

Development of a soft sensor to estimate the rheological properties of self-assembled systems: application to wormlike micelles (WLMs)

Silabrata Pahari* Jiyoun Moon** Mustafa Akbulut*
Sungwon Hwang** Joseph Sang-Il Kwon*

* *Artie McFerrin Department of Chemical Engineering Texas A&M University, College Station, TX 77845 USA (e-mail: kwonx075@tamu.edu)*

** *Education and Research Center for Smart Energy and Materials, Inha University, Incheon, Republic of Korea*

Abstract: The application of synthetic supercolloids extends across multiple industries. Owing to their unique rheology, there is an increasing demand for these products. Therefore, the large-scale production of these colloids must be efficiently done. Although some very new studies have shed light on the controlled production of these colloids, no studies have focused on the online estimation of system rheology during the production. Furthermore, it is desired to have accurate estimates of the process variables from only a few measurements. Hence, it is essential to design a proper soft sensor that can estimate the process states accurately with a few measurements. Motivated by these requirements, a moving horizon state-estimator (MHE) was designed in this work. Specifically, the MHE-based soft sensor was designed with a nonlinear model developed to relate the process inputs to the system rheology. Finally, the developed framework was implemented to a case study of wormlike micelles produced from cetrimonium bromide (CTAB) and sodium chloride (NaCl).

Keywords: Soft sensor, colloids, wormlike micelles (WLMs), moving horizon state-estimator (MHE), rheology

1. INTRODUCTION

Amphiphilic surfactant molecules self-assemble to form supramolecular structures in polar solvents (Liu et al., 2021; Bhat et al., 2021). One such self-assembled structure is wormlike micelles (WLMs) (Pahari et al., 2021a,c). Since WLMs are formed via dynamic interactions between such self-assembling monomers, they undergo continuous breakage, and recombination processes (Zou et al., 2015; Pahari et al., 2021a). Owing to the dynamic nature, WLMs exhibit unique viscoelastic properties, which are of interest across multiple industries (Pahari et al., 2021b). However, the large-scale production of WLMs, for instance in pharmaceuticals, energy, and food industries (Pahari et al., 2021c), requires the online estimation of key rheological properties such as zero-shear viscosity. Although recent studies have provided insights into the controlled production of the WLMs, only a few studies have highlighted the online estimation of the system's viscosity during the operation (Pahari et al., 2021c). Furthermore, during the production, zero-shear viscosity is not directly measured, but rather small-angle X-ray scattering is utilized to obtain the mean length of WLMs (Jensen et al., 2014). Thus, it is essential to develop a soft sensor which estimates the dynamic variation of zero-shear viscosity from available measurements (i.e., mean length of WLMs) to efficiently and effectively regulate the large-scale production of WLMs.

Hence, in this work, an integrated framework to estimate the zero-shear viscosity of WLMs during the production is proposed. Given that operation variables (e.g., pH, salt concentration, and temperature of a solution) considerably affect the production of WLMs, it is important to develop a mathematical model which can predict the evolution of the system's rheological properties with the varying reaction conditions (Danov et al., 2020). Specifically, two models are required to predict the temporal variation of the system's rheology during the WLMs synthesis: 1) a model that captures the growth of the WLMs length; and 2) a model that computes the viscosity of the system by the obtained WLMs length.

For this, a population balance model proposed in (Pahari et al., 2021c) was adopted to capture the temporal variation of the WLMs length, and a pointer-based algorithm based on the tube-reptation theory (Zou and Larson, 2014) was implemented to capture the viscosity of the WLMs. Herein, the pointer-based algorithm was chosen since it is relatively fast while showing a higher prediction accuracy compared to the models presented in previous studies (Zou et al., 2015; Zou and Larson, 2014). Subsequently, the population balance model and the rheology model are combined to design a moving horizon estimator (MHE) (Alessandri et al., 2010), which solves an optimization problem by providing weights to the process, measure-

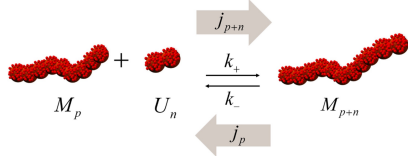


Figure 1. An illustration showing the growth of the WLMs by fusion of aggregated monomers.

ment noise, and a priori state estimates while considering practical process constraints (Haseltine and Rawlings, 2005; Ferrari-Trecate et al., 2002). The MHE can incorporate constraints on estimated process states and does not require the linearization of the system. Moreover, the size of the prediction horizon for the state estimator can conveniently be manipulated to keep the solution of the optimization problem computationally tractable (Zavala et al., 2008). Finally, the developed optimal state estimator is utilized to estimate the viscosity of the WLMs system of cetrimonium bromide (CTAB) and sodium chloride (NaCl) (Pahari et al., 2021c).

