international journal of refrigeration 34 (2011) 1360–1365

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Thermal conductivity measurement of oil in Water (O/W) nanoemulsion and oil in H_2O/LiBr (O/S) binary nanoemulsion for absorption application

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ARTICLE INFO

Article history:
Received 17 January 2011
Received in revised form
31 March 2011
Accepted 25 April 2011
Available online 1 May 2011

Keywords:
Nanoemulsion
Water
Lithium bromide
Stability
Thermal conductivity
Absorption system
Binary mixture

ABSTRACT

Binary nanoemulsions, oil-droplet suspensions in binary solution (H_2O/LiBr), are developed to enhance the heat and mass transfer performance of absorption refrigeration systems. In this study, a novel four-step method is used to prepare the stable oil-in-binary solution (O/S) emulsion. To stabilize the nanoemulsions in a strong electrolyte, four different polymers are used as a steric stabilizer. The droplet size and the thermal conductivity of binary nanoemulsions are measured by the dynamic light scattering method and the transient hot-wire method, respectively. It is found that the measured thermal conductivities of the oil in water (O/W) nanoemulsion and binary nanoemulsion (O/S) with a stabilizer enhance up to 6.4 and 3.6%, respectively compared with the Maxwell's model. It is also found that GA (Gum Arabic) gives the highest thermal conductivity enhancement. It is finally confirmed that the initial stable condition of the O/S nanoemulsion can be recovered by the re-dispersion in actual absorption systems.

Mesures de la conductivité thermique d'une nanoémulsion huile dans eau (O/W) dans une nanoémulsion binaire huile dans H_2O/LiBr (OS) pour une application d'absorption

Mots clés : Nanoémulsion ; Eau ; Bromure de lithium ; Stabilité ; Conductivité thermique ; Système à absorption ; Mélange binaire

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doi:10.1016/j.ijrefrig.2011.04.008

Nomenclature

DAQ	data acquisition system
k	thermal conductivity of the O/S nanoemulsion, $\mathrm{Wm^{-1}\,K^{-1}}$
k_{Mw}	Maxwell's effective thermal conductivity, $\mathrm{Wm^{-1}\,K^{-1}}$
R_1	fixed resistance, Ω
R_2	fixed resistance, Ω
R_V	variable resistance, Ω
Subscripts	
Mw	Maxwell's effective thermal conductivity

1. Introduction

Nanofluids, which are defined as the stable suspensions of highly conductive nanoparticles in the base fluids, have been extensively paid attention to improve the low thermal conductivity of the conventional working fluids (Keblinski et al., 2002; Xue, 2003; Jang and Choi, 2004; Koo and Kleinstreuer, 2004; Bhattacharya et al., 2004).

However for applying them into the absorption systems, there is a problem of rapid sedimentation of solid nanoparticles because of the strong electrolyte solution of LiBr or NH_3. Keblinski et al. (2002) and Xue (2003) investigated that the ions in solutions led to decrease of thickness of electrical double layer (EDL). Due to this phenomenon, a smaller repulsion force between approaching particles causes the rapid coagulation and sedimentation of nanoparticles. To overcome these problems of binary nanofluids, the binary nanoemulsion, oil-droplet suspensions in binary solutions (O/S), has been studied to apply them into the absorption systems (Sul et al., 2010).

In this study, nano-sized n-decane droplets in water and H_2O/LiBr solution are prepared to analyze the thermal property and stability of the nanoemulsions, by measuring the thermal conductivity and droplet size respectively. Furthermore visualization and Tyndall effect are observed to explain the thermal conductivity characteristics with stability. The thermal conductivity and droplet size are measured by the transient hot-wire method and the dynamic light scattering method, respectively. The objectives of this study are to evaluate the stability of nano-sized oil-droplet and to measure the thermal conductivities of single component nanoemulsions (O/W) and binary nanoemulsions (O/S) for absorption application.

