionic surfactants do not produce ions in aqueous solution. As a consequence, they are compatible with any types and are excellent candidates for complex mixtures. Above all, ions such as OH^- can be easily adsorbed on the emulsion droplet thus producing a charge [31]. Nonionic surfactants are much less sensitive to electrolytes than ionic surfactants. Ionic surfactants such as sodium dodecyl sulfate (SDS) and hexadecyltrimethyl ammonium Bromide (HTAB) can also be used in O/W emulsion, but the system is sensitive to the presence of electrolytes. Surfactant mixtures, for instance, ionic and nonionic, or mixtures of nonionic surfactants can be more effective in stabilization of the emulsions.

Figure 4

The strength of the protective layer is related to the concentration of surfactant [32]. Adding adequate surfactant can achieve the best emulsification effects. Li et al. [32] experimentally tested the effects of surfactant/oil ratio on droplet size of paraffin and found a direct relationship. As summarised in Tab. 1, the increase in the surfactant/oil ratio led to a reduction in droplet size. They also established that mini-emulsions with diameter around 0.5μm were thermodynamically stable, as the emulsions with droplet size over 1μm were easy to cream and flocculate. When flocculation happens, droplets cluster together and form clumps. To have droplet size around 0.5μm, the ratio needs to be larger than 1:4. To have droplets smaller than 0.1μm, much larger amount of surfactant was demanded. However, excessive amount of surfactant will affect the quality of emulsion and introduce bubbles which are not easy to remove and also reduces the stability of emulsion. Normally surfactant/oil ratio of 0.1-0.3 will be the optimal range [33].

Table1

2.3 Preparation of Emulsions

High-energy methods

Preparation of emulsions using high-energy stirring technique involves a mechanical process whereby large droplets are broken into small ones. High energy methods produce coarse droplets around 5–100μm, and further reductions in the droplet size would require a substantially greater amount of energy input. The most common device is the rotor-stator system which applies shear stress to induce deformation of pre-emulsion droplets and breaking into smaller and uniform sizes, whose principle was shown in Fig. 5 [17]. Diameter of the droplets depends heavily on the applied energy. The viscosity ratio of the dispersed to continuous phase also has limited effect on droplet size.

Figure 5

The dispersion speed which is related to energy input, largely affects the quality of produced emulsion. If the dispersing speed is not high enough, i.e. energy input is insufficient, it would fail to mix the paraffin and the surfactant fully and result in an uneven distribution of droplet size. If the speed is too high, it would have little impact on droplet size, thus wasting energy. High speed dispersion is more likely to introduce large amount of bubbles which will affect stability of the emulsion [34]. As shown in Tab.2 and Fig.6 [35], when the dispersion speed was higher than 800rpm, there was little difference in droplet size distributions, even though the stability of emulsion did improve as the fluidity was deteriorating. Therefore, a speed range of 800-1000rpm was considered to be adequate for a the complete process [35].

Table 2

Figure 6

It is recommended to reduce the dispersing speed after an intense mixing to allow surfactant to be fully absorbed onto the paraffin droplets [33]. In industrial applications, low speed stirring around 200rpm is applied to pre-mix the paraffin and water in order to avoid slopping out before increasing the speed to 500-1000rpm to fully emulsify the paraffin. Dispersion for a longer period of time than 30 minutes is not effective and is considered to be a waste of energy as 30 minutes would be enough to completely emulsify a product and longer emulsification time has little influence on the droplet size [33].

Low-energy method

PCME can also be prepared using low energy methods called spontaneous emulsification. Spontaneous emulsification makes use of the chemical energy stored in molecules to complete the transition between O/W emulsions and W/O emulsions without external energy input [25].

Phase inversion method is the most often considered approach of spontaneous emulsification method. Emulsion prepared by phase inversion tends to be fine and well-dispersed [36]. Phase inversion makes use of changing the spontaneous curvature (molecular geometry) or relative solubility of non-ionic surfactants in water and oil. Due to the hydrophobic effect, surfactant molecules tend to spontaneously associate with each other in water to form a monolayer which allows the most efficient packaging of the molecules. In an emulsion, the surfactant monolayer is presented in an oil-water interface. The type of emulsion that a particular surfactant tends to favour depends on its spontaneous curvature. Fig. 7 [25] is a molecular representation of the spontaneous curvature change of surfactant during phase inversion and the resulting type of emulsion. Phase inversion can be achieved either by changing the temperature (phase inversion temperature, PIT) [37, 38] or by changing the volume fractions of water/oil (emulsion inversion point, EIP) [2, 12, 39-41]. The most important part of phase inversion is crossing the inversion line which is the solid black line shown in Fig. 8, and the speed at which it crosses the line [42].

Figure 7

Figure 8

The phase inversion temperature (PIT) method (vertical arrow in Fig. 8) was first described by Shinoda and Saito [37, 43] as an alternative to high shear emulsification methods. The essential processes of PIT method are shown in Fig. 9, in which oil, water and non-ionic surfactants are pre-mixed together at room temperature [44]. At low temperatures, the surfactant tends to be more soluble in water and the surfactant monolayer exhibits positive curvature which packs oil droplet in middle. When this emulsion is heated gradually, the surfactant gradually becomes lipophilic (soluble in oil) and at a particular PIT, the solubility of the surfactant in the oil and water phases is approximately the same, and surfactant monolayer then exhibits zero curvature.

At temperatures higher than PIT, the surfactant becomes more soluble in the oil phase than in water phase, thus the surfactant gets completely dissolved in the oil phase and the original O/W macro-emulsions becomes the W/O emulsion. Mechanical power is applied at a constant temperature above PIT temperature to break large drops. When this system is cooled below the PIT, surfactant molecules move from the oil phase into water phase rapidly which leads to the spontaneous formation of small oil droplets.

Figure 9

In the emulsion inversion point (EIP) methods (horizontal arrow in Fig. 8) the change from one type of an emulsion to another is through a catastrophic phase inversion (CPI). In this case a W/O emulsion with a high oil content is first formed with some specified types of surfactants before the water content is gradually increased with continuous stirring (Fig. 11). Above critical water content, the emulsion reaches the phase inversion point where it changes into an O/W system [44]. The size of the droplets depends on various process variables, such as the dispersing speed, the surfactant concentration and the rate of water addition, etc. The surfactant used in EIP method is limited to small molecule surfactants to stabilize both W/O and O/W emulsions.

Figure 10

Adding water to surfactant and oil mixture followed by inversion is indeed a widely used method. As both of the lipophilic and hydrophilic surfactants are used, this method is sometimes modified as in the mixing film synthesis [12, 41]. As mentioned before, the inversion can take place in a catastrophic or transitional way. The catastrophic inversion is due to a change in WOR, and the transitional one is because of a change in formulation, which can be done by varying the temperature, or changing the weight composition of the surfactants in the emulsion as in the mixing film synthesis. In this method, the lipophilic surfactant (e.g. Span60) is pre-mixed with the oil (called mixture A). Therefore, the PIT temperature is very low. The hydrophilic surfactant (e.g. Tween60) is mixed with water forming mixture B. Mixture B is then added to mixture A at a specified temperature. This process increases both the concentration of hydrophilic surfactant and the PIT. With this method, it is possible to trigger a transitional inversion at constant temperature [45].

Schalbart et al. [45] used three different low energy methods (EIP, mixing film and PIT) to prepare tetradecane emulsions and found the PIT to be the most effective approach. During the preparation, all the components which were pre-mixed at room temperature were heated to 72°C, and then were cooled down to room temperature by adding 54g cool water. In this way, the emulsion crossed the inversion line twice which achieved a narrow droplet size distribution in the range of 200-250nm. They maintained stability with low viscosity values (2-4 times of water) for more than six months at room storage temperature.

2.4 Main characteristics of PCME

2.4.1 Thermophysical properties: Heat capacity

Total heat capacity of PCME consists of not only the latent heat of the paraffin, but also the sensible heat capacity of the water and that of the paraffin. In the temperature range from T1 to T2, total heat capacity of PCME Δhe is the sum of latent heat capacity of the emulsion Δhf,e, the sensible heat capacity of water Δhw and that of paraffin ΔhPCM as follows [23]:

$$\Delta h_e = \Delta h_{f,e} + \Delta h_w + \Delta h_{PCM} = X_{PCM} \Delta h_{f,PCM} + X_W C_{p,W} (T_2 - T_1) + X_{PCM} \overline{C_{p,PCM}} (T_2 - T_1) \quad (1)$$

Where, Xw and XPCM are the weight fractions of paraffin and water, Δhf,p is the heat of fusion of paraffin in the temperature range of T1 to T2. Cp, w and $\overline{C_{p,PCM}}$ are the specific heat capacity of water and the average specific heat capacity of the paraffin, respectively.

Total heat capacity of the emulsion can be estimated experimentally. Experiment to determine the heat capacity of the emulsion under certain similar operational conditions in practical applications has been carried out in a test rig (Fig. 11) by Huang [23]. The rig consisted of a storage tank, a thermostat, a plate heat exchanger and a Laing heating pump. A flow meter and thermocouples were used to determine the flow rates and the temperatures of the primary heat transfer fluid and the sample. All of the elements and pipes were well insulated to reduce the heat loss. The values from the test rig did agree well with those estimated according to Eq.(1).

Figure1

2.4.2 Thermophysical properties: Thermal conductivity

Concluding from past investigations [25, 39, 46, 47], PCMEs exhibit substantially higher thermal conductivities than PCMs [48, 49]. The size, shape and components of dispersed phase all have effects on conductivity. Emulsions with small particles have higher thermal conductivity than ones with large particles. Emulsions with spherical shape particles exhibit slightly higher thermal conductivity compared with the ones having irregular particles. In addition, high temperature could enhance the conductivities by increasing the molecular activeness. Although there are some empirical correlations such as the Eurken's model [50] and laws of mixtures [39] available for calculating thermal conductivities of PCME, they are not considered to be sophisticated and robust enough for high level accurate results.

Even though PCMEs have higher conductivities than PCMs, they are still relatively lower than that of water which various researches have tried to enhance with different types of materials. For instance, Zou [51] looked at the possibility of increasing the thermal conductivity of paraffin emulsions with 1wt% Al nanoparticles. The results showed about 29.4% enhancement in thermal conductivity which was almost equal to the conductivity of water. Ho [52] prepared a nanoparticle-in-paraffin emulsion by emulsifying 5wt% and 10wt% of alumina (Al_2O_3) particles in n-octadecane emulsion and achieved corresponding thermal conductivity enhancements of 2% and 6% respectively at 30°C. However, the alumina also contributed to an increase in the dynamic viscosity and was therefore considered to be unsuitable for low energy application in air conditioning systems. Another main disadvantage in using metallic materials is that they displace a considerable amount of

PCM and increase the weight of the dispersed phase thus causing sedimentation [50, 52]. As a result some investigations involving the use of lightweight materials such as carbon fibres and nanofibres have been carried out [53-55]. For instance, Elgafy and Lafdi [53] employed carbon nanofibres to enhance thermal performance of PCME. As shown in Fig. 12, the thermal conductivity at room temperature did increase with increasing mass fraction of carbon nanofibres (CNFs) and the cooling rate during the solidification process also increased significantly. However, the problem of settlement of nanoparticles after several freeze-thaw cycles was observed by Fleischer et al. [55] and attributed to the change in density which occurred during the period of liquid-solid transition.

Figure 2

2.4.3 Sub-cooling

Sub-cooling phenomenon is one of the issues which affect the application of PCME. It lowers the crystallization temperature of a liquid or a gas, thus latent heat is released at a lower temperature or in a wider temperature range [56]. A large sub-cooling is not acceptable because it would enlarge the operating temperature range of a PCS system and thus deteriorates the system performance and reduces energy efficiency.

The level of sub-cooling for PCMEs highly depends on the PCM used. However, PCMs behave differently from microscopic geometry to macroscopic geometry. Even though the used paraffin may have negligible sub-cooling, the PCME still crystallizes below freezing temperature [24, 46, 57]. For instance, the tetradecane and hexadecane emulsions prepared by Huang et al. [15] showed temperatures of 4.3K and14.7K sub-cooling respectively, while the PCM tetradecane and hexadecane only have 0.5K and 1.9K degree of sub-cooling.

Nucleation theory

Gunther et al. [58] tried to interpret the cause of sub-cooling with nucleation theory which describes the formation of small particles of the new phase in the middle of the mother phase in early stage of phase transitions. When the temperature of bulk liquid is reduced below melting point, the formation of solid phase would be spontaneous and release energy. When a particle of radius r is formed, a phase interface between the bulk liquid and solid agglomerate would be created. The creation of the interface would need energy input to fight against the effect of surface tension force in order to prevent it from reducing the size of the liquid surface. However for very small solid particles in the bulk liquid, the energy released during phase transition tend not to be adequate enough for overcoming the effect of surface tension force. This limitation therefore blocks the nucleation process and prevents spontaneous solidification from happening.

The thermodynamic potential that describes this effect is the Gibb's potential G. The difference in G between the old and the new phases, $\triangle G$, is a function of cluster radius, and its maximum defines the critical radius r_{crit} as sketched in Fig. 13[59]. $\triangle G(r)$, called the nucleation barrier, is a potential barrier that needs to be overcome to initialize macroscopic nucleation. This means, only for clusters larger than theoretical radius the radius grows spontaneously and solidification proceeds [58]. The crystallization process can be regarded as a two-step process [60]. The first one corresponds to the apparition within the liquid phase of a "supercritical" aggregate. It is the process to develop a cluster larger than the critical radius. The second phase corresponds to crystalline growth, initiated by this supercritical cluster and leading to the total crystallization of the system.

Figure 3

The nucleation in bulk PCM is known as heterogeneous nucleation. In bulk PCM, crystallization will occur more rapidly as one nucleation event per PCM module is sufficient to assure the functionality of PCM. However, when the PCM is finely divided into emulsion droplets, the volume of the single droplets is very small; freezing process in emulsions is predominantly a homogeneous nucleation which leads to the lower crystallization temperature of PCME. At some point, the droplet size is smaller than critical radius, the nucleation is blocked. One of the solutions is by using nucleating agents.

Nucleating agent

Substances that have a particularly small phase tension, so-called nucleating agents, can be added to the liquid to enhance nucleation. Nucleating agents in principle are impurity or surface in contact with the liquid. They offer the necessary seeds inside of the paraffin droplets to start the nucleation and thus are acting as a nucleating catalyst. The nucleating agent and its fraction have important effects both on the melting and nucleation temperature.

In the case of PCME prepared by Huang et al. [15], a nucleation agent was added before emulsifying. Paraffin wax with a higher freezing peak point than PCM was selected as the nucleating agent. The sub-cooling witnessed a 6.9K drop with nucleation agent. They found that with increasing fraction of the nucleating agent, the melting peak shifts to lower temperature range, but the freezing peak increases, so the sub-cooling phenomenon is reduced.

Effect of droplet size

The smaller the droplets are, the higher degree of sub-cooling the emulsions probably will have [57, 61, 62]. To analyse the relationship of droplet size on nucleation process and sub-cooling, Huang [15] prepared different phase change emulsions with different droplet sizes. Droplet sizes and their distributions played vital roles in both the melting and nucleation temperature. Both temperatures decreased with the reduction in droplet size. The influence of the droplet diameter on the melting temperature was found smaller than 2K, but the influence on the nucleation temperature was as high as 15K for the emulsion with the smallest droplets.

The effect of surfactant

The degree of sub-cooling depends not only on the droplet size but also the type of surfactant. Huang et al. [15] prepared hexadecane emulsions with three different surfactants (SDS, Tween40, surfactant mixture) and found no significant impact on the melting temperature. However, the nucleation and sub-cooling temperatures did change. The hexadecane emulsion with surfactant mixture had two nucleation and sub-cooling temperatures of 11.6 /6°C and 5.7/ 11.3K respectively. The nucleation temperature of sample prepared with SDS surfactant achieved the lowest emulsion nucleation temperature of about 2.6°C with sub-cooling temperature of 15K. For the sample with Tween40, nucleation temperature increased to 6°C and resulted in a smaller sub-cooling temperature of 11K.

There is extensive evidence to show that adsorption layers of surfactants could trigger nucleation. Surfactant molecules at the interface, acting as a template, increase the ordering of oil molecules to form nuclei of a critical size to initiate crystallization [62, 63]. Experiment by Golemanov et al. [57] revealed that emulsions with surfactants with longer alkyl tails (i.e. with 16 or 18 Carbon atoms) had a lower degree of sub-cooling, and that addition of oil-soluble co-surfactant could further suppress the sub-cooling phenomenon. This finding indicated that the dense adsorption layers of long-chain surfactant molecules could act as templates for oil crystallization.

2.4.4 Stability

Stability is always the priority of PCME studies. For practical uses, PCME should be stable for long-term storage and even under shear rate. Emulsions may degrade via a number of different mechanisms as in Fig. 14 [46]:

1) Creaming ; the process of forming a concentrated layer at the superior part of sample as a result of gravity
2) Flocculation; the process through which small oil particles stick together and form clumps
3) Coalescence; the process though which two or more droplets melt and form a bigger droplet
4) Ostwald ripening; the process of forming a bigger droplet due to solubility difference
5) Phase inversion though which continuous phase become disperse phase while disperse phase becomes part of continuous phase

In the majority of cases the predominant degradation mechanism is coalescence. As a result of thermodynamic instability, emulsions will finally tend to increase in droplet diameter. Even though creaming and flocculation do not normally change the droplet size distribution, yet they are the signals to coalescence since coalescence requires the droplets to be close proximity. Ostwald ripening, on the other hand, does not require the droplets to be close, since the ripening occurs by transport of dissolved matter through the dispersion medium [64].

Figure 4

Solutions to Instability

In an ideal suspension, instability should never occur. Unfortunately, majority of PCMEs tend to separate, especially under thermal-mechanical cycles. For practical applications, it is acceptable that the emulsion changes the properties in a tolerable range [24]. The PCMEs can be considered as stable when neither distinct growth in droplet sizes nor phase separation occurred during the storage period, and in practical applications, it is tolerable when emulsions remained in dispersion and kept the heat capacity under the designed operational conditions [65]. Schalbart et al. [45] tested tetradecane-in-water emulsion and only two samples achieved good storage stabilities against creaming at room temperature for six months. But Ostwald ripening destabilisation was observed resulting in a slight increase in the droplet size. Huang et al. [65] evaluated the stability of their

PCMEs under different conditions. The droplet size distribution changed slightly after 28 months storage at a room temperature. However, slight coalescence was observed in the properties after 50 thermal-mechanical cycles.