The paper is organized as follows: the details of the population balance model and the application of the pointer-based algorithm are presented. Then, the MHE is formulated by considering the nonlinear model proposed for the growth and rheology of WLMs. Lastly, results obtained by implementing the proposed framework to the CTAB/NaCl system are highlighted and further discussed.

2. MODEL FORMULATION

2.1 WLM growth and rheology models

In this section, the population balance model is implemented to obtain the dynamic evolution of the mean length of WLMs. Herein, inputs such as salt concentration, pH, and temperature of the solution are considered during the WLMs synthesis. Subsequently, the mean length of WLMs obtained from the population balance model is employed in the rheology model based on the pointer-based algorithm to obtain the viscosity of WLMs.

First, the major idea of the population balance equations lies in a unimer exchange mechanism (Fig. 1) which is observed by SAXS experiments of (Jensen et al., 2014). Note that a detailed derivation of the population growth model can be found in (Pahari et al., 2021c). According to the proposed model, the growth of the WLMs is propelled by the step-wise consumption of spherical aggregates. Specifically, the growth of the WLMs is governed by the fusion of aggregates as follows:



where M_p is the WLM aggregate of size p , U_n is the aggregate of size n , and M_{p+n} is the combined aggregate of size $p+n$. The rate of formation of the aggregates of size $p+n$ is given as follows:

$$j_{p+n} = k_+ \phi_n \left(\phi_p - \frac{\phi_{p+n}}{\phi_n c_{sa}} \exp\left(-\frac{p}{k_1 n}\right) \right) \quad (2)$$

where ϕ_p denotes the concentration of aggregates of size p , k_+ is the rate constant for insertion, c_{sa} is the correction term for the potential energy, k_1 is the parameter value determined from equilibrium, and p is the aggregation number. The rate constant k_+ is obtained as follows:

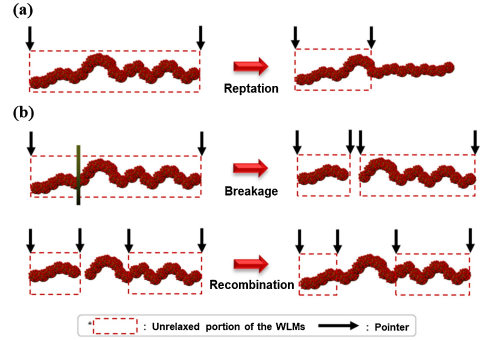


Figure 2. The relaxation mechanisms of WLMs: (a) reptation and (b) breakage and recombination.

$$k_+ = \frac{2xk_bT}{3\eta} \left(\frac{(1+n^{\frac{1}{3}})^2}{n^{\frac{1}{3}}} \right) \quad (3)$$

where x is a pre-factor determined from thermodynamic equilibrium, n is the number of monomers in the spherical aggregate, and η denotes the solution viscosity. Finally, the growth of aggregate of size p is obtained from the following differential equation.

$$\frac{d\phi_p}{dt} = j_p - j_{p+n} + \dot{N}(p) \quad (4)$$

where ϕ_p is the number of aggregate of size p , and $\dot{N}(p)$ is the additional flux of ϕ_p due to the breakage and recombination of WLMs owing to their dynamic nature. The proposed model has been found to show good agreement with experimental results (Pahari et al., 2021c). By following the previously proposed framework, the value of $\dot{N}(p)$ is computed as follows:

$$\dot{N}(p) = -c_1 p \phi_p - c_2 \phi_p \int_0^\infty \phi'_p dp' + 2c_1 \int_p^\infty \phi'_p dp' + c_2 \int_0^\infty \int_0^\infty \phi'_p \phi''_p \delta(p' + p'' - p) \quad (5)$$

where c_1 and c_2 are the rate constants for the breakage and recombination events in the WLMs, respectively. A detailed explanation of the terms in (5) can be found in (Pahari et al., 2021c). Here, WLMs are assumed to grow while minimizing their energy, and this assumption is validated by experimental results (Marrucci, 1985) which imply that energetically stable exponential distributions are obtained at equilibrium. From those equations, both the length distribution of the WLMs with respect to time and the mean length of the WLMs can be obtained.