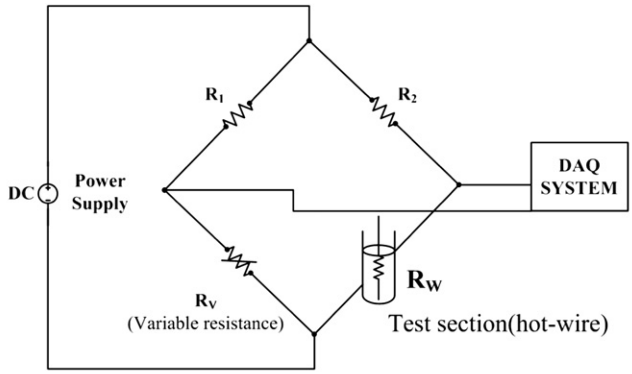


Fig. 1 – Schematic diagram of the transient hot-wire method.

2. Experiment

2.1. Transient hot-wire method

The time rate of temperature change in metal-wire during the electric heating process varies with the thermal conductivity of the surrounding fluids which are binary nanoemulsions in this study. In the transient hot-wire method, the time rate of change in the electric resistance of metal-wire is measured by its temperature dependence. In contrast to the steady state measurement method, the transient hot-wire method can be free from the effect of natural convection due to its promptness in the measurement (Nagasaka and Nagashima, 1981; and Labudová and Vozárová, 2002).

Fig. 1 shows the schematic diagram of the transient hot-wire method. In this study, the Pt-wire (isonel-insulated platinum wire), of 19 cm in length and 25 μm in diameter is used as the metal-wire. The Pt-wire is coated with the isonel layer to prevent the current leakage to the test solution (Sul et al., 2010). The experimental setup consists of the Wheatstone bridge circuit in connection with the power supply, two high accuracy standard resistors of 20 Ω, a high accuracy variable resistor, and the test section including Pt-wire exposed in the test fluids. The maximum experimental errors of the present study are estimated as −0.32% for DI water, 0.33% for 30 wt% H_2O/LiBr and −0.45% for the 50 wt% H_2O/LiBr. And the maximum standard uncertainties obtained by the Gum method (Labudová and Vozárová, 2002) which is statistical analysis are 0.10% for DI water and 0.068% for H_2O/LiBr binary solution, respectively.

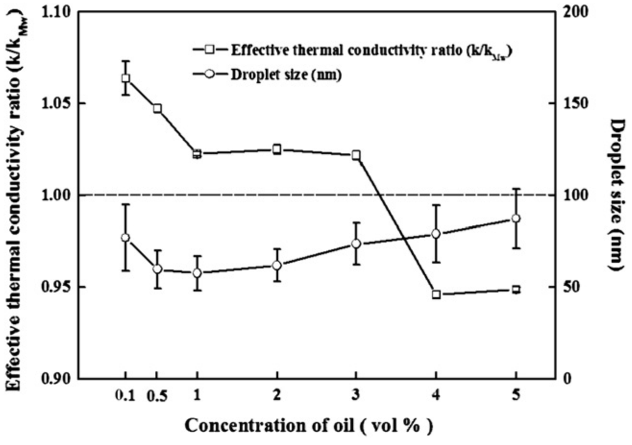


Fig. 2 – Variation of effective thermal conductivity and droplet size of the oil in water nanoemulions with oil concentration.