The standard procedure for testing the stability of paraffin dispersions is to subject them to shear rate. Fig. 15 is a schematic drawing of the test apparatus designed by Vilasau [66] to test the stability of emulsion under shear stress. This stability test consists of a centrifugal pump connected to a column with a free fall. The stability under freeze-thaw cycles could also be achieved by circulating the dispersion through a model heat-exchanger system. If the dispersion was unstable, a clear separation could be witnessed after a number of cycles; this number would be used as a measure of dispersion stability. However, the circulation method requires special equipments, it is also time-consuming, especially for the more stable systems, and no precise quantification of dispersion stability is possible. Moreover, in the actual air-conditioning systems, the working fluid is typically exposed to strong mechanical stresses, which may lead to coalescence that are otherwise stable under static conditions or under pressure variations of lower magnitude [57].

Figure 5

Zou et al. [41, 46] suggested two principles to overcome the instability.

a) Seek an optimal concentration of PCM. Higher concentration will easily cause agglomeration. However, reducing concentration will deteriorate the latent heat capacity of PCME. So, a proper concentration should be studied.

b) Reduce the diameter of droplet. The speed of separation can be described using Stockes equation[33]:

$$V = (\Delta\rho \cdot \mathrm{d}^2 \cdot g) / 18\,\delta_c \qquad (2)$$

Where V, $\Delta\rho$, g and δ_c represents separation speed, density difference between two phases, gravity acceleration and viscosity of continue phase respectively.

According to the Eq.(2), a stable emulsion which means a low separation speed, needs to have a higher viscosity, small density difference and droplet diameter. However, for an emulsion, it is difficult to reduce density difference; so, the easiest way is to reduce droplet size which also reduces the influence of gravity. Droplet size can be control by formulation and the stirring conditions prevailing, as well as on composition of the surfactant-oil-water system.

Factors affecting stability

The stability of PCME is closely related to surfactant. Surfactant forms an absorption layer around oil droplet. If the layer is not strong enough, droplets will cream. Therefore, surfactant selection is the top priority to produce small and even paraffin droplets.

Golemanov et al. [57] tested the effect of surfactant on emulsion stability. They found that solid-liquid phase transition of the dispersed paraffin particles reduced the dispersion stability significantly. Irregularly shaped crystals could destabilize significantly the system during the freezing-thaw cycles. It was pointed out that non-ionic surfactants were more stable than others. The surfactant mixtures comprising hydrophilic and hydrophobic components were found efficient in stabilizing the dispersions, which was attributed to the formation of denser adsorption layers between two phases. HLB number, used to choose surfactants for conventional emulsions, may not be effective for emulsion with particles which undergo freeze-thaw cycles. The chain length of the surfactants was also very important for such systems.

Vilasau [66] analyzed the stability of PCME with mixed ionic/non-ionic surfactant system. Emulsions were prepared as a function of three parameters: 1) ionic surfactant fraction (=ionic surfactant/total surfactant), keeping the total surfactant concentration a constant. 2) The total surfactant concentration, keeping constant ionic fraction, and 3) the homogenization pressure. They found that the most stable emulsions were those with high ionic surfactant ratio. Moreover, stability increased at high surfactant concentration and high pressure which produce emulsions with small sizes.

In the same study, the stability was also assessed against electrolyte concentration, since paraffin emulsions were generally diluted using water containing high concentration of electrolyte for industrial applications. In the study, emulsions were diluted in water (1:1000) and electrolyte, Sodium Chloride (AnCl) and Calcium Chloride Chloride ($CaCl_2$) were added. Samples were mixed and then kept at 25°C for 24hrs. Afterwards, critical coagulation concentration (CCC) was used as a measuring parameter of stability. Generally, a higher CCC was preferred. The results indicated that diluted emulsions presented low stability against electrolyte (CCC_{NaCl} and CCC_{CaCl2} were 17 and 4mM, respectively). It was probably caused by the charges presented on the particles. With the Ca^{2+}, stability was much lower than emulsion with NaCl. Fig. 16 [66] indicates the relationship between CCC_{CaCl2} and ionic surfactant weight fraction. The emulsion prepared without ionic surfactant appear flocculated after emulsification (ΦI=0). Addition of ionic surfactant leads to an increase in CCC_{CaCl2}. CCC peaked at ionic surfactant weight fraction of 0.56. It suggested the coexistence of non-ionic and ionic surfactant were better at stabilizing emulsions, as non-ionic surfactant can maximize CCC.

Figure 6

2.4.5 Rheological behaviour

In emulsion studies, two factors must be considered: droplet size distribution and viscosity. It is of vital importance to control the droplet sizes distribution of emulsions as viscosity tends to increase as the droplet sizes decrease [61]. Dispersions with fine droplets normally are more stable than those with large droplets. However, smaller droplets lead to a larger sub-cooling degree [33]. Therefore, a compromise on droplet sizes should be reached to ensure an emulsion with low viscosity, small sub-cooling degree and good stability.

Viscosity is an important parameter of emulsions in terms of stability. If viscosity of an emulsion remains unchanged after pumping then it is considered to be kinetically stable. Within air conditioning systems, emulsions would be continually pumped while undergoing heating and cooling cycles. It is therefore important that the viscosity is stable and low enough to ensure less pump energy consumption.

Theoretically, the Einstein equation can be used to describe the viscosity of emulsions [67]:

$$\delta = \delta_{PCM}(1 + 2.5\phi) \qquad (3)$$

Where, δ and δ_{PCM} are the viscosities of emulsion and dispersed phase.

For O/W type of PCME,

$$\phi_W = V_{PCM} / (V_{PCM} + V_W) \qquad (4)$$

Among which, V_P+V_w is a constant. With the water content reduces, viscosity of emulsion increases.

Huang et al. [24] measured viscosities of the different concentrated levels of RT10 emulsions. They realized that the fraction of the dispersed phase was one of the important parameters that affect the rheological behaviour of an emulsion. They noticed that the samples with55–75wt% paraffin were much more viscous than ones with 15-50wt% paraffin. A PCME is required to have a low viscosity for applications in air conditioning systems. Thus, the paraffin weight fraction over 50wt% was not recommended. PCMEs containing 30–50wt% paraffin would be favourable alternative to water in energy storage applications because it had an energy storage density two times higher than that of water but still kept a low viscosity.

In 2010, Huang [65] further studied the relationship between temperature and viscosity by testing three types of PCMEs, named as Cryosol 6,10 and 20. As shown in Fig. 17, the viscosities were different for the three types of PCMEs and thus demonstrated the impact of the dispersed material. The studied emulsions were shear-thinning fluids. The viscosities dropped firstly with shear rate increasing when the shear rate was lower than 30s^{-1} and then maintained the same after that. Temperature ramp tests were also carried out aiming at determining the viscosity during the phase transition. The samples were cooled from 30°C to 0°C at a rate of 2°C /min at a constant shear rate of 50s^{-1}. The result as shown in Fig. 18 indicated that temperature had a significant impact on the emulsions due to the phase transition of the paraffin. Sudden jumps in viscosities of emulsions were witnessed at corresponding peak freezing point. The most likely cause was that at the freezing point, PCM got frozen and solid PCM particles deformed little under shear stress and thus caused higher viscosities.

Figure 7

Figure 8

Zhao et al. [9] studied the rheological behaviour of 49.8wt% and 16.3wt% tetradecane emulsions with rotational viscometer. The tested emulsions showed basic characteristics of non-Newtonian fluid and formed the solid-liquid dispersion after solidification. High concentrated emulsions had higher viscosities. Fig. 19 shows the viscosity changes against temperature. Change in viscosity appears to be linear with temperatures from phase change point (6°C) to 50°C. The variation with temperature was smaller in high concentrated emulsion, which the author speculates was caused by the water content difference. The viscosity of 49.8wt% PCME was 5-10 times of the viscosity of 16.25wt% emulsion after solidifying. Before solidifying, viscosity of 16.25wt% PCME almost kept constant, while for the 49.8wt% one, the viscosity increased dramatically.

Figure 19

Dai et al. [19] set up a series of experiments to explore the factors affecting viscosity, e.g. water content, surfactant and dispersing speed. The experiment exhibited that the viscosity reduced with increasing water content, which agrees well with other researchers. The viscosities of emulsions increased remarkably from 0.55 to 2.94mm^2/s when the concentration of surfactant was increased from 2.6% to 4.7% and was consistent with the formation of a stronger surfactant monolayer. This is due to the fact that stronger surfactant monolayer requires more energy to move the PCM molecules [68]. The viscosity also doubled when the dispersing speed increased from 400 to 1300rpm.

2.5 Heat transfer

In comparison with conventional single phase heat transfer fluid containing no PCM, substantial heat transfer enhancements do occur in phase change emulsions. Investigation by Huang et al. [65] did reveal that the presence of micro-sized PCM particles in slurries can enlarge the surface-to-volume rate, and therefore increase their heat transfer rates as compared with bulk PCMs [65]. In addition, as PCMEs remain fluidity during phase change process, the convection heat transfer, instead of conduction heat transfer, is the domination process during solidification [39].

The following section focuses on review of heat transfer phenomenon including experimental and numerical studies on both laminar and turbulent flow.

2.5.1 Theoretical studies

In spite of numbers of experimental studies with phase change material suspension, theoretical models for heat transfer are limited. Chen and Chen [69] used a Dirac δ-function based model to investigate the heat transfer process over a plate at a constant temperature.

Charuyakorn [70] developed a comprehensive model for laminar heat transfer in a circular duct and between parallel plates. The model included the enhancement of thermal conductivity due to particle/fluid interactions. Heat gain due to phase change process was also involved in the energy equation as a source term. However, the experimental result of Geol [71] agreed little with their numerical prediction.

Zhang [72] modified the Charuyakorn's [70] model. This model was validated with the result of Geol [71]. This analysis pointed out the biggest reason causing the difference between Geol and Charuyakorn was the effect of sub-cooling. However, the authors did not provide any correlation or similar criteria for future design.

Alisetti et al. [73] introduced an "effective heat capacity model" for heat transfer in PCM slurries. In the effective heat capacity method, the phase change effects are directly incorporated into the energy equation by assuming the specific heat capacity of the phase change material to be a function of the temperature. The model overcomes the limitations of previous models [69, 70, 72] which are using complicated source terms or special analytical techniques. This model is easier to apply in standard computer fluid dynamic (CFD) packages without complicated terms or special analytical techniques [74]. Roy et al. [75] used effective heat capacity model to predict the forced heat transfer process for fully developed laminar flows. The model was verified by comparing its numerical predictions with previous theoretical results as well as well as experimental data. The numerical study showed that the effect of sub-cooling would be quite significant at very low heat fluxes or when the inlet temperature was much lower than the melting point.

Roy and Avanic [76] adopted the "effective heat capacity model" to simulate the turbulent heat transfer of PCME in a circular tube with constant wall heat flux. The Stefan number was found to be primary parameter influencing heat transfer. For low to moderate Stefan numbers, wall temperature reduced considerably over distance. The locations where phase change effects were dominated could be estimated from numerical results. Further experimental studies with DSC tests were suggested to characterize PCMs to accurately calibrate the numerical models.

2.5.2 Experimental studies

Roy and Avanic [77] presented an experimental study of laminar forced convection heat transfer in a circular duct with a phase change material emulsion (n-octadecane/water emulsion). The bulk Stefan number considered was up to 3.0 and the concentration of phase change material up to 30vol%. The experimental results were used to further verify previous theoretical models [70, 72] and to evaluate any differences in the heat transfer process between an emulsion type suspension and microencapsulated phase change material suspension as in Geol [71]. The result suggested the heat transfer characteristics for PCMEs were similar to those of microencapsulated phase change slurries. It meant the capsules of MPCM had little effect on heat transfer. The results also showed that the overall heat transfer characteristics did not change drastically for different concentrations. From an applications point of view, the results confirmed that the sub-cooling of the fluid and its melting temperature range were important issues and must be considered in future experiments.

Zhao [9] carried out an investigation on non-Newtonian heat transfer performance for a new O/W type emulsion in a circular tube. From Fig. 20, two different concentrations of PCMEs (13 and 40wt%) had the similar heat transfer characteristics. At the same flow velocity, Reynolds number for 40wt% was lower than that for 13wt% emulsion, but the Nussult numbers for two emulsions were at the same level. After phase change, the emulsions became solid-liquid two phase flows. Nusselt numbers for both emulsions were slightly increased compared to the results when PCMs were in pure liquid phase. It could be concluded that convective heat transfer performances were enhanced by phase change, but they were not affected by PCM concentration.

Figure 9

Zhao et al. [10] further tested the laminar flow heat transfer in coiled tubes and gave the dimensionless equation for convection heat transfer. Fig. 21 demonstrates the heat transfer characteristic for different concentrated emulsions. The line in the diagram represents the heat transfer characteristic of water. The result showed that the Nusselt numbers of different concentrated emulsions were higher than that of water and increased with the increasing concentration. For same concentration, the Nusselt number was higher when solid phase presented. It was probably due to the conductivity of solid PCM was higher compared to liquid phase and the presence and perturbation action of solid PCM promoted the heat transfer inside the tube.

Figure 10

Choi et al. [78] investigated the heat transfer process of a hexadecane emulsion in a turbulent flow through a circular tube. They found a significant reduction of pressure drop at the melting point of the PCM as well as significant variations in both the local convective heat transfer coefficient and the effective thermal capacity of the PCME along the test section. This made it difficult to apply the log-mean-temperature-difference (LMTD) method for the analysis of heat transfer in the PCM slurry. The investigators therefore proposed a three-region melting model. Using this three-region melting model, the bulk mean temperature profile was determined along the heating test section as shown in Fig. 22. In Region I, the average emulsion temperature was below melting temperature, the bulk mean temperature increased linearly along flow direction. In the second region (Region II), phase change happened and the bulk mean temperature was constant at the melting temperature. In the final third region (Region III), PCM was completely melted and the mean temperature increased linearly again. Local convective heat transfer coefficient was found increasing in Region I, and reducing in Region II, and increasing again in Region III. Based on the model, the authors provided an explanation of the mechanism of the convective heat transfer enhancement due to the PCM particles. Along the flow direction, the emulsion temperature increased. As a result, the viscosity dropped and Reynolds number increased, leading to a slight increment in the heat transfer coefficient. They also pointed out that the layer of melted PCM close to wall became thicker when the heat flux was very high. This phenomenon prevented the radial movement of solid PCM from the centre to the wall and resulted in a lower convection coefficient.

Figure 22

Choi and Cho [79] studied the influence of the aspect ratio (AR, height/width ratio) of a rectangular channel on the cooling characteristics of $C_{22}H_{46}$ emulsion flow with a linear array of discrete square heat sources with high heat flux. Other factors such as concentration, heat flux and Reynolds number were also investigated. The result is shown in Fig. 23. At a high heat flux of 40W/cm^2, the influence of the aspect ratio of the rectangular channel on the local heat transfer coefficients, for both water and the 5wt% paraffin slurry, was greater than those at a low heat flux. Local heat transfer coefficient for 5wt% PCME was larger than that for water. The thermal enhancement was the result of both the particle migration and subsequent collision against the wall in turbulent flows and the latent heat of the PCM. The local heat transfer coefficients for a rectangular channel with an aspect ratio of 0.10 were larger than those for the rectangular channels with aspect ratios of 0.20 and 0.50. The reason was that the average flow velocity for a rectangular channel with an aspect ratio of 0.10 was the largest among three channels at the same Reynolds number because of the smallest hydraulic diameter. The differences of the local heat transfer coefficients between the PCME and water increased as the aspect ratio reduced.

Figure 11

Inaba et al. [7, 80] dealt with the natural convection heat transfer characteristics of PCME in rectangular enclosures. The PCM mass concentration of the emulsion varied from 30wt% to 5wt%, and the experiments have been done three times T_1<313K when PCM was in solid phase, 313K<T_2<323K when PCM was in the phase changing region and T_3>323Kwhen PCM was in liquid phase. The result showed that the PCM mass concentration had little impact on the Nusselt number when PCM was in solid phase. Fig. 24 shows the Nusselt number against Rayleigh number at various mass concentration and enclosures [7]. In the phase transition range, the Nusselt number increased with increasing PCM concentration at low Rayleigh numbers, but at high Rayleigh numbers ($>10^5$) the Nusselt number decreased with PCM concentration increasing. The effect of aspect ratio on heat transfer was greater for the PCM in the solid region than the effect for PCM in liquid region because the viscosity of the PCM slurry reduced when PCM particles were melted. There was little difference in natural heat transfer characteristics of the PCME at concentration slower than10wt%. Fig. 25 shows the convection heat transfer coefficient versus temperature difference between the heating and cooling plates T_H-T_C (T_C=313K) for different PCM concentrations in the enclosure of AR =21: 8. As indicated in Fig. 25, the overall heat transfer coefficient declined with the increasing PCM concentration, because the viscosity of PCME increased along with PCM concentration increasing. The heat transfer coefficient peaked at T_H-T_C=6K (or T_H=319K) which corresponded to the temperature with the highest apparent specific heat of PCM. It was mainly due to the involvement of the phase transition process of PCM. The heat transfer coefficient then dropped dramatically from temperature difference from 6K to 10K, since the latent heat transferred reduced with heating plate temperature T_H increasing over 320K.

Figure 12

Figure 13

2.6 Applications in HVAC system

Currently, most PCMEs are in the development stages and therefore there are no adequate publications regarding their application at either commercial or industrial level available. It is however widely agreed that PCMEs have great potential as cold storage material and heat transfer fluid for heating and cooling systems.

Huang et al. [65] outlined some potential applications based on different phase transition temperatures and operating systems. One concept was based on conventional cold distribution network for an air conditioning system which was to operate within a temperature range of 6–12°C. High volumetric cold water piping system was to be used to retrieve the cold energy from a PCME of melting temperature between 0 and 6°C. The alternative approach was to directly apply PCME such as pentadecane/water emulsion at a melting temperature of between 7 and 10°C, in the cooling pipe systems. This would enable the volumetric flow rate to be reduced and ultimately achieve lower energy consumption for the circulating pumps. However, applying viscous PCME in pipelines is likely to cause higher pressure drop than water, which should be considered in practical applications.

