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# LIGHT-TUNING OF HEAT TRANSFER PERFORMANCE FOR LOW REYNOLDS NUMBER FLOW OF MICELLAR SOLUTION

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### ABSTRACT

Viscoelastic fluids in low Reynolds number flow regime have the interesting and important potential for heat transfer performance in contrast to Newtonian fluids. To provide a high efficiency heat exchanger, the authors are aiming at controlling the heat transfer rate actively, in particular, with photo-rheological fluids (PRFs), the properties of which can be tuned by light. In this study, ortho-methoxy cinnamic acid (OMCA) known as a photo-sensitive molecule was added to an aqueous mixture of cetyl-tri-methyl-ammonium bromide (CTAB) and sodium salicylate (NaSal) which is known for inducing the formation of wormlike micelles. OMCA has trans- and cis-arrangements of substituents, and trans-OMCA irreversibly undergoes a photo-isomerization to cis-OMCA upon exposure to UV light. This transformation alters the molecular packing at the micellar interface and shortens wormlike micelles, so that the viscoelasticity of the aqueous solution as a working fluid of heat transfer becomes weaker as the exposure time increases, i.e. trans-OMCA decreases while cis-OMCA increases. As a result of the experiment, both mean heat transfer coefficient and pressure loss penalty were decreased with an increase in the exposure time. This change is supposed to be caused by weaker viscoelasticity of the aqueous solution that significantly influences flow structure, as OMCA undergoes a photo-isomerization.

**KEYWORDS:** Viscoelasticity, Photo-Rheological Fluids, Micellar Solution, Heat Transfer Characteristics, Low Reynolds Number Flow

# **1. INTRODUCTION**

Surfactants, which are sometimes surrounded with counter-ions in aqueous solution, can assemble themselves into various molecular associations, such as spherical micelles, wormlike micelles, vesicles, and lamellar structures. Among these aggregate structures, especially, micelles have attracted great interest in fundamental research and practical application over the past few decades [1]. Under specific experimental conditions, such as surfactant concentration, salinity, and solution temperature, small spherical micelles can grow into long, thread-like, and flexible entangled wormlike micelles. The entanglement of such aggregates results in remarkable viscoelastic properties. This is analogous to that of flexible polymers in aqueous solution. The network of wormlike micelles, however, constantly breaks and recombines, which is different from polymers' behaviours. Moreover, recently, much attention has been paid to smart wormlike micelles, whose macroscopic physicochemical properties undergo morphological changes in response to external stimuli. Among various external stimuli, light irradiation presents superior advantage in small scale application and easy operation. Thus, Photo-Rheological Fluids (PRFs), whose rheological properties are changed by light, have gathered attention and been researched in some engineering fields [2, 3].

In recent years, industrial equipment is getting smaller and smaller, so in miniaturized channel devices, flow becomes laminar in low Reynolds number regime and results in depressing heat transfer performance in comparison to turbulence flow. To solve this problem, there is one effective way to use a viscoelastic fluid as

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a working fluid. Tatsumi et al. [4, 5] experimentally and also numerically investigated the flow and heat transfer characteristics in a millimeter-scale serpentine channel using a polymer solution as a viscoelastic working fluid and showed that the polymer solution increases both heat transfer coefficients and wall friction factors since the viscoelasticity of the fluid causes flow perturbations and generates unsteady secondary flows. In order to enable the heat transfer enhancement more effectively, we propose to use an aqueous solution of PRFs and control its heat transfer performance by light irradiation in response to the need of the occasion and circumstances. This control can be achieved if the viscoelasticity of the fluid is changed by external light stimulus successfully.

In this study, we selected ortho-methoxy cinnamic acid (OMCA) as a photo-sensitive molecule which has trans- and cis-arrangements of substituent. Trans-OMCA is added to an aqueous mixture of cetyl-tri-methyl-ammonium bromide (CTAB) and sodium salicylate (NaSal) which are known for inducing the formation of wormlike micelles [6]. Trans-OMCA irreversibly undergoes a photo-isomerization to cis-OMCA upon exposure to UV light. We prepared also CTAB/NaSal/OMCA solutions of several determinate trans- and cis-OMCA mixing ratio for reference, and compared the rheological properties and heat transfer characteristics of both the former irradiated trans-OMCA solution and the latter different mixing ratio solution to investigate the effectiveness of light irradiation.