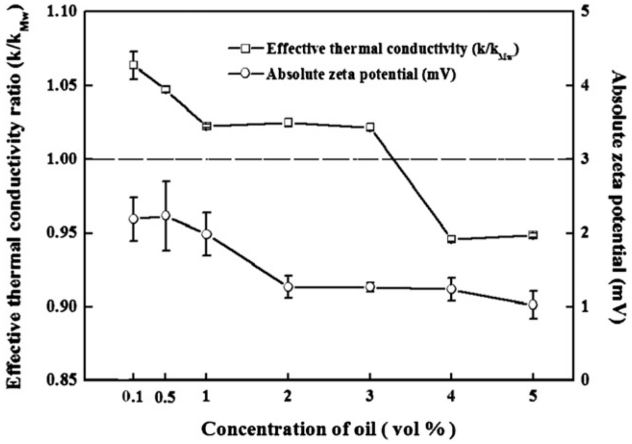
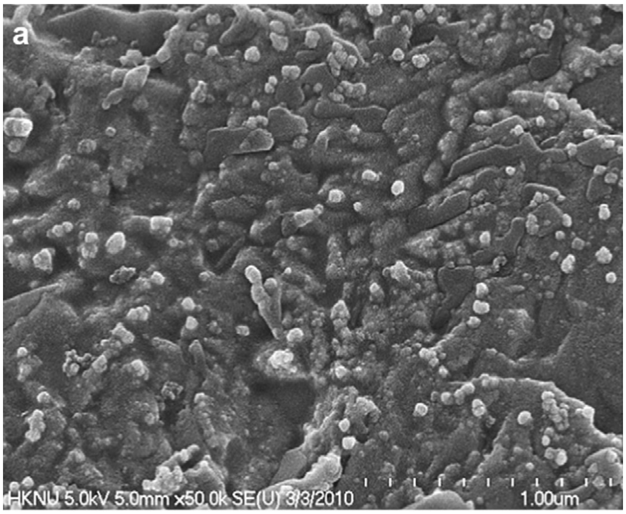
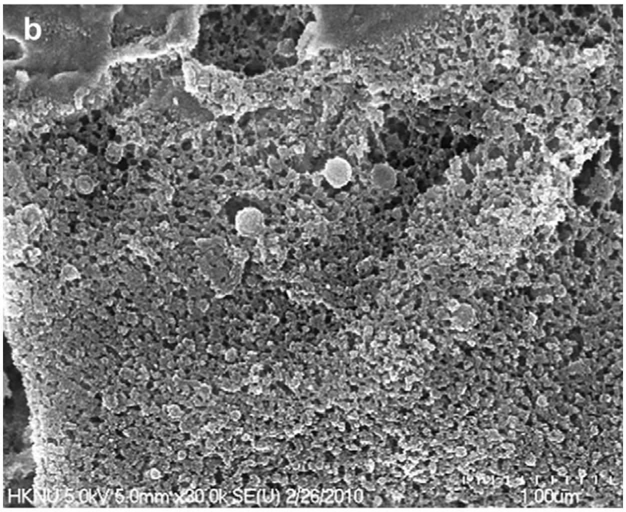


Fig. 3 – Variation of effective thermal conductivity and absolute zeta potential of the oil in water nanoemulsion with oil concentrations.



0.1 vol% of oil in water nanoemulsion



5 vol% of oil in water nanoemulsion

Fig. 4 – Cryo-sem of O/W nanoemulsions.

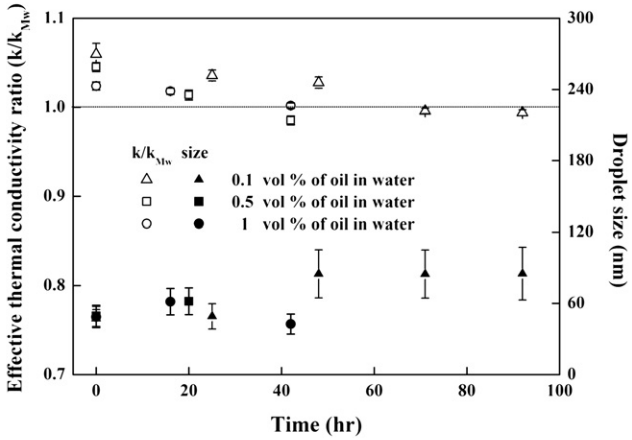


Fig. 5 – Variation of effective thermal conductivity ratio and droplet size with time when 0.1, 0.5, 1 vol% of oil are dispersed.

2.2. *Preparation for nanoemulsions*

The nanoemulsions are prepared using n-decane (oil), which has the thermal conductivity of 0.136 $Wm^{-1}K^{-1}$ at room temperature. It is much lower than those of water (0.5948 $Wm^{-1}K^{-1}$ at 25 °C) or $H_2O/LiBr$ (0.4481 $Wm^{-1}K^{-1}$ at 25 °C in 50 wt% $H_2O/LiBr$). And two kinds of non-ionic surfactants are added; poly(oxyethylene)(4)lauryl ether (C12E4) of technical grade (Brij30, Sigma–Aldrich) and polyoxyethylene sorbitan monolaurate (TWEEN20). The ratio of C12E4 and TWEEN20 is calculated by HLB system and found to be 81:19 (Sul et al., 2010; Jacqueline et al., 2006). The ratio of oil to surfactant is determined to 2:1 for the best stability (Sul et al., 2010). And four different polymers are used as a polymeric stabilizer in this study; Gum arabic (GA), Polyvinyl alcohol (PVA), Guar gum (GG) and Xanthan gum (XG).