The idea of utilising PCME instead of water for cooling of ceilings and walls in capillary tubing system was also considered for increasing thermal mass of building components [65]. However, the PCME should have a relatively low viscosity to prevent blockage of the tube. Pollerberg and Dötsch [81] investigated the possibility of using PCME as a heat transfer medium. The study compared three scenarios for a cooling supply network (based on tetradecane emulsion, ice slurry and water) by considering the cost of cold generation and distribution. They found the ice slurry to have the lowest distribution cost but cost of PCME was still lower than that of cold water. As the evaporation temperature had to be low in order to solidify tetradecane, the COP of the chillers deteriorated and consequently increased the generating cost. In general, the PCME was able to compensate the additional generating cost through reduction in distribution cost, and made it the overall cheapest option under the three scenarios.

Besides the economic aspects, there were technical aspects which were considered by Pollerberg and Dötsch [81]. First of all, the material used in the distribution network was based on the type of paraffin. For instance, paraffin is a solvent for rubber, so the seals of EPDM need to be replaced with fluororubber. The second important point is the water endangering potential of paraffin and additives was taken into consideration since they are considered as threats to the safety of portal water. Furthermore, the recycling was suggested, as PCMEs are not considered as hazardous substances.

In a study carried out for California Energy Commission [82], PCME was applied to a domestic air conditioning system as shown in Fig. 26. In this study, PCME was used as a cold storage material for peak shifting. The PCM had a phase change range from 10 to 15°C. The system consisted of a blower, heating coil, two heat exchangers for PCM emulsion, an air conditioning unit, a PCME slurry storage tank, pumps and mixer. One of the heat exchangers was used for heating the emulsion (upstream of the AC unit) and the other was for cooling the emulsion (downstream of the AC unit). During off-peak time, the slurry would be pumped through the heat exchanger, and the cool air from air the conditioner unit would remove heat from the emulsion. At peak time, solidified PCME would be passed through the heat exchanger to cool warm air prior to it entering the air cooling coil. Generally speaking, the bench-scale test was successful and the slurry did not clog the pipes. Test results showed that 40% of peak load can be absorbed by PCME system. In addition, the system was able to operate at an efficiency level 10-12 times greater than existing air conditioning systems during the hottest period of the day.

Figure 26

PCME with melting point over 70°C can be a good candidate as a new category of heat storage material and latent heat transfer fluid in the area of waste heat recovery, boiler and heating system. Ishikawajima Harima Heavy Industries Co, Ltd. [83, 84] proposed to use PCME to recover waste heat from a heat and steam generator of a lithium bromide (LiBr) absorption air conditioning system. The selected phase change temperature range wasbetween84-91°C which according to their report helped to reduce the spatial and temporal mismatches between waste heat emission and cooling demand. In comparison with water based system, the proposed system could save up to 82% of the energy used for pumping the fluid.

Zou [84] described an electrical boiler which uses a PCME as shown in Fig. 27. It consists of a heat exchanger and a storage tank. Hot water from the boiler heats up the PCME inside the storage tank which in turn heats up secondary working fluid, normally water, to provide heating for users.

Figure 147

Zou [84] investigated the use of PCME for space heating. The heat transfer fluid for space heating works at 70-95°C. 30wt% tetratetracontane emulsion whose melting point is 85-87°C was therefore selected as heat transfer fluid in this study. The latent heat of fusion of the PCME was taken as 60kJ/kg and the equivalent specific heat around 6.6kJ/kgK, which was 1.5 times of that of water. The results showed that to be able to deliver the same amount of heat, the volume flow rate of PMCE would be equivalent to 0.67 times of that of hot water, which could save 45% of the energy consumed by the pump. Detailed comparisons are listed in Tab. 3.

Table 3

3. Conclusion

This review was focused on the characteristics, challenges and advancement in the development and application of PCM emulsions in HVAC systems. The review has outlined the composition, preparation methods and analysis of properties of various PCM emulsions (PCMEs), which are crucial to the development of PCMEs as heat transfer fluids.

It was noticeable from the review that the heat transfer performances of PCMEs were higher than pure water due to their better thermophysical properties. However, the mechanisms of heat transfer enhancements and the degree of each factor were not well established due to lack of adequate experimental studies. Several numerical models have also been developed but not fully validated. In HVAC systems, most cooling coil/ heating coils are fin-and-tube heat exchangers in which flow behaviour of PCMEs are expected to behave differently from straight pipes. Factors such as frost formation and overall heat transfer of PCMEs on the performance of heat exchangers are also unclear.

Peak load shifting, energy cost saving and pump power reduction have also been reported from limited sources of short term experimental studies. Long term experimental studies are therefore needed to evaluate their overall performances.

Regarding the applications of PCMEs, there are few practical examples at industrial level but yet to become commercially viable. In principle, applications of PCMEs in HVAC systems for either as cooling medium or cold storage material seem feasible. There are, however, some vital problems which need to be overcome before a competitive edge over water can be achieved. These scientific barriers are summarised as follows:

1) The issue of higher viscosities in PCMEs needs to be improved in order to minimise higher pumping power.
2) Thermal stability of PCMEs needs to be enhanced in order to prolong period of usage.
3) Level of sub-cooling needs to be reduced in order to enhance system performance.
4) Sub-cooling, stability and viscosity are related to each other and how to reach a balance among these three factors

require more investigations.

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Research Highlights:

- Composition, preparation methods and analysis of properties of various PCM emulsions (PCMEs) have been outlined in this report
- Heat transfer performances of PCMEs were higher than pure water due to the latent heat associated with the phase change process and combination of other influential factors
- There are few practical examples at industrial level using PCME as cold storage materials or heat transfer medium.
- Some vital problems which need to be overcome, such as viscosity, sub-cooling and instability have been identified and explored in detail.

Table Caption

Table 1: Effect of surfactant/oil ratio on emulsion droplet size distribution by Li [32]
Table 2: Effect of dispersing speed on emulsion stability by [35]
Table 3: Parameter comparisons by [84]

Table 1: Effect of surfactant/oil ratio on emulsion droplet size distribution by Li [32]

Surfactant blends and emulsify temperature	Droplet size under different surfactant blends/ liquid paraffin ratio (μm)					
	1:2	1:3	1:4	1:5	1:6	1:7
System I @60°C	0.29		0.34	0.67	0.81	0.97
System II @60°C		0.34	0.53	0.78	0.92	1.21
System II @45°C			0.41	0.45	0.81	2.69
System III @60°C			0.33	0.71	0.92	1.15

System I: Tween80 (58.8%) +Span80 (41.2%)
System II: Tween80(58.8%)+Span80(41.2%):liquid paraffin=3.8:1
System III: Tween80(26%)+Span80(34%):liquid paraffin=3:2

Table 2: Effect of dispersing speed on emulsion stability by [35]

Dispersing speed (rpm)	Stability in storage	Fluidity
200	Worse	Diluted fluid
500	Worse	Semi-fluid
800	Good	Semi-fluid
1000	Good	Viscous emulsion
1500	Good	Pasty emulsion

Table 3: Parameter comparisons by [84]

	Hot water	Phase change emulsion
Equivalent specific heat (kg/kgK)	4.2	6.6
Volumetric flow rate (%)	100	67
Flow velocity (m/s)	3	2
Viscosity (mPas)	0.4	4.1
Friction loss per unit length (%)	100	83
Pump power consumption (%)	100	55

List of Figure Captions

Figure Captions:

Figure 1: Structure of oil-in-water, water-in-oil and water-in-oil-in-water emulsions [18]

Figure 2: Relationships between heat of fusion and droplet distribution with different concentration of emulsion [24]

Figure 3: Illustration of PCME and surfactant [24]

Figure 4: Surfactant classification based on [29, 30]

Figure 5: Scheme of principle of emulsification with a rotor-stator device [17]

Figure 6: Different dispersing speed vs. droplet size distribution (1#,2# and 3# represents dispersing speeds of 800, 1000 and 1500rpm) [35]

Figure 7: Phase inversion (a) surfactant morphology, (b) type of assembly, (c) emulsion type [25]

Figure 8: Schematic illustration of phase inversion for preparation of O/W emulsions [42]

Figure 9: Schematic diagram of the formation of emulsions by the PIT method [44]

Figure 1: Schematic diagram of the formation of emulsions by the EIP method [44]

Figure 2: The test rig for studying the heat capacity of the emulsion [23]

Figure 3: The thermal conductivity at room temperature vs. CNFs content ratio [53]

Figure 4: Maximum of ΔG defines the critical radius beyond which radius growth is possible [59]

Figure5: Instability in PCME [46, 64]

Figure 6: Stability test facility of emulsion under shear designed by Vilasau [66]

Figure 7: Determination of the critical coagulation concentration of $CaCl_2$ (CCC_{CaCl2}) as a function of the ionic surfactant weight fraction [66]

Figure 8: Viscosity of Cryosol 6, 10 and 20 versus shear rate at 25°C [65]

Figure 9: Viscosity of Cryosol 6, 10 and 20 versus temperature at $50s^{-1}$ [65]

Figure 19: Viscosity against temperature phase change emulsions [9]

Figure 10: Convective heat transfer characteristic of Phase Change Emulsion [9]

Figure 11: Heat transfer characteristic of PCME in coiled tubes [10]

Figure 12: Measured local heat transfer coefficient and bulk mean temperature [78]

Figure13: Local heat transfer coefficients with respect to row number @ Re=15000 [79]

Figure 14: Nusselt number against Rayleigh number at various mass concentration and enclosures [7]

Figure 15: Heat transfer coefficient vs. temperature difference between two horizontal boundaries for PCME with various mass concentrations for AR=21.8 and PCM in phase changing region [7]

Figure 16: Schematic of air conditioning systems [82]

Figure 17: PCME integrated with electrical boiler [84]

Figure 1

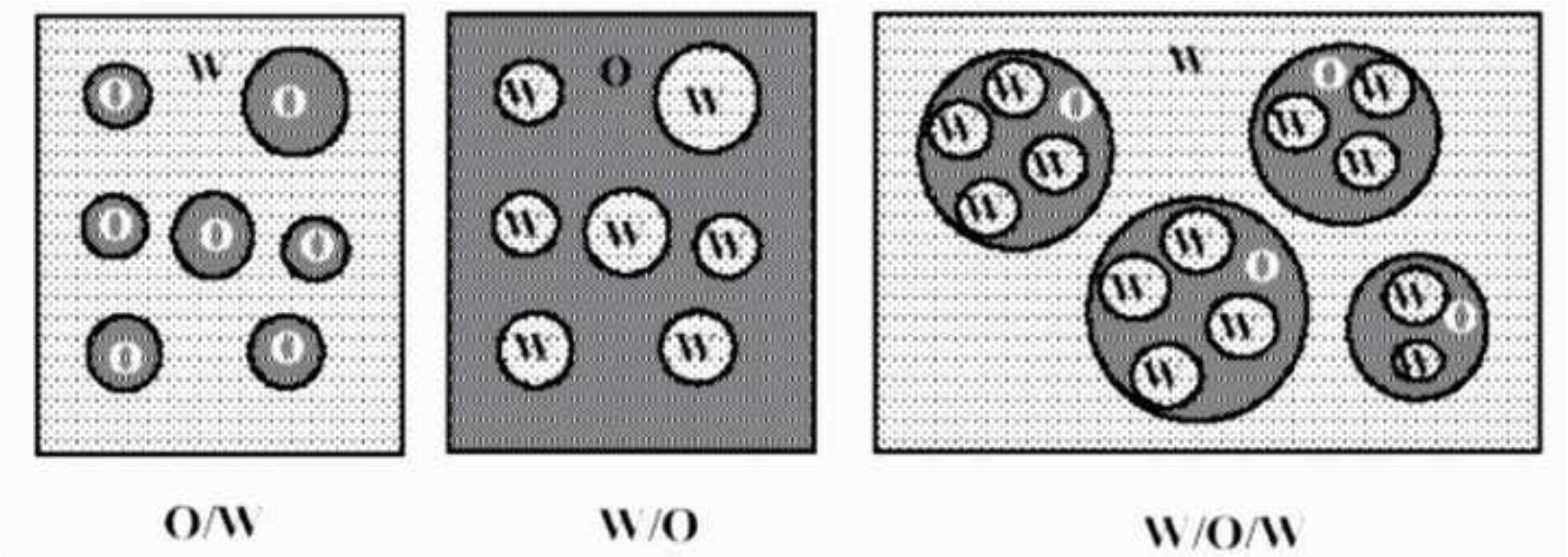

Figure 2

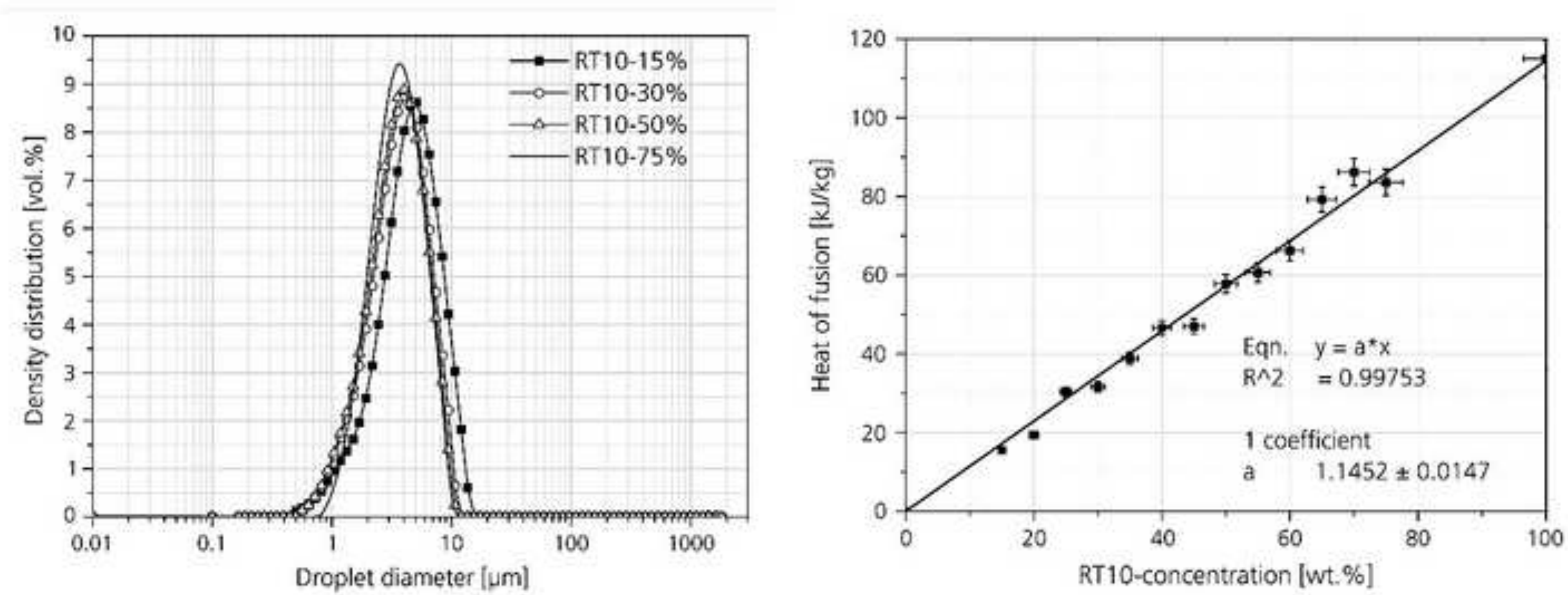
Density distribution [vol.%]
10
9
8
7
6
5
4
3
2
1
0
0.01
0.1
1
10
100
1000
Droplet diameter [μm]
RT10-15%
RT10-30%
RT10-50%
RT10-75%
Heat of fusion [kJ/kg]
120
100
80
60
40
20
0
0
20
40
60
80
100
RT10-concentration [wt.%]
Eqn. y = a*x
R^2 = 0.99753
1 coefficient
a 1.1452 ± 0.0147

Figure 3

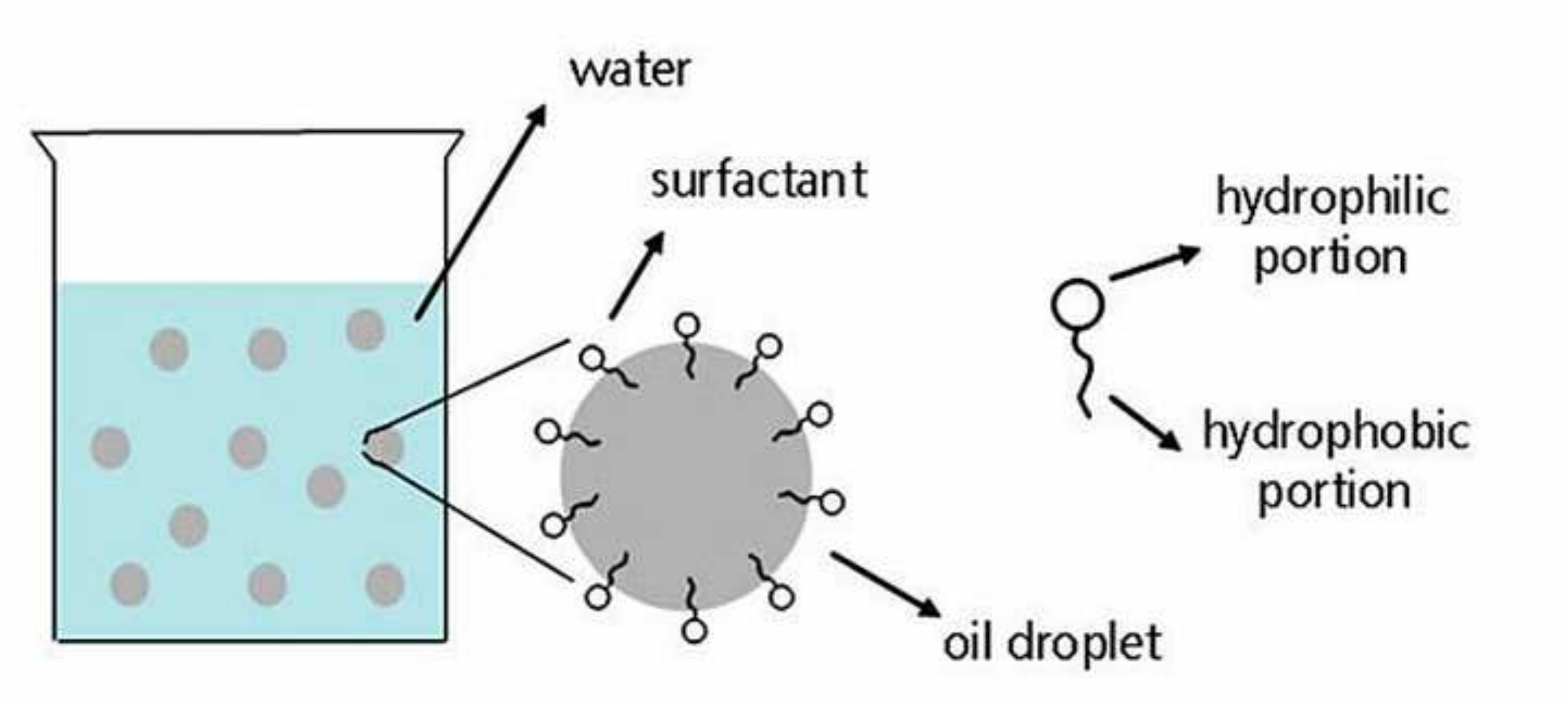
water
surfactant
hydrophilic portion
hydrophobic portion
oil droplet