# 2. EXPERIMENTAL APPALATUS AND METHODS

**2.1 Rheological Measurements of CTAB/NaSal/OMCA Solutions** CTAB, NaSal, and OMCA are commercially available, and their mixed solution was stirred for 1 day at 20°C. The concentration of CTAB/NaSal/OMCA solution was set to be 1.0wt% CTAB, 0.2wt% NaSal, and 0.2wt% OMCA in high-purity  $H_2O$ . For light-triggered trans-to-cis transition, the solution samples, each of which weighs 300g, were placed in a plastic tumbler and irradiated with a 100W mercury lamp (Olympus U-LH100HGAPO) under stirring with a magnetic stirrer at 200rpm for a desired time. The top of the tumbler was covered with cling film to avoid evaporation of the solution, while the bottom and side of the tumbler were covered with aluminum foil to reflect the light back into the tumbler. The distance between the sample and lamp was fixed at 75mm.

To confirm isomerisation, hydrogen nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of the solutions before and after 24-hour UV irradiation were recorded on a magnetic resonance spectrometer (Bruker NMR spectrometer, DPX-400). The measurements were carried out at room temperature. All samples including 0.2wt% OMCA only and were prepared using D<sub>2</sub>O as the solvent instead of high-purity H<sub>2</sub>O. Spectral analysis of the solutions decanting into a quartz cell was also carried out using a spectrophotometer (SHIMADZU UV-Visible spectrometer, UV-2450) at room temperature. The solutions were diluted to the concentration of 0.01mM OMCA solutions before the analysis since the absorbance at the original concentration was too high in the UV-Vis spectrophotometric analysis. Rheological properties were determined using a rheometer (ANTON PAAR, MCR301) equipped with a cone plate, 50mm in diam. The measurement temperature was controlled at 30°C. Dynamic frequency spectra of elastic and viscous moduli, *G'* and *G''*, were determined in the linear regimes of each sample by dynamic stress-sweep measurements.

**2.2 Heat Transfer and Pressure Loss Measurements** Figure 1 shows the schematic diagram and dimensions of a test section for the experiments. The test section forming a serpentine channel had a square cross section of  $5\text{mm} \times 5\text{mm}$  and consisted of 10 semicircle units connected periodically in the streamwise direction. The inner and outer radii of curvature of the semicircle unit were  $R_i = 5\text{mm}$  and  $R_o = 10\text{mm}$ , respectively. The length along the serpentine channel, *L*, was ca. 470mm. The wall of the test section was made of copper blocks isothermally heated up by constant temperature water circulation. The working fluid was supplied from the pressurized tank to the channel, and the mass of the fluid flowing from the outlet was weighed on an electronic scale to measure the mass flow rate,  $\dot{m}$ . The bulk mean temperatures of the fluid at the inlet and outlet of the test section,  $T_{b,i}$  and  $T_{b,o}$ , were calculated using the fluid temperatures measured at each corresponding location and the fully developed velocity profile of a square channel. A single pair of sheath thermocouples was used to measure the inlet fluid temperature while the outlet fluid temperature was

measured by 5 K-type bare thermocouples located evenly in the height direction at the center of the channel width direction. The wall temperature,  $T_w$ , was an arithmetic-averaging temperatures measured at 4 locations where thermocouples were affixed in copper wall blocks.

An average Nusselt number,  $Nu_m$ , was defined as follows:

$$Nu_{\rm m} = \frac{h_{\rm m}D_{\rm h}}{k} \left(h_{\rm m} = \frac{\dot{m}c_{\rm p}}{A_{\rm s}} \times \ln\frac{T_{\rm w} - T_{\rm b,i}}{T_{\rm w} - T_{\rm b,o}}\right)$$
(1)