The nanoemulsions are prepared by the four-step method with the ultra-sonication process (Sul et al., 2010) and after then, mean droplet size and zeta potential are measured by dynamic, electrophoretic light scattering device (ELS-Z, Otsuka, JPN).

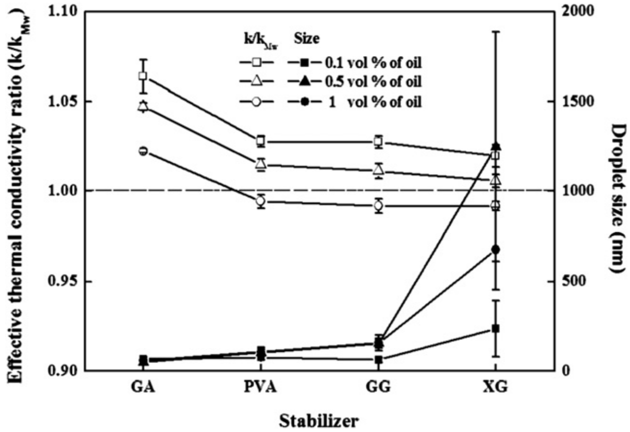


Fig. 6 – Comparisons of effective thermal conductivity ratio and droplet size of 0.1, 0.5, 1 vol% of oil in water nanoemulsions by stabilizer types.

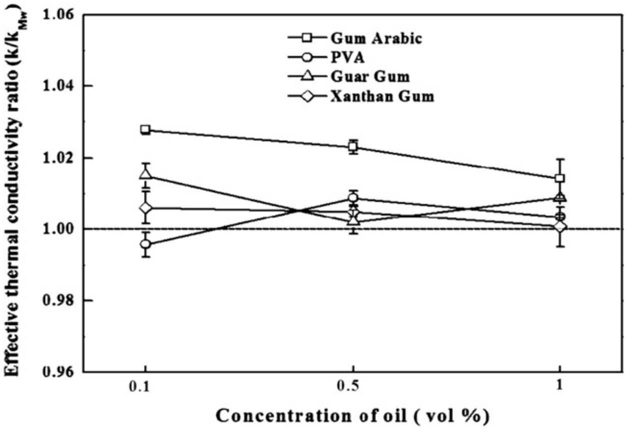


Fig. 7 – Comparisons of the effective thermal conductivity ratio of oil in 10 wt% H_2O/LiBr binary nanoemulsions by stabilizer types.

3. Results and discussion

3.1. *Oil in water nanoemulsions (O/W)*

Figs. 2 and 3 show the effective thermal conductivity ratio, droplet size and zeta potential as a function of oil concentration, respectively. The effective thermal conductivity ratio represents the ratio of thermal conductivity of nanoemulsion to that of Maxwell's model (Xue, 2003). The Maxwell equation is used because the main purpose of the present study is to show how much the effective thermal conductivity of nanoemulsion increases compared with the theoretical prediction. If the enhancement of the effective thermal conductivity is not significant, the theoretical prediction can be used. It is found that the effective thermal conductivity of oil in water nanoemulsions enhances up to 6.4% at 0.1 vol% of oil droplets. By considering the thermal conductivity of n-decane, this result implies that there is other positive effects by nano-sized oil-droplet such as Brownian motion or emulsion-laden flow (Koo and Kleinstreuer, 2004). However as the concentration of n-decane increases, the thermal conductivity decreases and the thermal conductivity become lower than that of the base fluid for higher ranges than 4 vol% of oil. And also the zeta potential decreases as the concentration of n-decane increases. This means there is a smaller repulsion force between approaching droplets, and it causes the Ostwald ripening, creaming and coalescence. In this failure of emulsions mechanism in the unstable range higher than 4 vol% of