Figure 4

Click here to download high resolution image

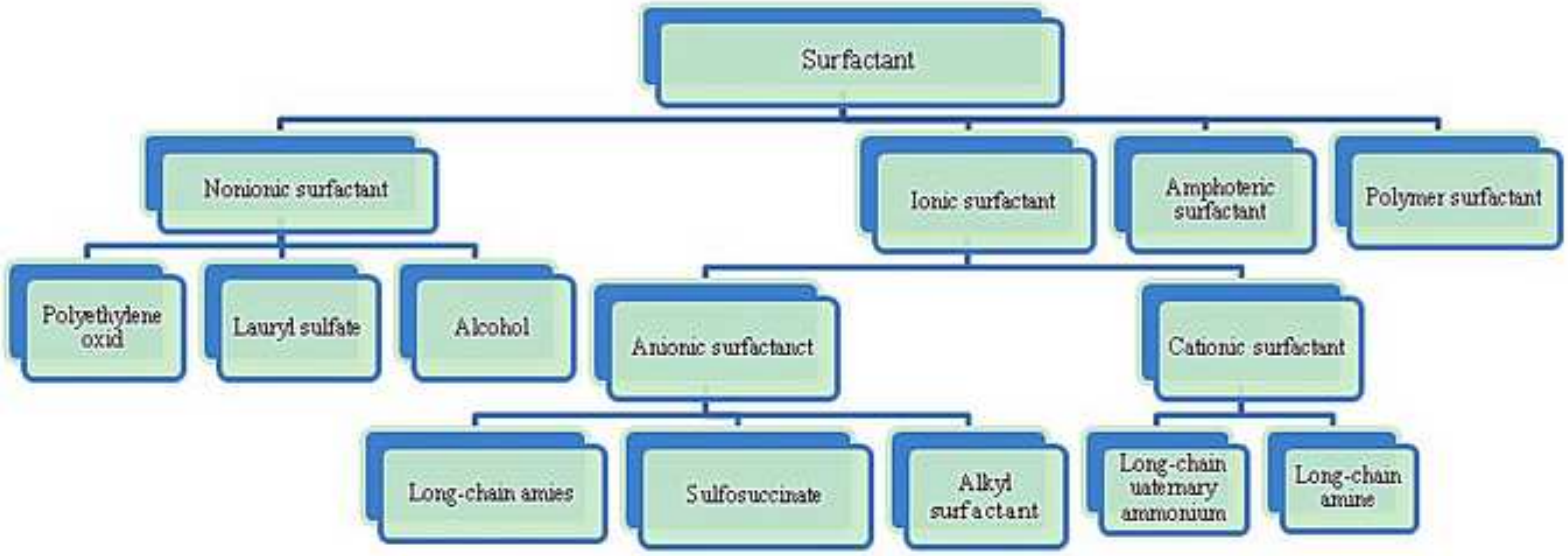

Figure 5

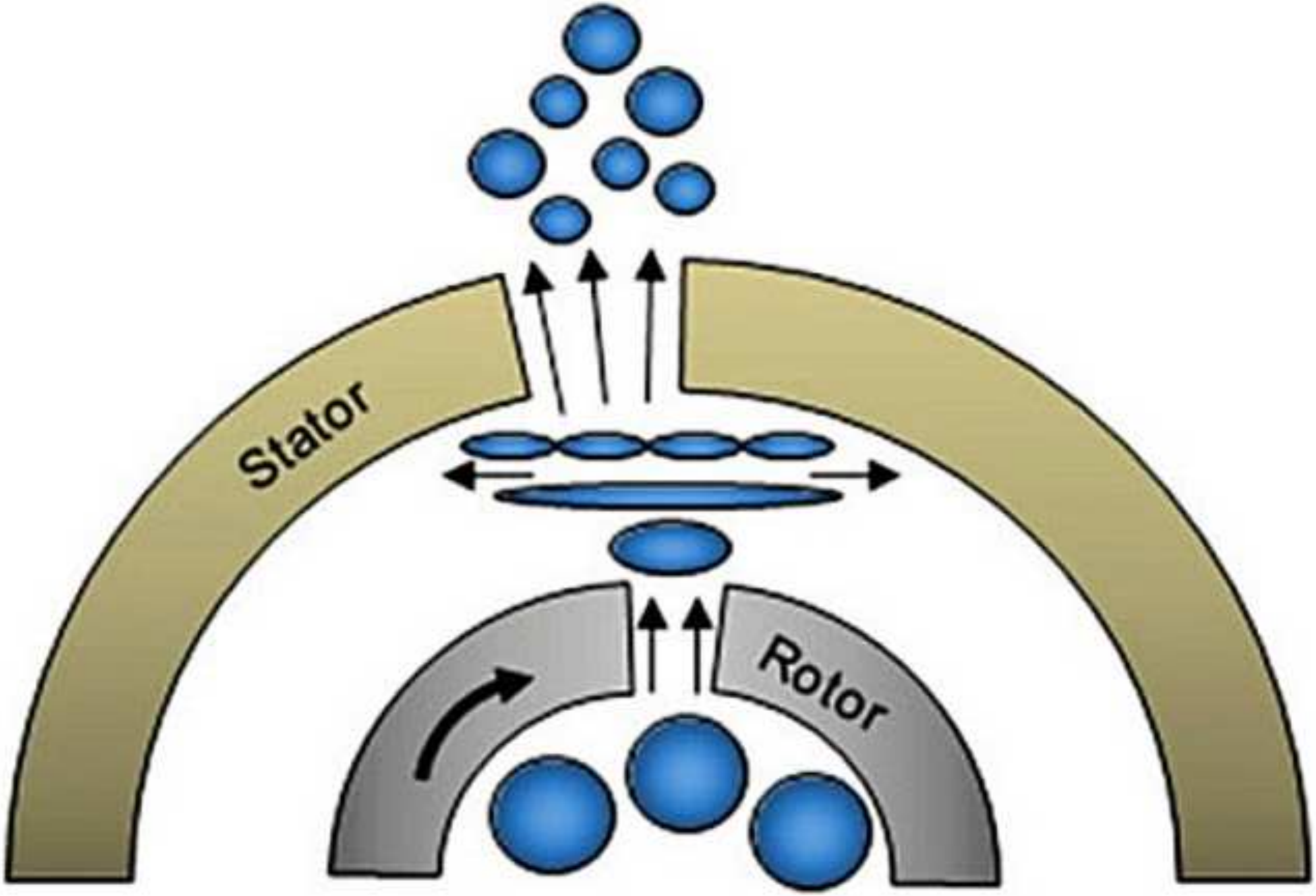

Figure 6

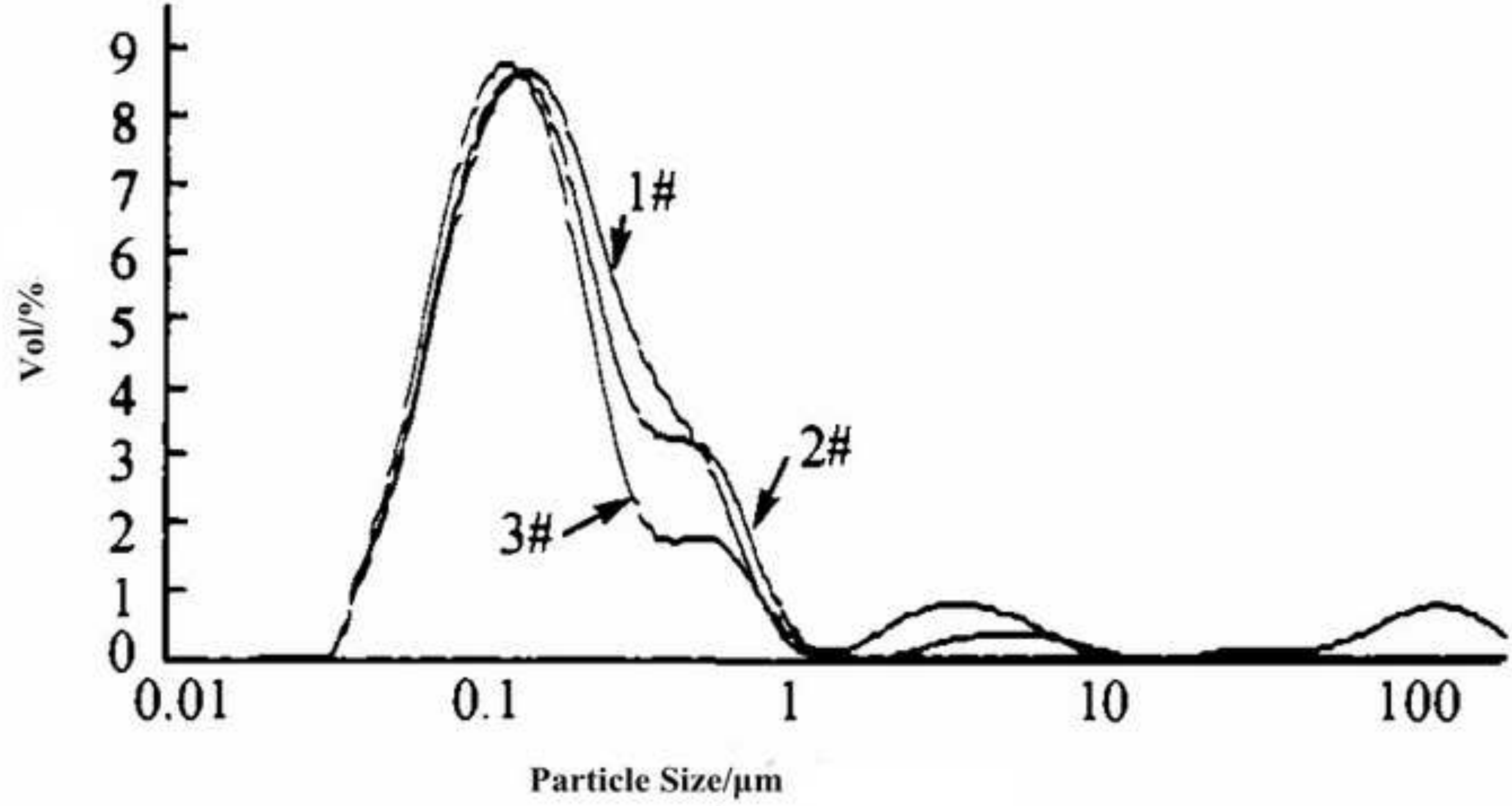

Figure 7

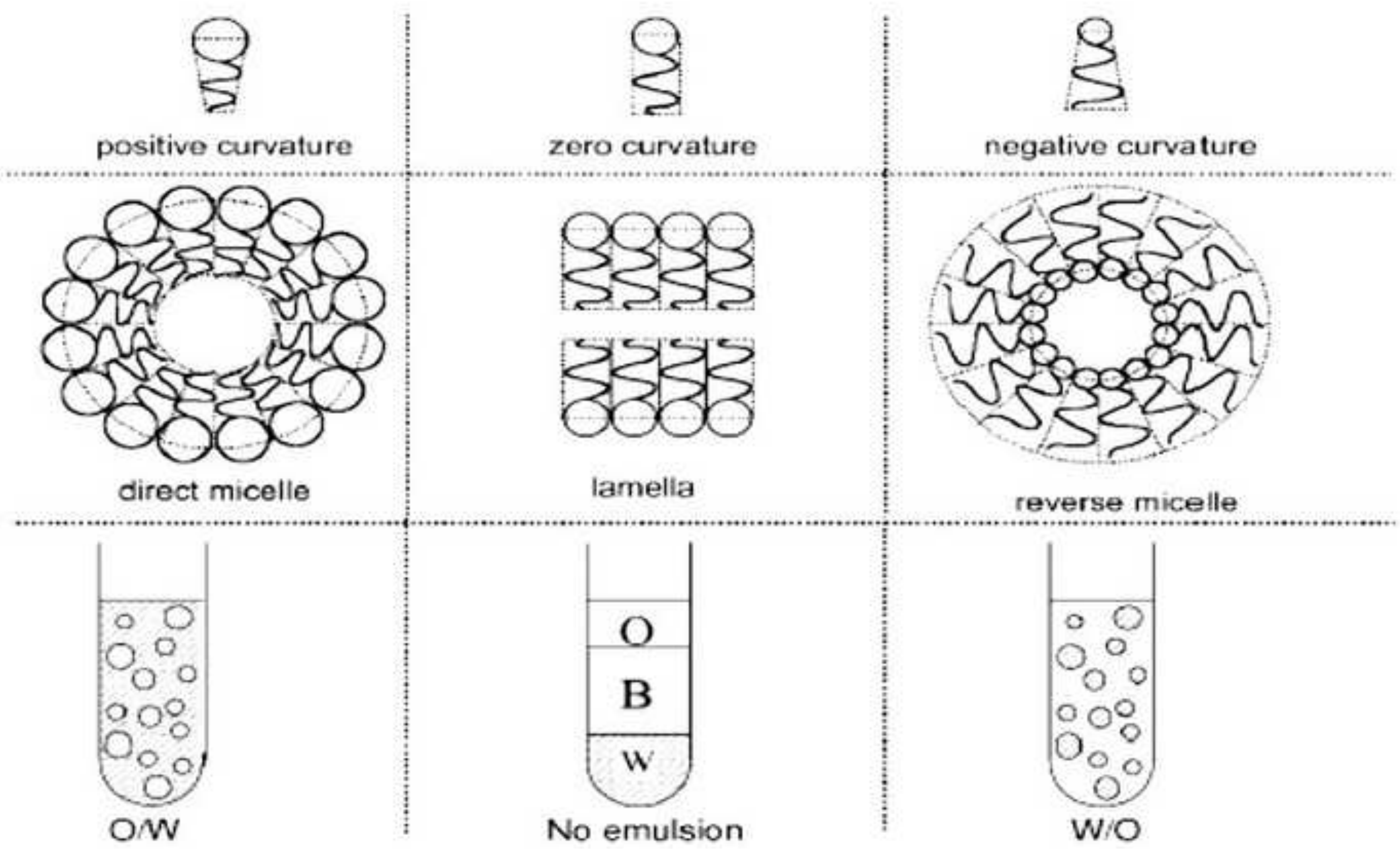
positive curvature
zero curvature
negative curvature
direct micelle
lamella
reverse micelle
O
B
W
O/W
No emulsion
W/O

Figure 8

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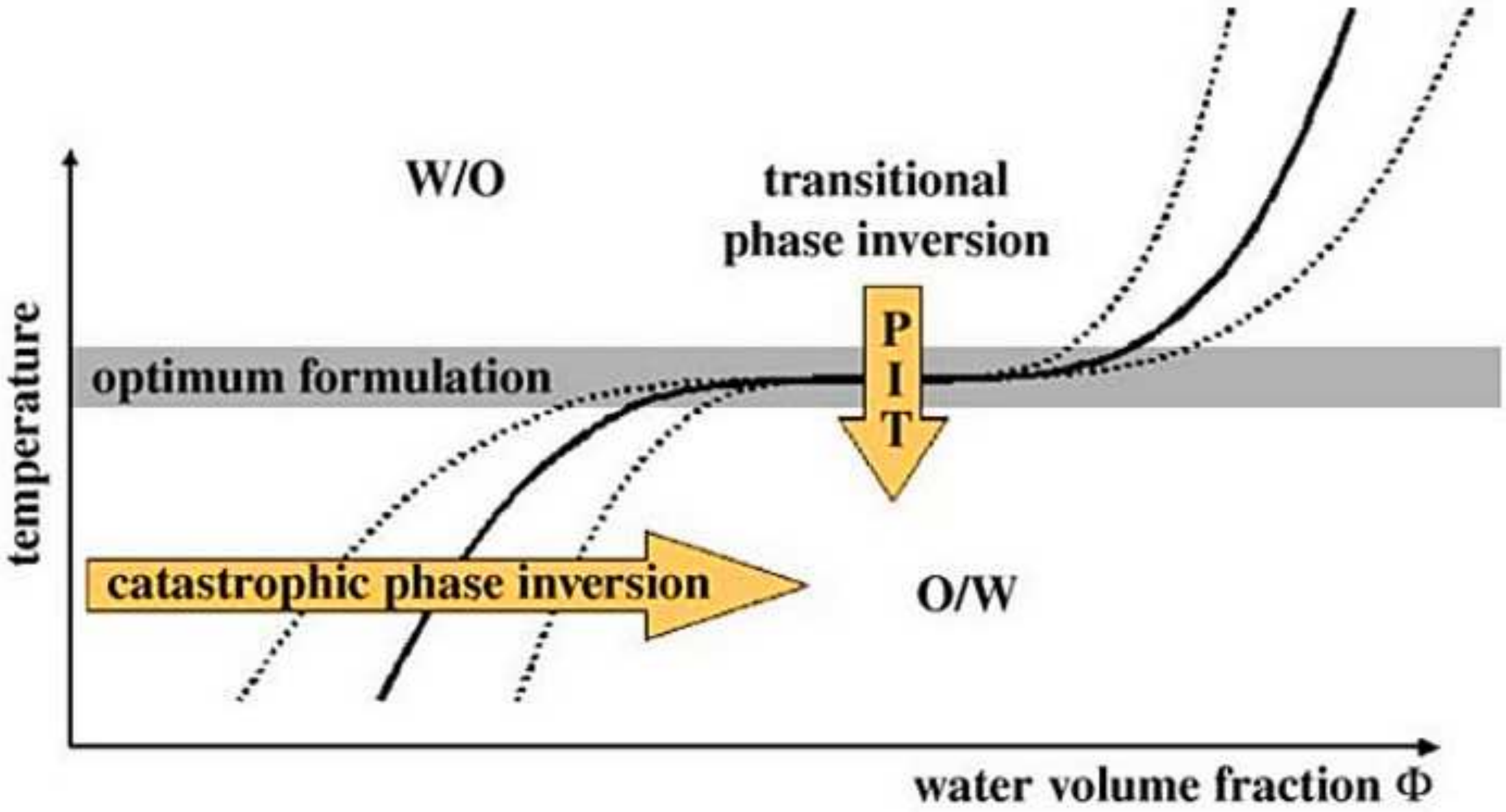