where  $D_h$  is the hydraulic diameter of the channel and  $h_m$  is the average heat transfer coefficient calculated by applying the bulk mean temperature and mass flow rate.  $A_s$  is the total area of heat transfer target wall.  $c_p$ and k indicate the specific heat capacity at constant pressure and thermal conductivity of the fluid, respectively. Fanning's friction factor, f, and modified Reynolds number,  $Re^*$ , were, respectively, defined as  $f = (D_h \Delta P) / (2\rho U_m^2 L)$  and  $Re^* = (\rho U_m^{2^-n} D_h^n) / \{8^{n-1}K (B + A/n)^n\}$  in order to evaluate pressure loss penalty. A and B are the geometrical constants. The values, n and K, are referred to the ones used to express shear viscosity,  $\mu$ , as a function of shear rate,  $\dot{\gamma} (\mu = K \dot{\gamma}^{n-1})$ . Both values were calculated from the results of static viscosity measurement using a rheometer.



Fig. 1 Apparatus of serpentine channel for heat transfer experiment.

#### **3. RESULTS AND DISCUSSION**

**3.1 PRFs Properties** Figure 2 (a) shows dynamic frequency spectra of CTAB/NaSal/OMCA solutions depending on the UV irradiation time. The data of G' and G'' are plotted against oscillatory shear frequency,  $\omega$ . In the case without UV irradiation (i.e. 100% trans-OMCA), G' is smaller than G" in the lower frequency region. With the increase of frequency, both G' and G'' increase and then intersect with each other at a certain frequency. After that, G' continues to increase and exceeds G'' as the frequency further increases, implying that the elastic property of the solution is more dominant than the viscous one in the higher frequency region. G' tends to eventually level off and reach an apparent plateau in its increase, while G" reaches a minimum and then increases slightly again. This trend follows the typical Maxwell model, indicative of the formation of viscoelastic wormlike micelles. With the increase of UV irradiation time, up to 8 hours, however, the dynamic frequency spectra deviate gradually from the manner of Maxwell model. The spectra in the case of every 10wt% different trans- and cis-OMCA mixing ratio under the constant OMCA concentration were also measured and compared with the irradiated trans-OMCA solution data. The case of 8 hour irradiation time, for instance, exhibits a considerably similar trend of the mixing solution of 20wt% trans- and 80wt% cis-OMCA. Static shear viscosity  $\mu$  as the function of shear rate  $\dot{\gamma}$  is shown in Fig. 2 (b).  $\mu$ decreases with an increase in  $\dot{\gamma}$ , showing shear-thinning behavior which typically characterizes viscoelastic fluids.  $\mu$  also decreases as a whole with an increase in the irradiation time. Following these obtained results, the mixing ratio of trans-OMCA is decreased with an increase in the UV irradiation time. Trans-OMCA

having a straight structure can promote the growth of micelles due to easy insertion to surfactant molecule aggregates and mitigate interfacial charge, while cis-OMCA cannot do because of its crooked structure. Thus, the decrease of trans-OMCA mixing ratio structurally weakens viscoelastic characteristics of the solution and leads to the degradation of viscoelastic wormlike micelles, depending on the degree of the exposure to UV light. The band spectrum of OMCA solution measured with the spectrophotometer changes remarkably, indicating the trans-to-cis transition of OMCA. <sup>1</sup>H NMR spectra revealing that 24 hour UV irradiation changes the 100% trans-OMCA solution to the cis-OMCA one including 4.5% trans-OMCA supplies evidence of another kind for the transition.



**Fig. 2** Rheograms for CTAB/NaSal/OMCA Solutions before and after the UV irradiation: (a) dynamic frequency spectra exhibiting elastic G' and viscous G" moduli as the function of oscillatory frequency  $\omega$ ; (b) static shear rheology plotting the shear viscosity  $\mu$  against the shear rate  $\dot{\gamma}$ .