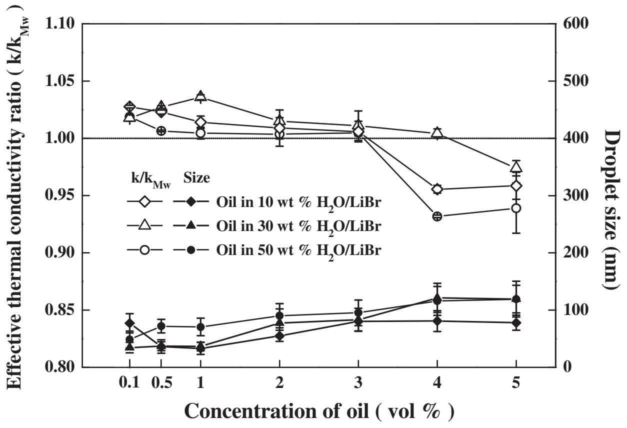
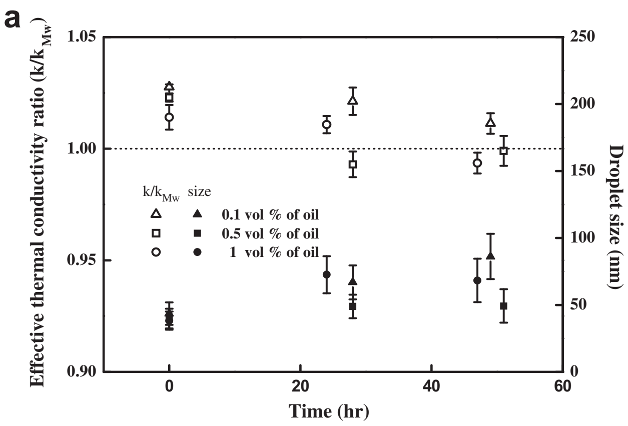
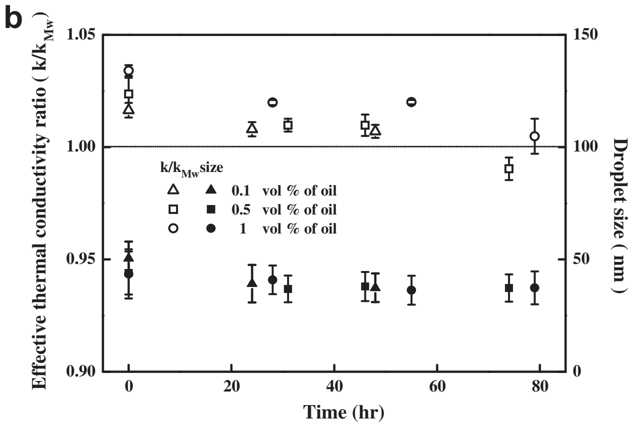


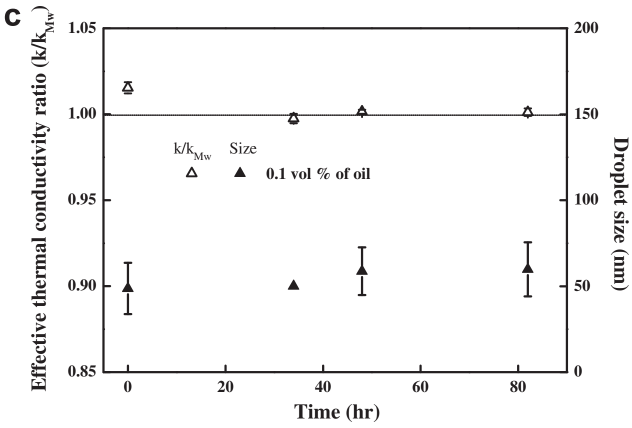
Fig. 8 – Variation of effective thermal conductivity and droplet size of the oil in 10, 30, 50 wt% H_2O/LiBr binary nanoemulsions with oil concentration.



Oil in 10 wt% H_2O/LiBr binary nanoemulsion



Oil in 30 wt% H_2O/LiBr binary nanoemulsion



Oil in 50 wt% H_2O/LiBr binary nanoemulsion

Fig. 9 – Variation of effective thermal conductivity and droplet size of the binary nanoemulsions with time for each concentration of H_2O/LiBr.