Figure 9

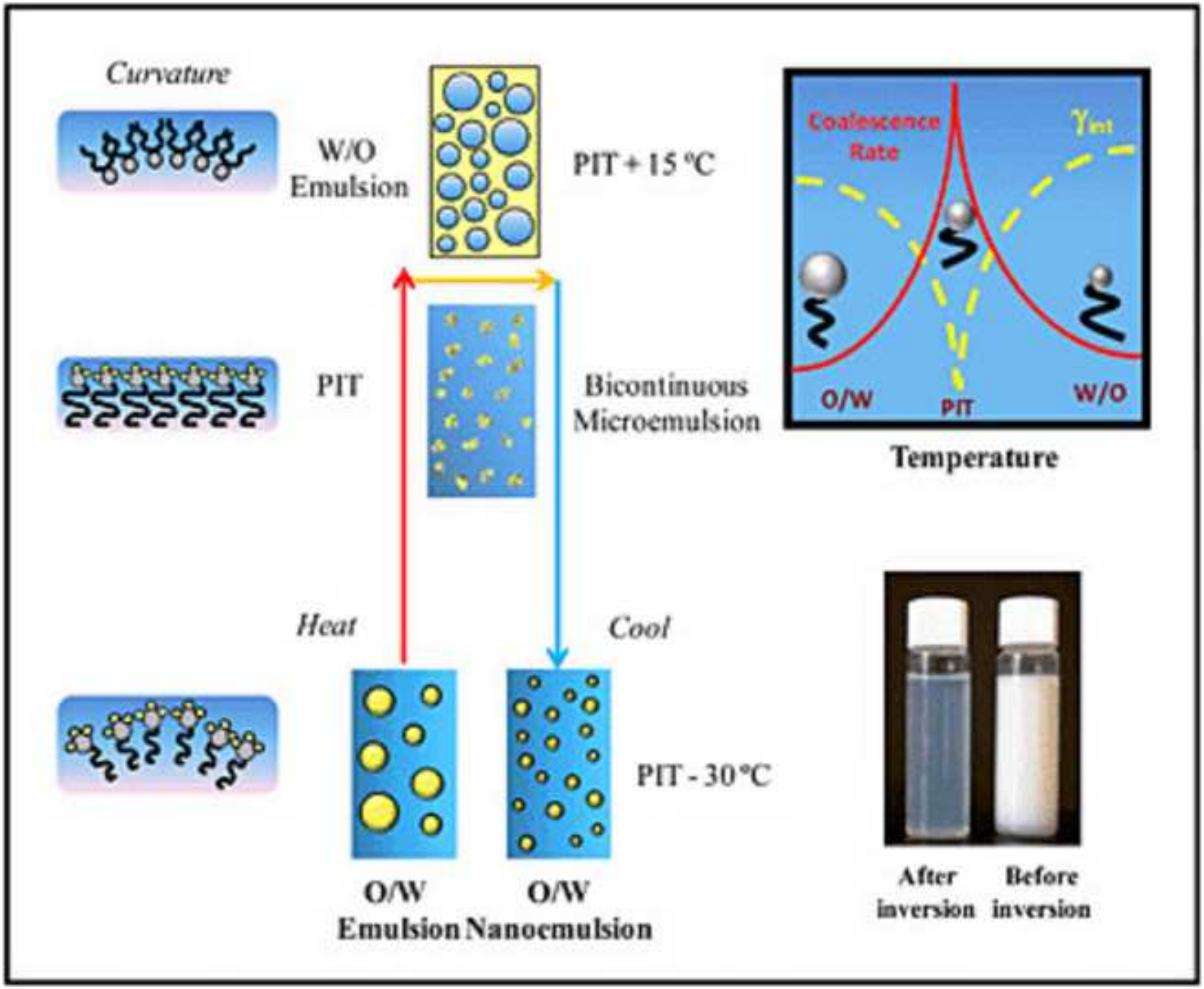
Curvature
W/O
Emulsion
PIT + 15 °C
Coalescence
Rate
γint
O/W
PIT
W/O
Temperature
PIT
Bicontinuous
Microemulsion
Heat
Cool
PIT - 30 °C
O/W
Emulsion
O/W
Nanoemulsion
After
inversion
Before
inversion

Figure 10

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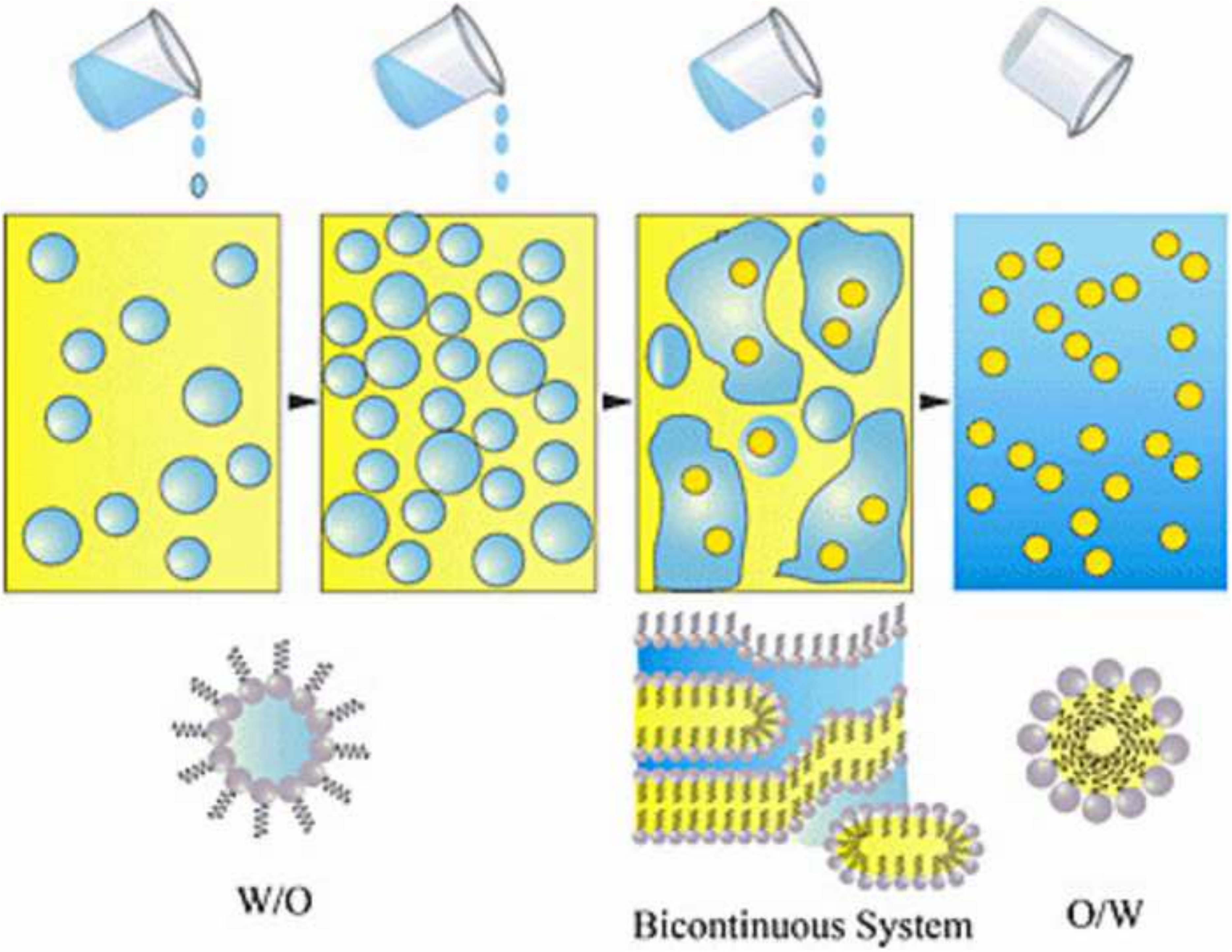

Figure 11

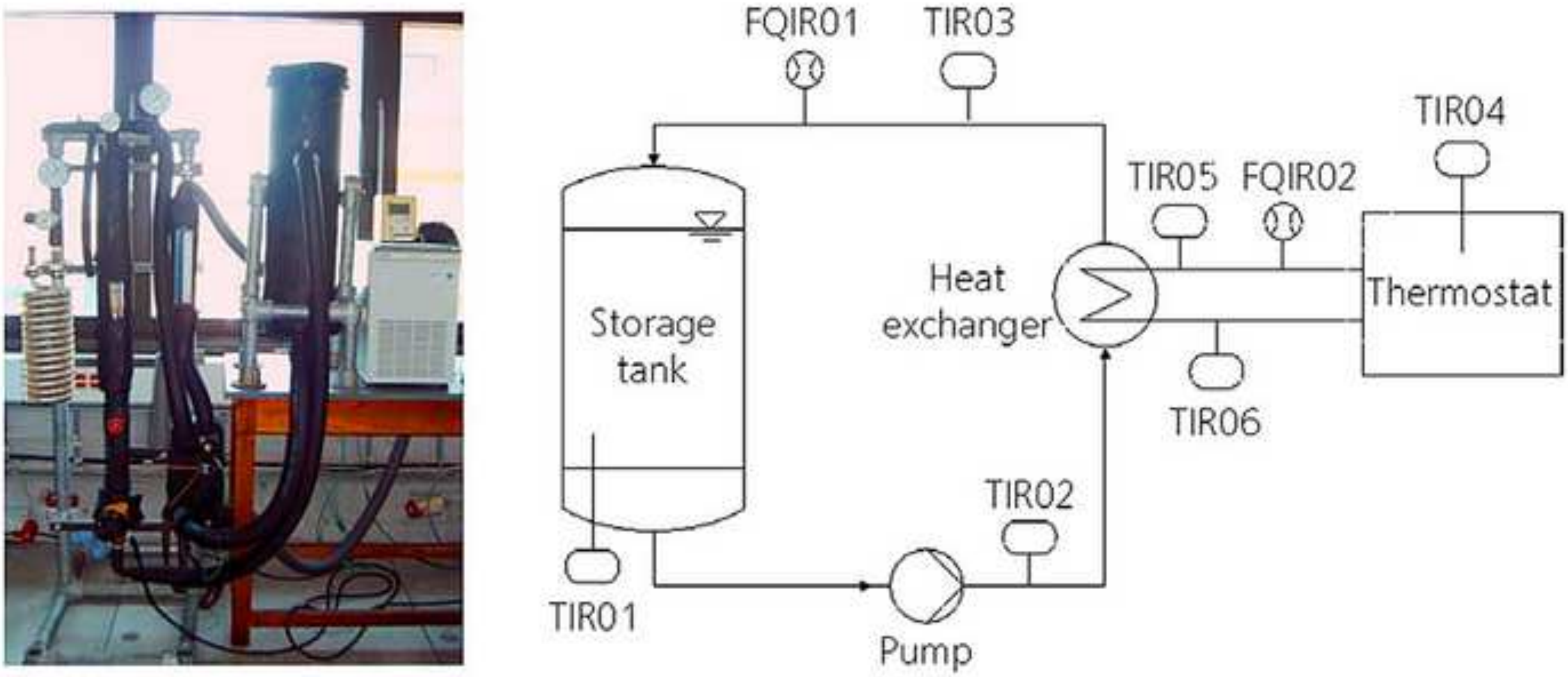
FQIR01
TIR03
TIR04
TIR05
FQIR02
Storage tank
Heat exchanger
Thermostat
TIR06
TIR02
TIR01
Pump

Figure 12

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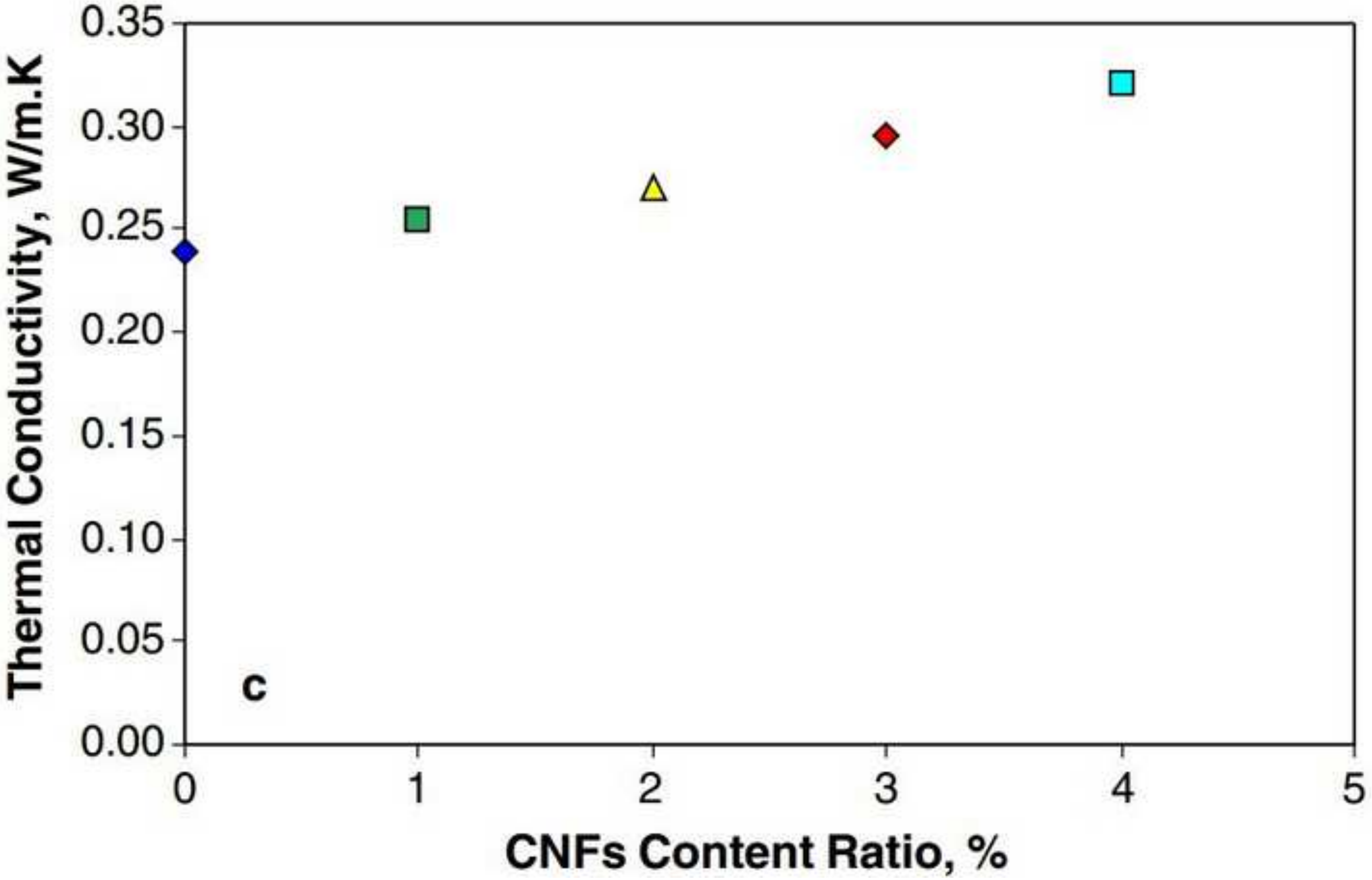