**3.2 Heat Transfer Characteristics** The flow conditions of heat transfer experiment are listed in Table 1 where the modified Reynolds number range of the solution having different irradiation time (0h ~ 8h) is  $Re^*$  = 1.2 ~ 17. Weissenberg number Wi representing the influence of stress relaxation phenomena was also tabulated there for reference. Figure 3 (a) and (b) shows, respectively, the average Nusselt number  $Nu_m$  and Fanning's friction factor f of CTAB/NaSal/OMCA solution plotted against  $Re^*$  at 4 different irradiation time conditions. The dashed and solid lines drawn in Fig. 3 (b), respectively, indicate the theoretically-obtained friction factor of steady flow in a square duct [7] and the modified one considering temperature dependence of viscosity for the solution after 8-hour UV irradiation. The maxima of both  $Nu_m$  and f are the case without UV irradiation in all  $Re^*$  region. With an increase in the UV irradiation time, the both data are decreased as a whole. This trend indicates that the elastic property of the solution without UV irradiation causes unsteady flow and enhances heat transfer while the property after UV irradiation is mitigated gradually, approaching the steady flow case with similar friction factors to the ones obtained theoretically. Temperature fluctuations of the solution measured with thermocouples at the channel exit correspondingly subsides with the UV irradiation time, indicating that the flow becomes unfluctuating. In addition to this experiment, we are examining another PRF including an azobenzene derivative as a reversible photo-isomerization molecule instead of OMCA. We expect this to control heat transfer performance with light, similar to OMCA but more effectively.

Solution	irradiation time (h)	$U_{\rm m}$ (mm/s)	$Re^{*}$	Wi
CNO-0h	-	36 - 130	1.2 - 17	71 - 840
CNO-2h	2	43 - 100	2.2 - 16	49 - 260
CNO-4h	4	31 - 90	1.9 - 14	19 - 180
CNO-8h	8	34 - 86	2.1 - 12	7.5 - 120

Table 1 Flow conditions of heat transfer experiment.



**Fig. 3** UV irradiation time dependence of average Nusselt Number  $Nu_m$  and Fanning's friction factor f: (a)  $Nu_m$  vs.  $Re^*$ ; (b) f vs.  $Re^*$ .

## 4. CONCLUSIONS

**Rheological Properties:** The viscoelasticity of 100% trans-OMCA solution is mitigated gradually with an increase in the UV irradiation time, which is caused mainly by the morphological transition from trans-OMCA to cis-OMCA accompanying the decrease of wormlike micelles.

**Flow and Heat Transfer Characteristics:** The average Nusselt number and Fanning's friction factor of CTAB/NaSal/OMCA solution are both conspicuously decreased by the UV irradiation which weakens the viscoelastic property of the solution and then causes the transition from unsteady flow to steady flow. If other chemical substances of reversible photo-isomerization are applied, the heat transfer performance can be effectively controlled by light irradiation.

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#### REFERENCES

- [1] Zana, R. and Talmon, Y., "Dependence of Aggregates Morphology on Structure of Dimeric Surfactants," *Nature*, 362, pp. 228-230, (1993). Journal Paper
- [2] Ketner, A. M., Kumar, R., Davis, T. S., Elder, P. W., and Raghavan, S. R., "A Simple Class of Photorheological Fluids: Surfactant Solutions with Viscosity Tunable by Light," *J. Am. Chem. Soc.*, 129, pp. 1553-1559, (2007). Journal Paper
- [3] Baigle, D., "Photo-Actuation of Liquids for Light-Driven Microfluidics: State of the Art and Perspectives," *Lab on a Chip*, (2012). Journal Paper
- [4] Tatsumi, K., Nagasaka, W., Nakajima, O., Heong, C. L., and Nakabe, K., "Flow and Heat Transfer Characteristics of Viscoelastic Fluid Flow in Serpentine Channel," *Trans. JSME Series B*, 79 (797), pp. 93-103, (2013). Journal Paper
- [5] Tatsumi, K., Nagasaka, W., Matsuo, T., and Nakabe, K., "A Numerical and Experimental Study on Flow and Heat Transfer Characteristics of Viscoelastic Fluid in a Serpentine Channel," *Proc. 15th Int. Heat Transfer Conf.*, IHTC15-9615, (2015). Conference Proceedings
- [6] Shikata, T, and Hirata, H., "Micelle Formation of Detergent Molecules in Aqueous Media: Viscoelastic Properties of Aqueous Cetyltrimetylammonium Bromide Solutions," *Langmuir*, vol. 3 (1987), pp. 1081-1086. Journal Paper
- [7] Kozicki, W., Chou, C. H., and Tiu, C., "Non-Newtonian Flow in Ducts of Arbitrary Cross-Sectional Shape," *Chemical Engineering Science*, 21, pp. 335-679, (1966). Journal Paper