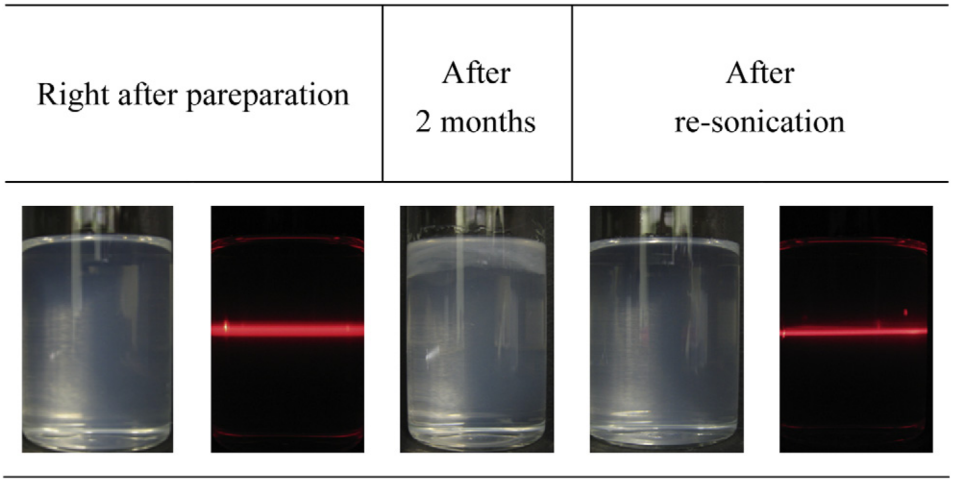


Fig. 10 – **Visualization and Tyndall effect of the right after preparation and after 2 months re-dispersion for 1 vol% of oil in 30 wt% H_2O/LiBr.**

oil, the droplet size of nanoemulsions increases as the oil concentration increases. Due to these changes of basic properties, the thermal conductivity decreases.

Fig. 4 shows the photographs of the nanoemulsions by the cryo-sem. Fig. 4(a) and 4 (b) show the cases of 0.1 and 5 vol% of n-decane dispersed in water, respectively. In the Fig. 4(a), there are scattered particles with a space to move, leading to an emulsion-laden flow. However in Fig. 4 (b), there are high density additives including oil, surfactants and stabilizer. In this case, the packing effect (which hinders the motion of droplets so that the emulsion-laden flow cannot be made) exists and it results in the decrease of the thermal conductivity.

Fig. 5 shows the effective thermal conductivity ratio and droplet size with time variation when 0.1, 0.5 and 1 vol% of oil are dispersed in water. Thermal conductivities are measured at normal temperature and pressure without any movement. The thermal conductivity gradually decreases near the base fluid as time elapses.

Fig. 6 shows the comparisons of the effective thermal conductivity ratio and the droplet size for each stabilizer: GA, PVA, GG, and XG. These stabilizers are soluble in water. For all stabilizers, the thermal conductivity decreases as the concentration of oil increases and it is found that GA gives the highest effective thermal conductivities ratio in the present study.

Fig. 7 shows the comparisons of effective thermal conductivity ratio at 10 wt% H_2O/LiBr for each stabilizer. For the base fluids of 10 wt% H_2O/LiBr, It is also found that the thermal conductivity enhancement is notable when the GA is used as the stabilizer rather than the other stabilizers. Because the GA can be solved in large range of electrolyte and pH without much change of viscosity, it is mostly used the most as a stabilizer. However for GG or XG, the viscosity increases at a large amount. The high viscosity change makes the less Brownian motion and it results in a lower thermal conductivity enhancement compared with GA case. And in the high concentration of PVA, the polymer molecules wrap the droplets and it makes the interaction. Due to this effect, the Ostwald ripening is occurred, resulting in a low thermal conductivity enhancement.