Figure 13

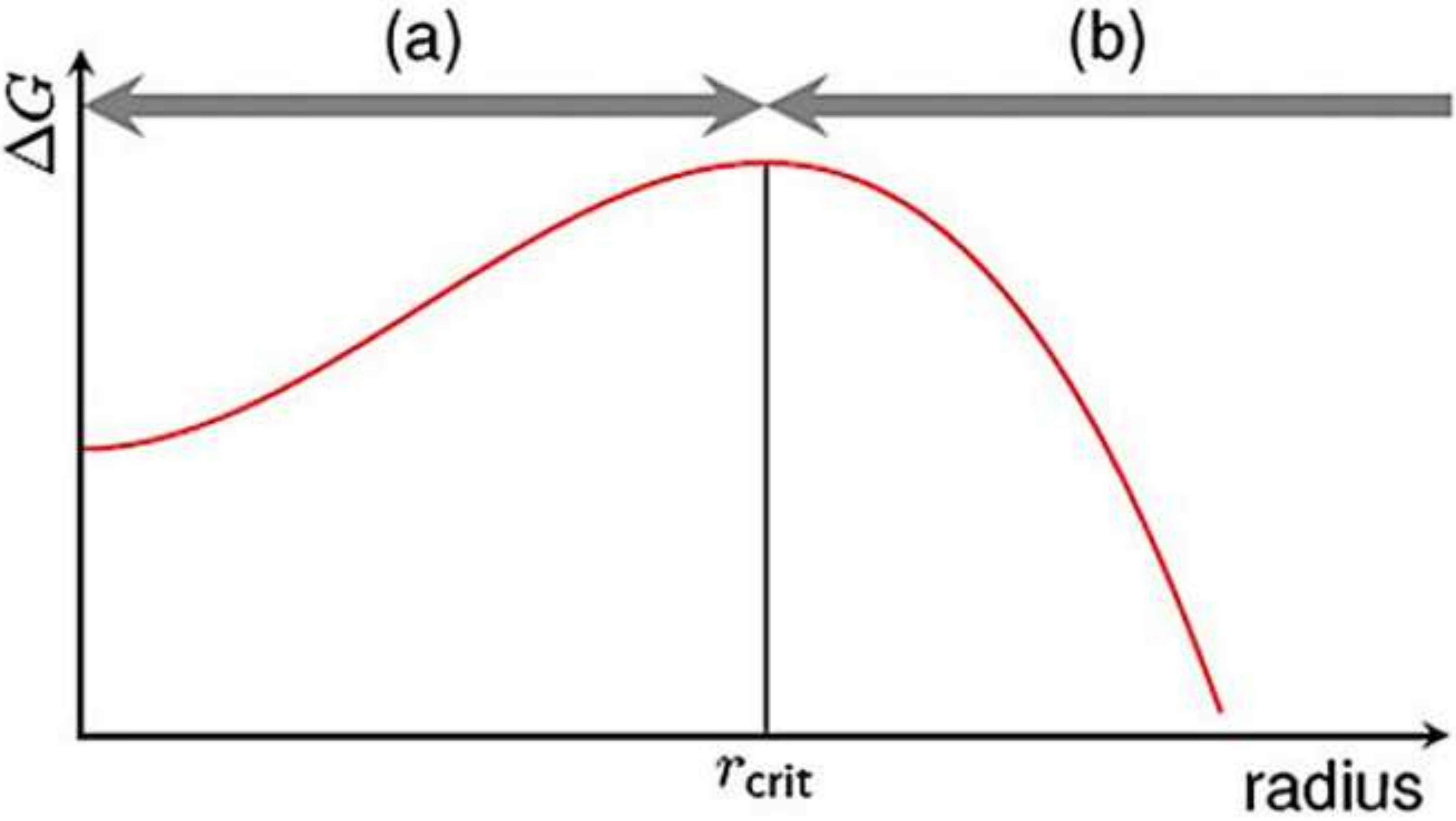

Figure 14

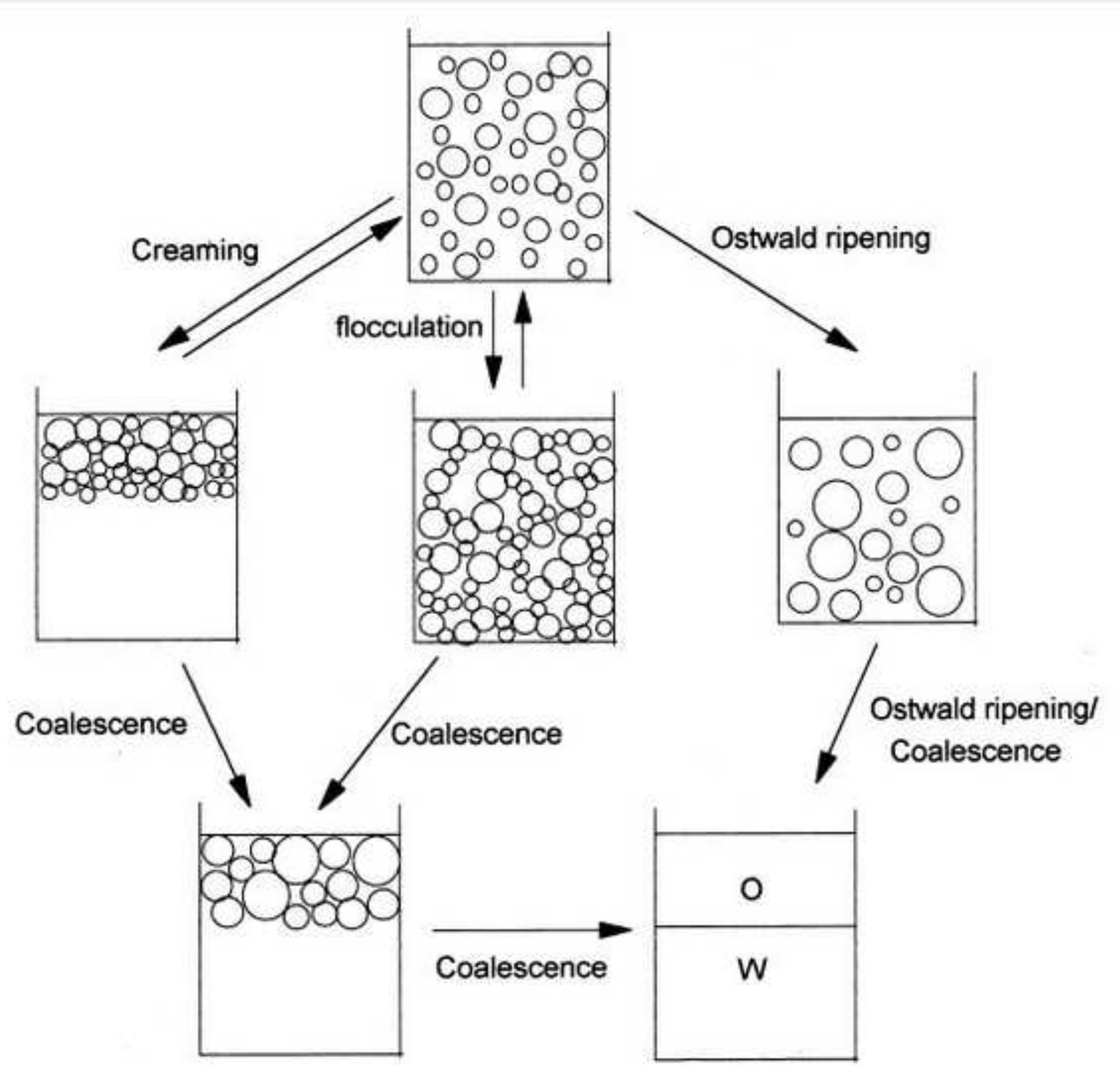
Creaming
flocculation
Ostwald ripening
Coalescence
Coalescence
Ostwald ripening/
Coalescence
Coalescence
O
W

Figure 15

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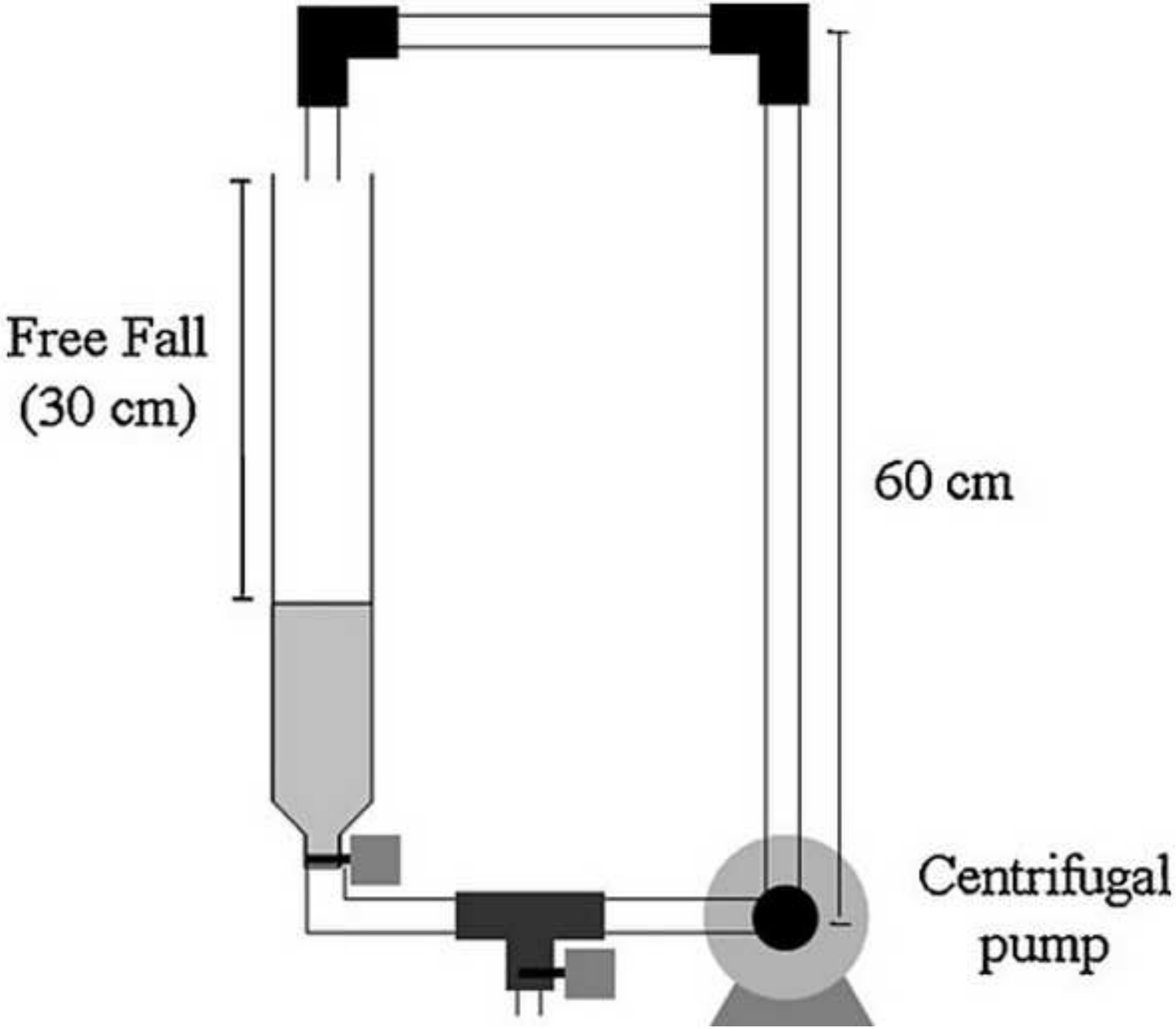

Figure 16

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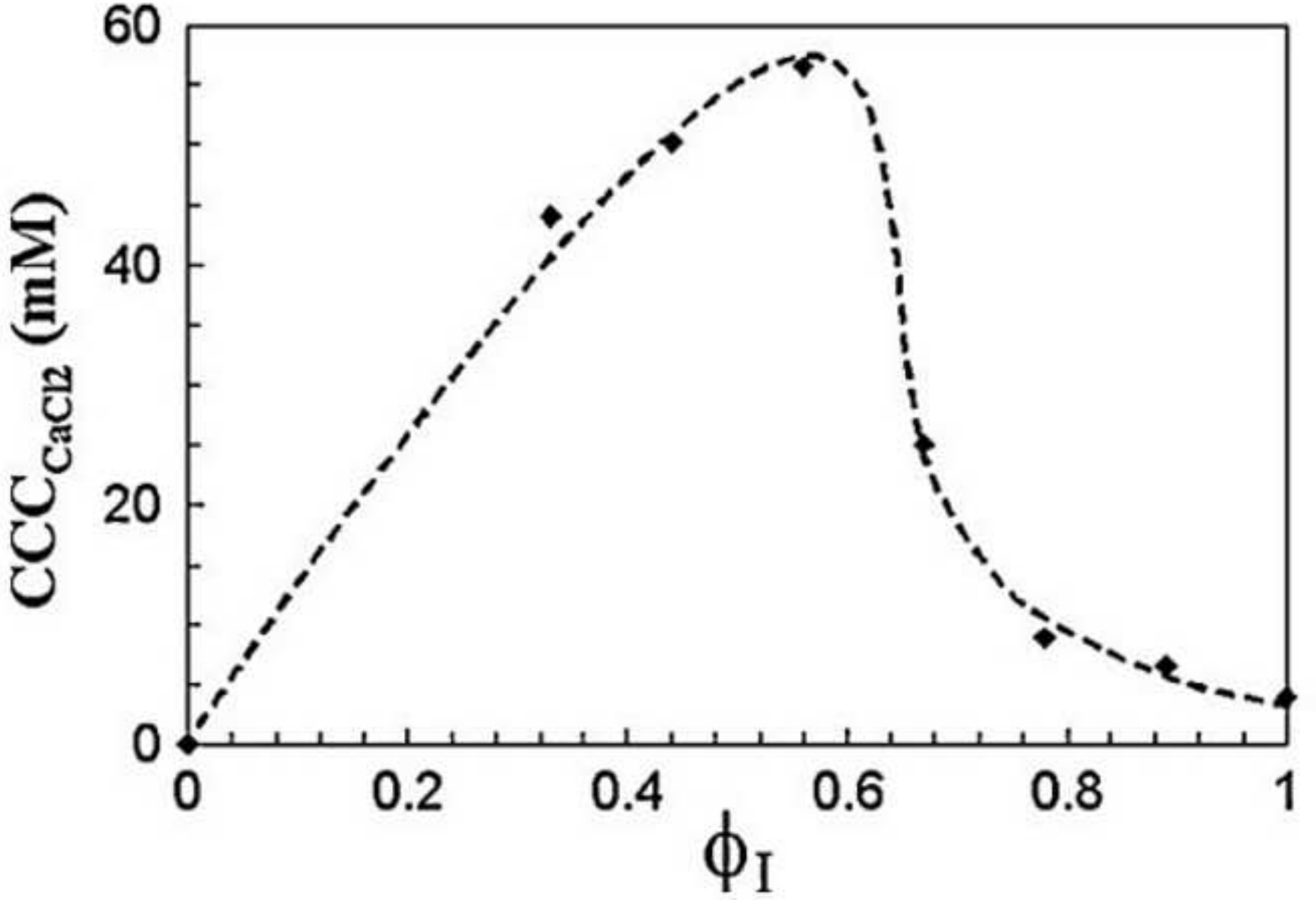

Figure 17

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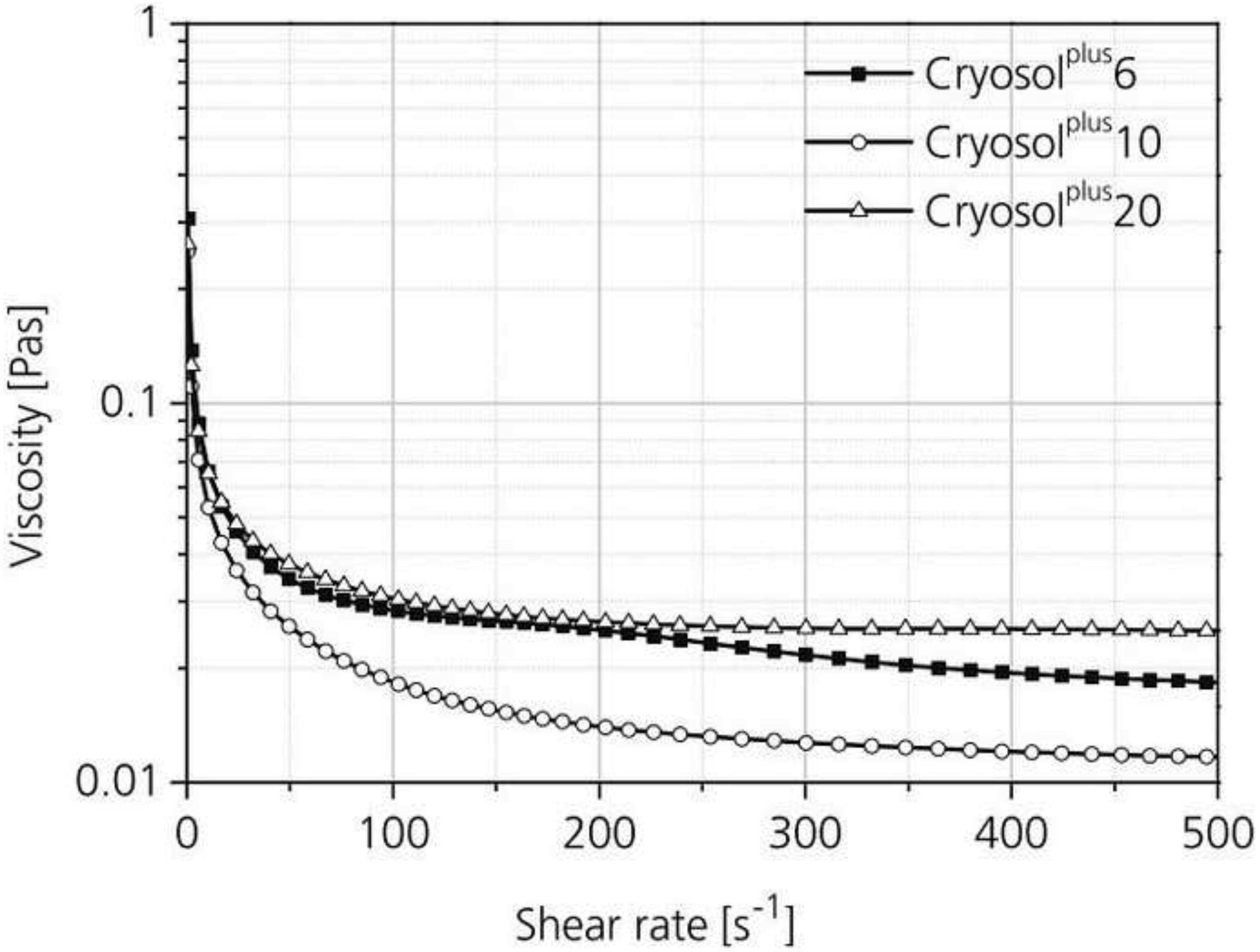