3.2. *Oil in solution (H_2O/Libr) nanoemulsions (O/S)*

Fig. 8 shows the thermal conductivity ratio and droplet size as a function of oil concentration for the binary nanoemulsions. It is found that the effective thermal conductivity ratio of oil in solution (H_2O/LiBr) binary nanoemulsions enhances up to 3.6% at 1 vol% of oil droplets in 30 wt% H_2O/LiBr. The thermal conductivity of the 30 wt% H_2O/LiBr(base fluid) and oil(n-decane) are 0.506 and 0.136 $W m^{-1} K^{-1}$ at 25 °C(measured temperature), respectively. Therefore it is found that the thermal conductivity of the binary nanoemulsions is enhanced by adding nano-sized droplets of n-decane oil which has a lower thermal conductivity than that of the base fluid, which was also reported by Sul et al. (2010) at different conditions. The measured thermal conductivity of the binary nanoemulsions is higher than that of the base fluid nevertheless the thermal conductivity of n-decane is less than that of the base fluid. It is considered that the n-decane droplets in the binary emulsion can enhance the motion of base fluid due to the emulsion-laden

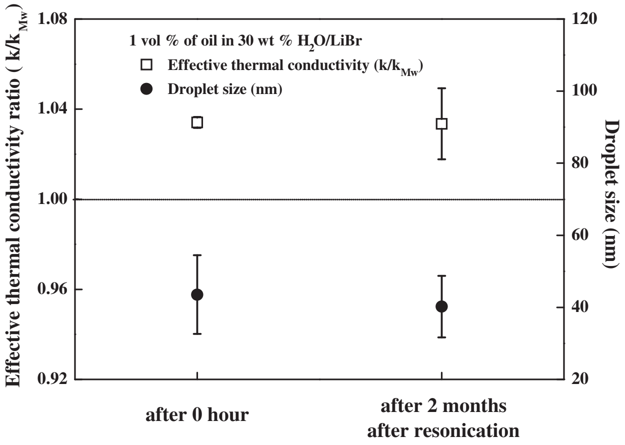


Fig. 11 – **Comparisons of the effective thermal conductivity and droplet size of the right after preparation and after 2 months re-dispersion process.**

flow. However if the concentration of n-decane increases more than 1 vol%, the thermal conductivity decreases near or lower than the base fluid due to the packing effect likewise the oil in water nanoemulsions.

Fig. 9 show the thermal conductivity and droplet size with time variation when 0.1, 0.5, 1 vol% of oil are dispersed in 10, 30, 50 wt% H_2O/LiBr. The thermal conductivity is measured at normal temperature and pressure without any movement. The thermal conductivity gradually decreases as time elapses likewise the oil in water nanoemulsions. The thermal conductivity of 1 vol% of oil in 30 wt% H_2O/LiBr binary nanoemulsions is kept higher than base fluid for about 60 h and then decrease near the base fluid. Because the thermal conductivity is enhanced the most right after preparation and decreases near the base fluid after long time, the re-dispersion process is carried out. After 2 months without any movement, the coalescence and creaming of oil are observed. Under the same condition, only an hour ultra-sonication is applied, and it is found that the stability is recovered as shown in Fig. 10. Fig. 11 shows the corresponding effective thermal conductivity ratio and the droplet size variation. It is finally confirmed that the initial stable condition can be recovered by the re-dispersion process in actual absorption systems.

4. Conclusions

In this study, the thermal conductivities of binary nanoemulsions (nano-sized n-decane in H_2O/LiBr solution) are measured with time variation for four different stabilizers. The droplet size and the thermal conductivity of binary nanoemulsions are measured by the dynamic light scattering method and the transient hot-wire method, respectively. Also the Tyndall effect is used to evaluate the stability of the binary nanoemulsions. The results from the present study are summarized as follows;

(1) The effective thermal conductivity of the oil in water nanoemulsion and binary nanoemulsion enhances up to 6.4 and 3.6% compared with the estimated one from the Maxwell's model, respectively.
(2) It is found that GA gives the highest thermal conductivity enhancement out of four different stabilizers in the present study.
(3) It is confirmed that the initial stable condition of the O/S nanoemulsion can be recovered by the re-dispersion in actual absorption systems.
(4) It is found that the thermal conductivity of the binary nanoemulsion be enhanced by adding nano-sized droplets of n-decane oil which has a lower thermal conductivity than that of the base fluid.

Acknowledgment

This work was partially supported by the National Research Foundation (NRF) grant (No. 2010-0029120) funded by the Korea government (MEST), and by the Technology Innovation Program grant (No. 10037329) funded by the Korea government (MKE).

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