Figure 18

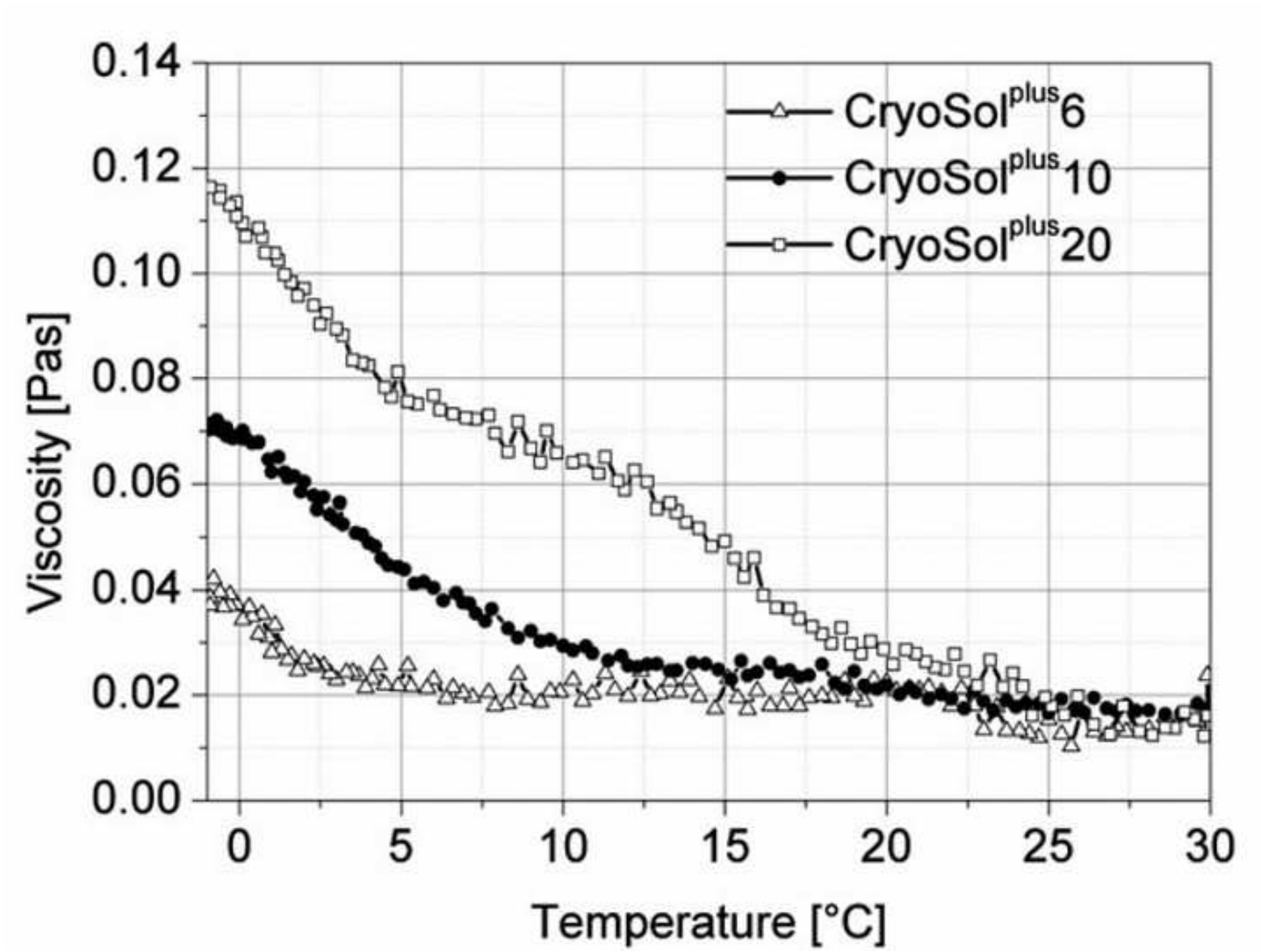
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Viscosity [Pas]
0
5
10
15
20
25
30
Temperature [°C]
CryoSolplus6
CryoSolplus10
CryoSolplus20

Figure 19

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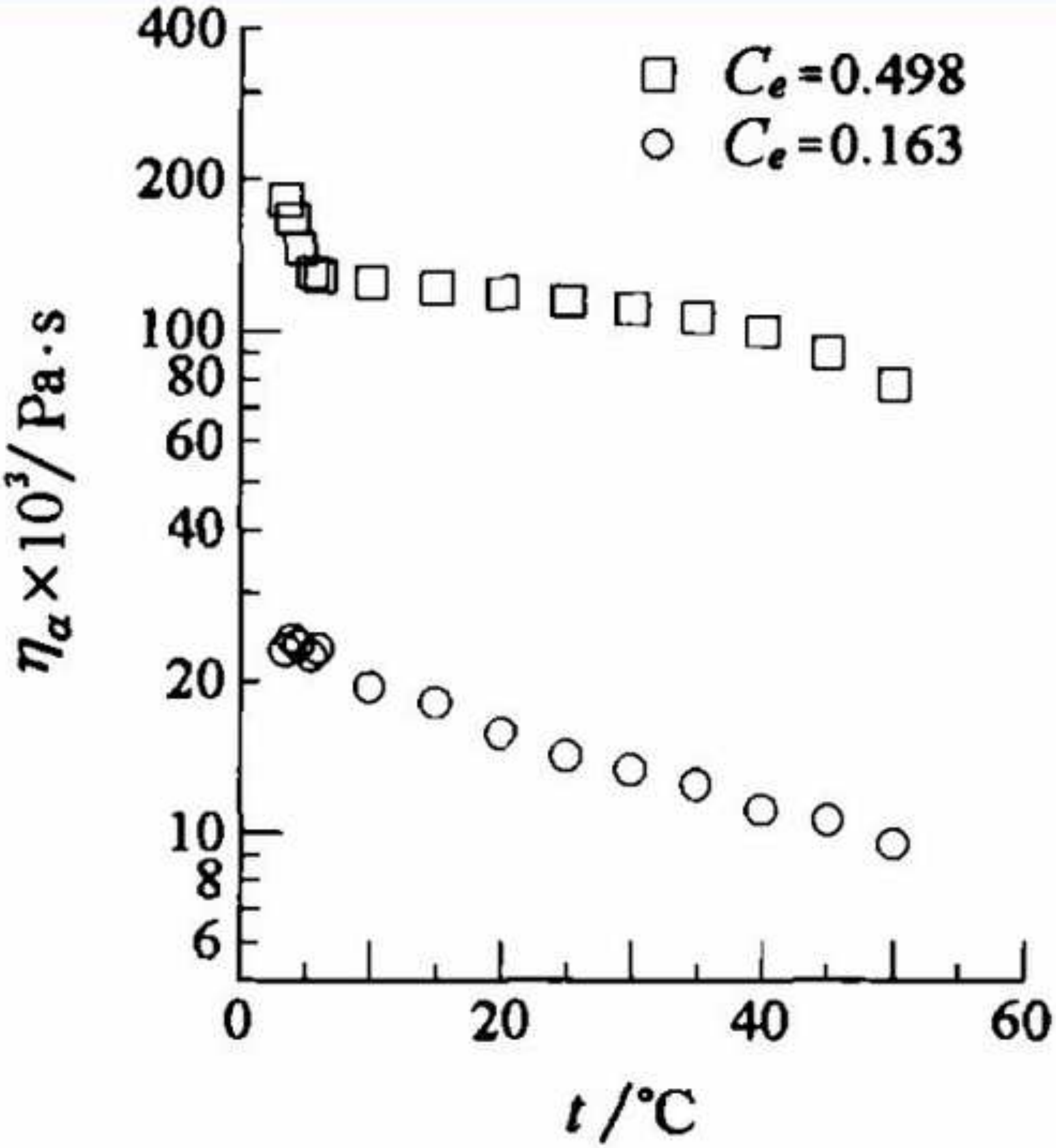

Figure 20

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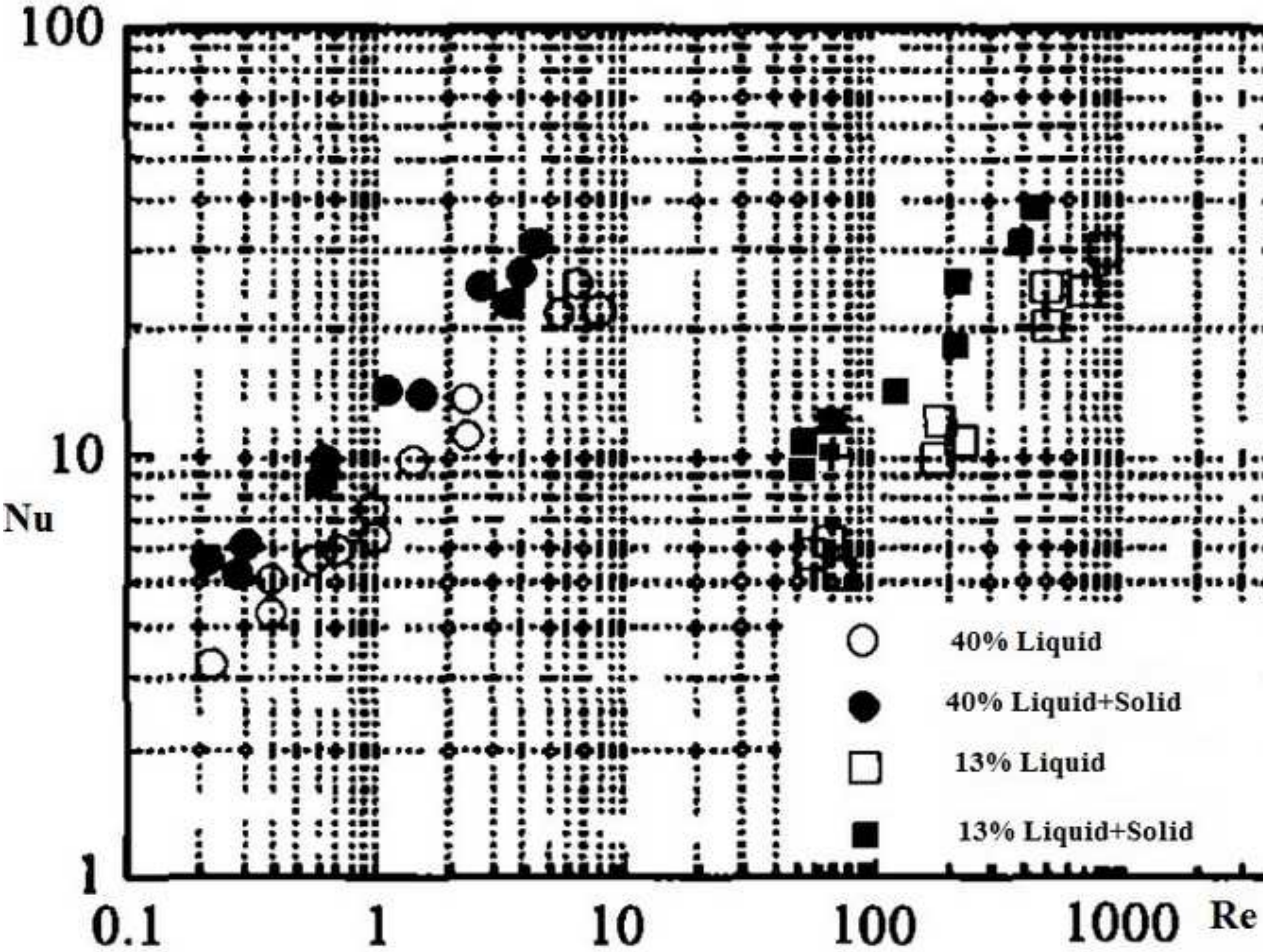

Figure 21

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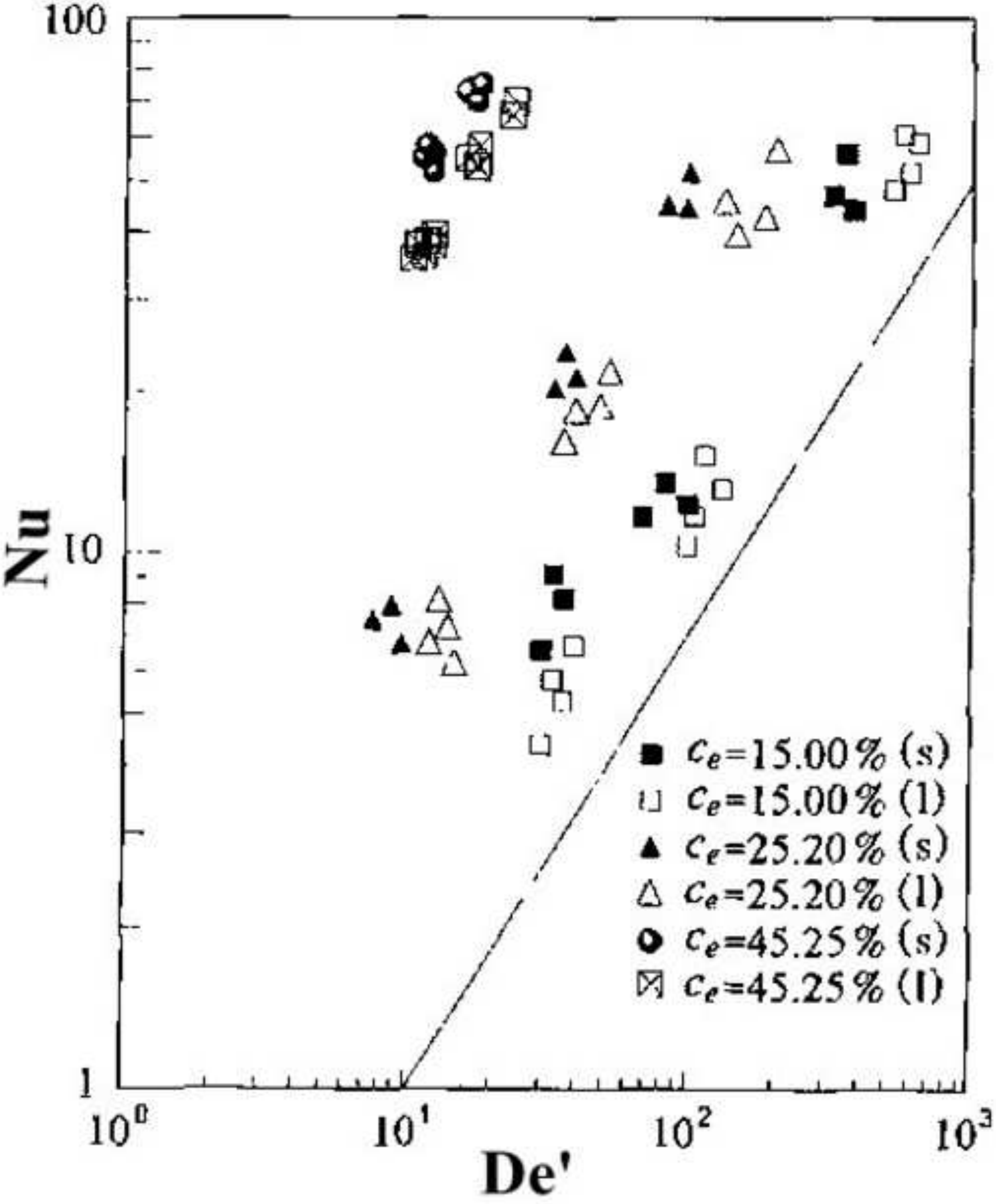

Figure 22

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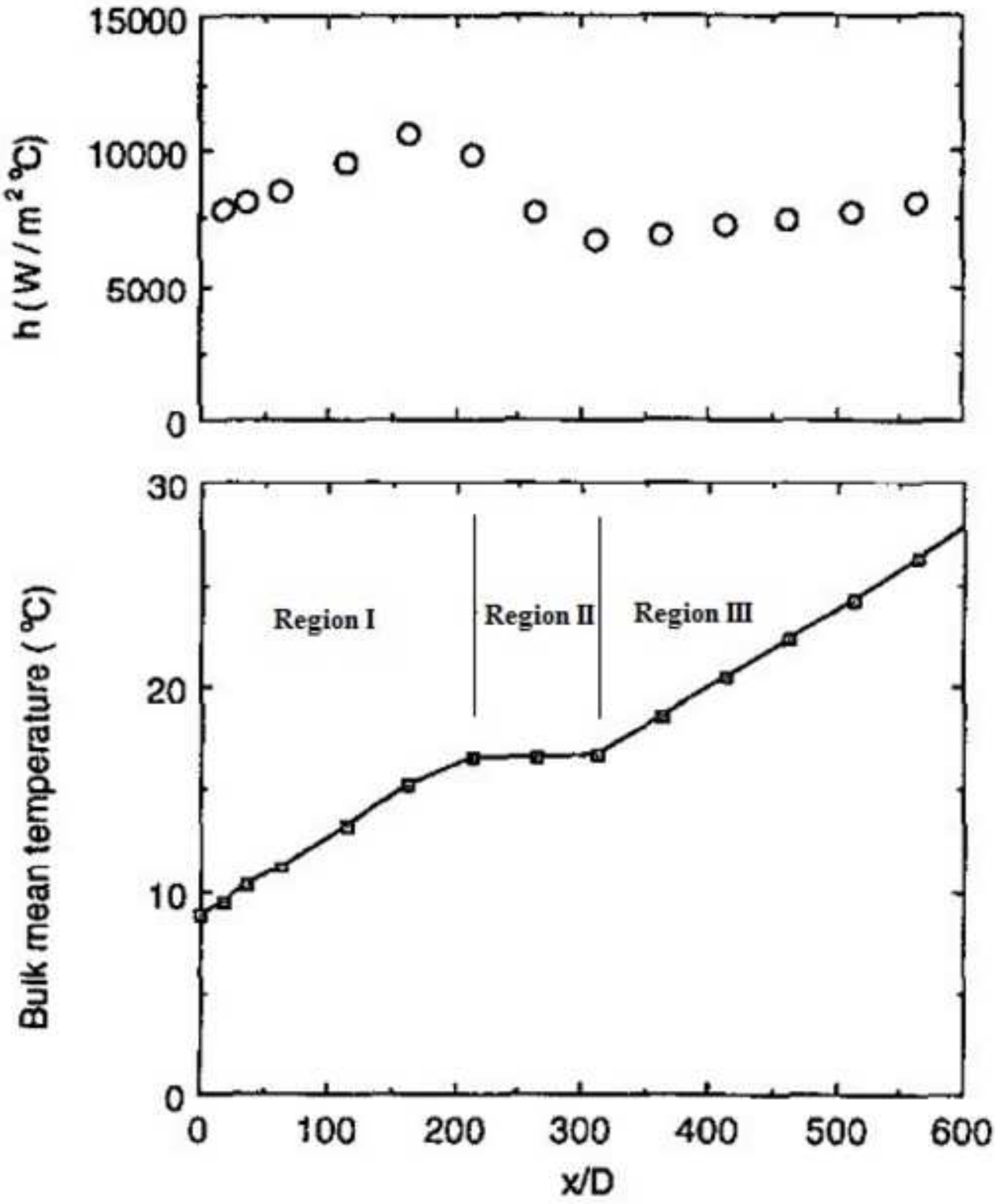

Figure 23
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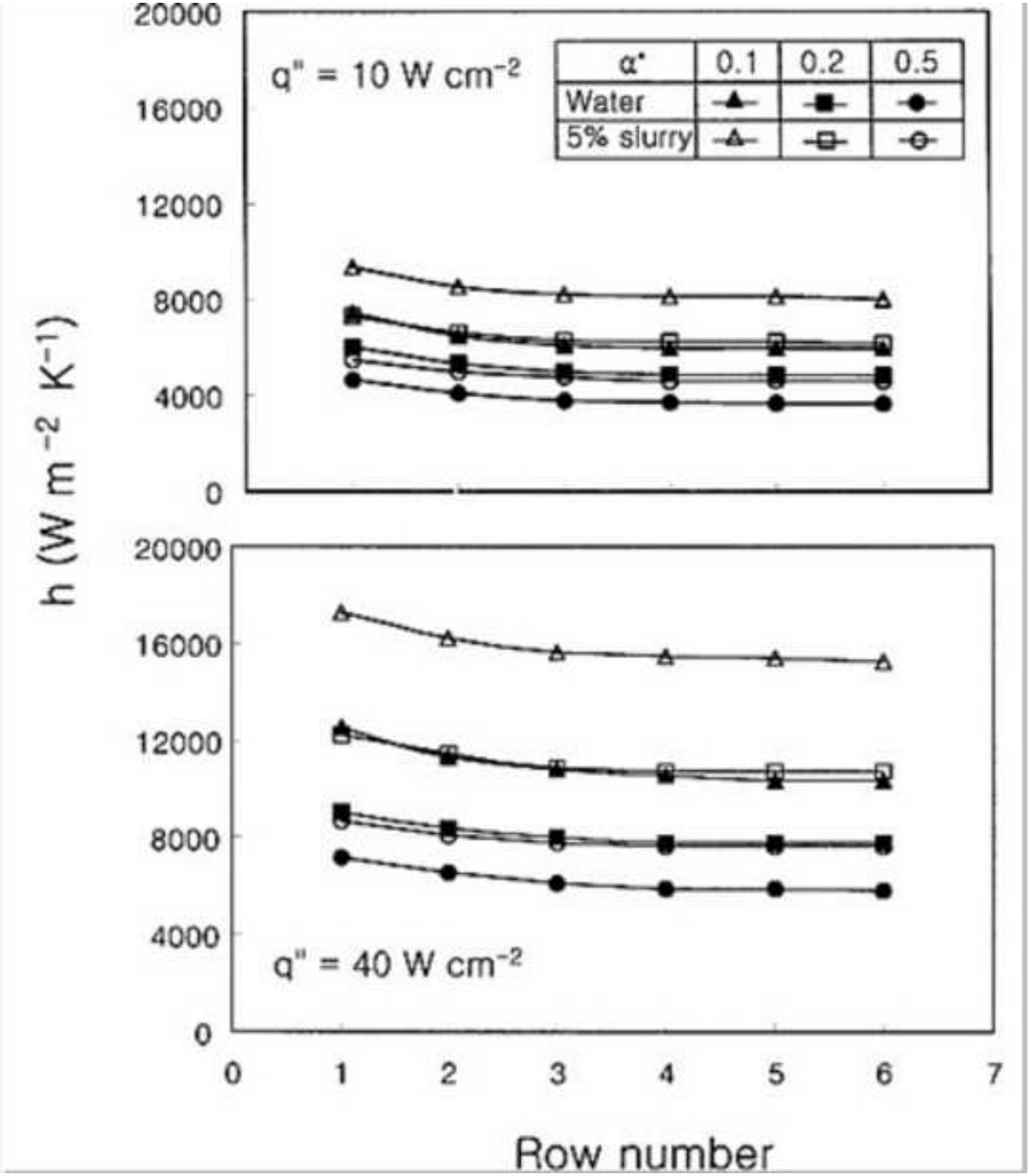

Figure 24

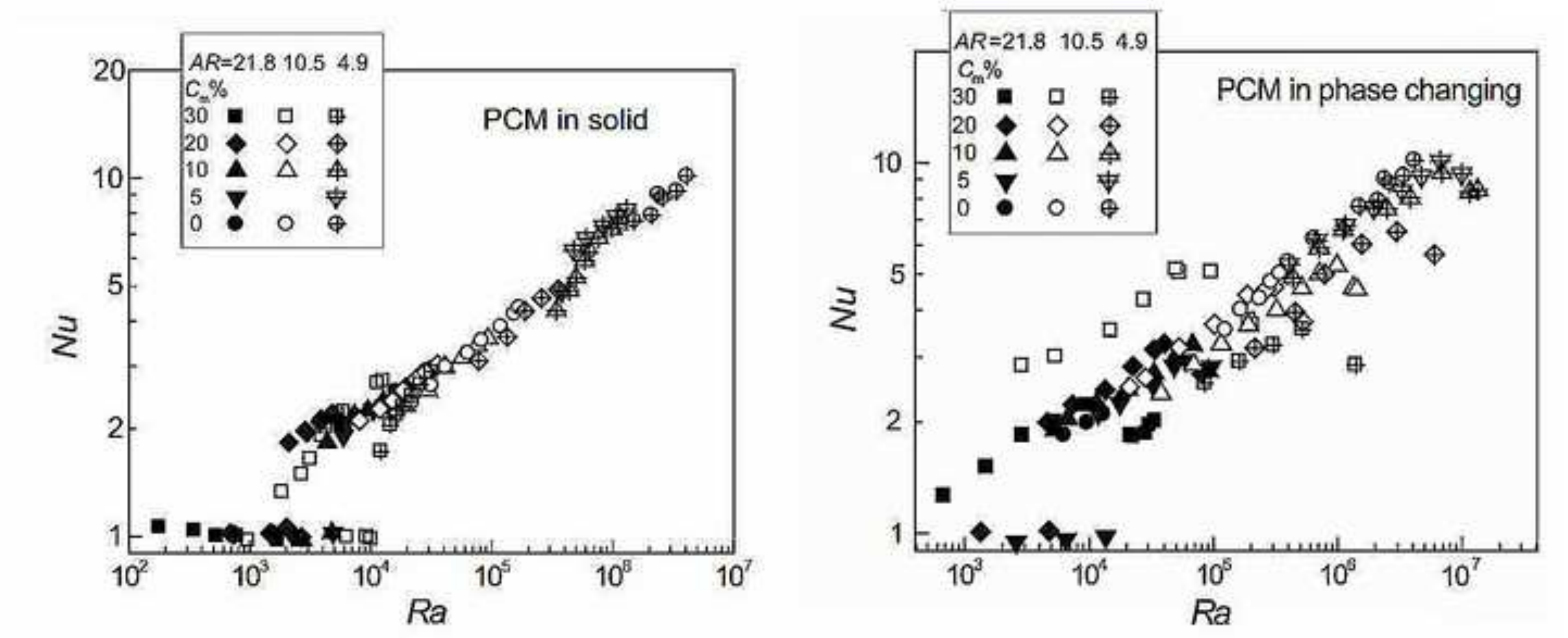
AR=21.8 10.5 4.9
C_m%
30
20
10
5
0
PCM in solid
Nu
Ra
20
10
5
2
1
10^2
10^3
10^4
10^5
10^6
10^7
PCM in phase changing
10
5
2
1
10^3
10^4
10^5
10^6
10^7

Figure 25

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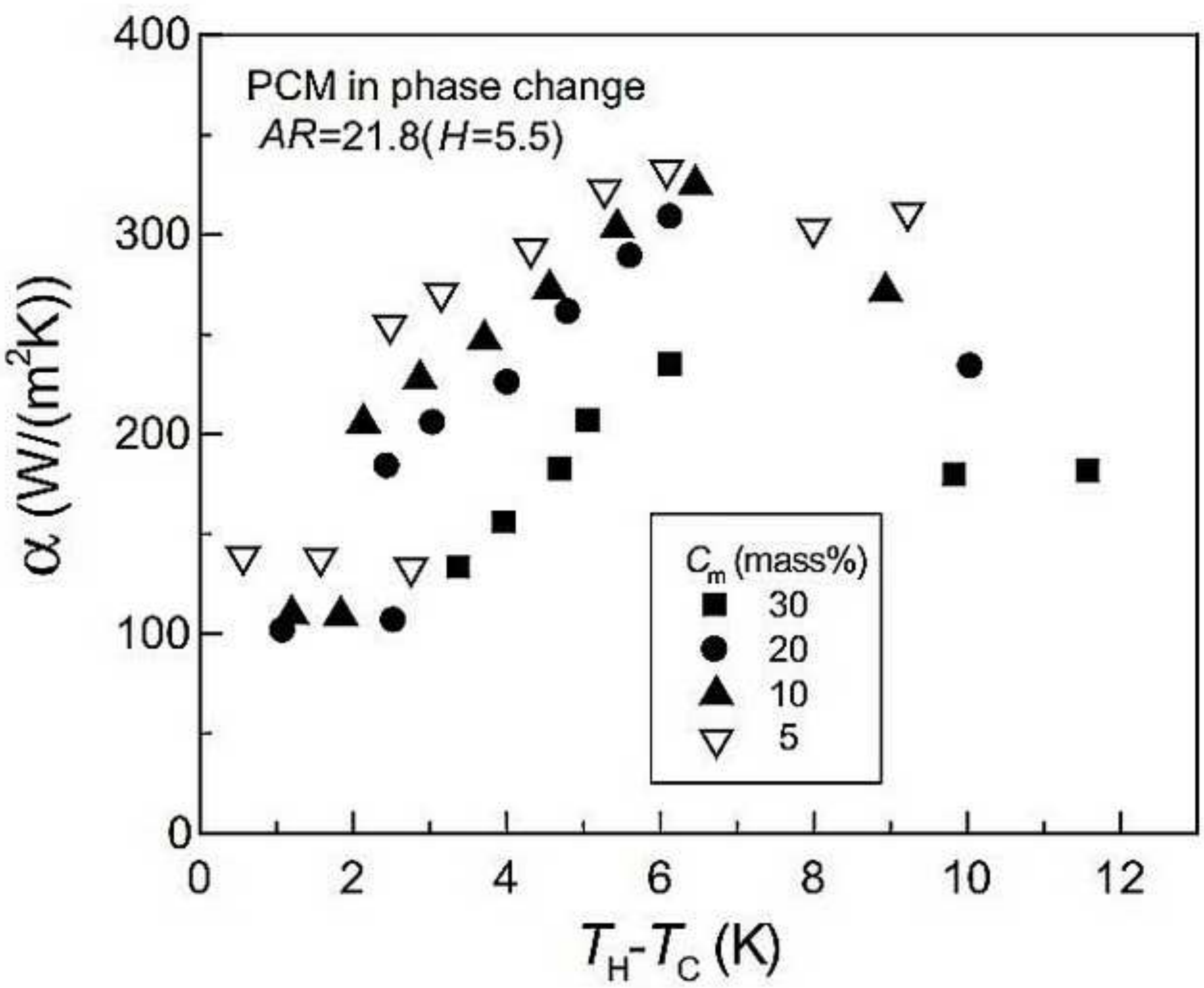


Figure 26

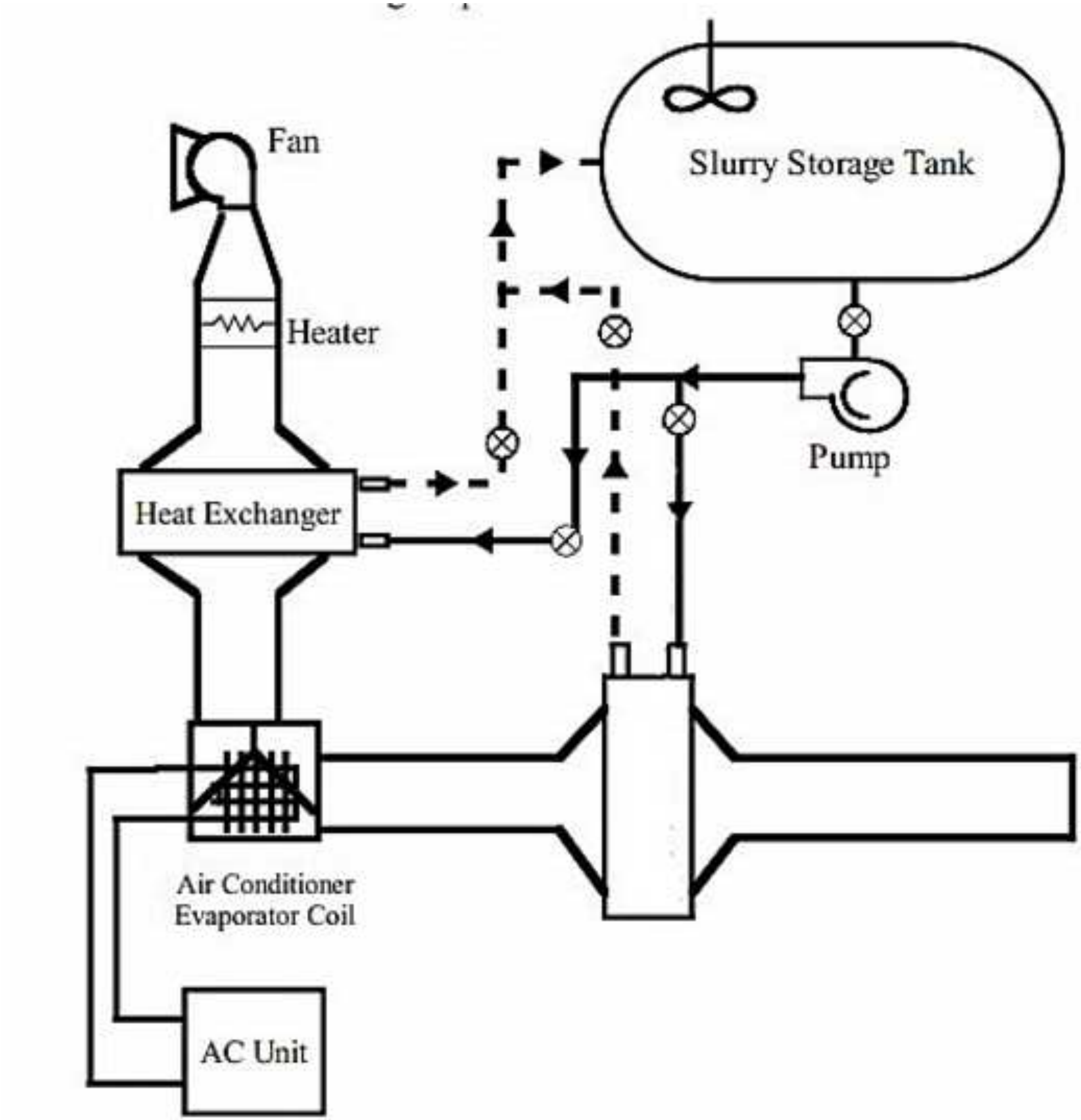
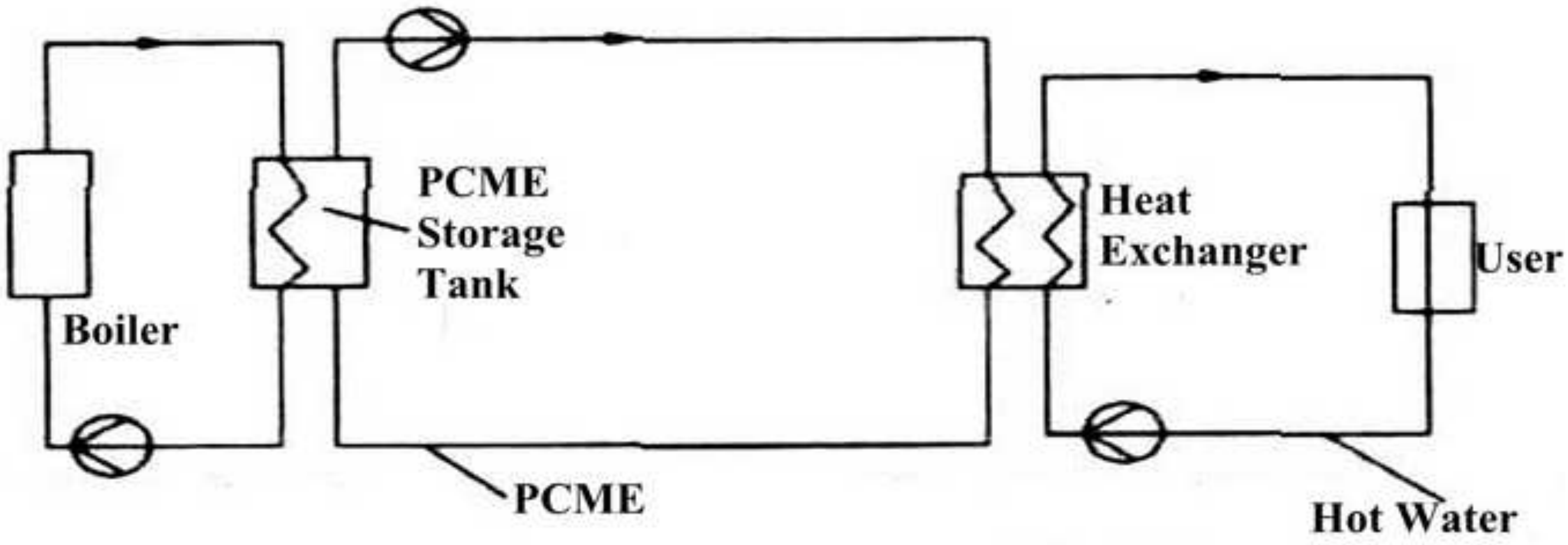

Fan
Slurry Storage Tank
Heater
Pump
Heat Exchanger
Air Conditioner
Evaporator Coil
AC Unit

Figure 27



PCME
Storage
Tank
Heat
Exchanger
User
Boiler
PCME
Hot Water