Subsequently, once the structural evolution of the WLMs is obtained, the transition in rheological properties during the synthesis can be successfully predicted via a stress-relaxation model. Owing to its fast computational capability, the pointer-based algorithm has been implemented to obtain rheological properties such as the zero-shear viscosity of the WLMs (Zou and Larson, 2014). In detail, the pointer-based algorithm tracks the ends (i.e., pointers) of unrelaxed portion of WLM chains. As shown in Fig. 2, crucial stress-relaxation mechanisms of WLMs such as reptation and union-scission induce the movement, creation, or annihilation of pointers. Hence, as the simulation proceeds, the curvilinear diffusion of the WLMs, which leads to stress-relaxation, is evaluated by the pointers. Additionally, it is also imperative to compute the time required for WLMs chains to escape the confining tube

(i.e., reptation time) (Marrucci, 1985). The equations for calculating the reptation time are as follows:

$$\tau_{rep} = \frac{\langle L \rangle}{\pi D_c} \quad (6)$$

$$D_c = \frac{D_o}{\langle L \rangle} \quad (7)$$

$$D_o = \frac{k_b T}{\zeta} \quad (8)$$

where $\langle L \rangle$ is the mean length of the WLMs, D_c is the curvilinear diffusion coefficient, and D_o and ζ are the diffusion and the drag coefficient per unit length of WLM chain, respectively. Herein, the drag coefficient is computed as follows:

$$\zeta = \frac{2\pi\eta_s}{ln(\frac{\epsilon}{d})} \quad (9)$$

$$\epsilon = l_p^{0.4} l_e^{0.6} \quad (10)$$

where ϵ is the excluded volume, d is the diameter of WLM, l_p is the persistence length of the WLMs, and l_e is the entanglement length of the WLMs. In every time step, all the WLMs present in the solution undergo reptation via the curvilinear diffusion. The time increment Δt is given by the following equation:

$$\Delta t = \frac{\tau_b}{N_{micelles}} = \frac{\zeta \tau_{rep}}{N_{micelles}} \quad (11)$$

where τ_b is the breakage time of WLMs, ζ is the ratio of breakage time to reptation time, $N_{micelles}$ is the number of micelles considered in the simulation domain, and τ_{rep} is the reptation time. Furthermore, the reptation of WLMs is simulated by the movement of the pointers in a randomly chosen direction.

Specifically, the corresponding length by which the pointers are moved to simulate reptation is computed by the following equation:

$$\Delta l_R = \sqrt{2D_c \Delta t} \quad (12)$$

where D_c is the diffusion coefficient of WLM chains. The stress relaxation function, $\mu(t)$, is calculated by evaluating the fraction of unrelaxed segment of WLMs in a dynamic fashion. Consequently, the simulation data is processed to obtain the storage and the loss modulus, respectively, as shown in (13) and (14).

$$G'(\omega) = G_N \omega \int_0^T \sin(\omega t) \mu(t) dt \quad (13)$$

$$G''(\omega) = G_N \omega \int_0^T \cos(\omega t) \mu(t) dt \quad (14)$$

where $G'(\omega)$ is the storage modulus, $G''(\omega)$ is the loss modulus, and G_N is the plateau modulus. Once the stress-relaxation models and the dynamic growth models are formulated, a MHE strategy which evaluates the temporal evolution of the zero-shear viscosity of WLMs during the synthesis can be formulated.

2.2 Moving horizon estimator (MHE)

In this section, a MHE is utilized as a soft sensor to obtain the zero-shear viscosity of the WLMs. In practice, the MHE is implemented to incorporate constraints in the estimation procedure and to avoid the linearization of a high-dimensional nonlinear system. Specifically, in

the MHE, an optimization problem is solved to estimate the zero-shear viscosity by considering the measurements of WLM length. Here, the cost function formulated for obtaining the estimates of a nonlinear system is given by the following equation:

$$J = \sum_{i=t-N+1}^t (X_i - \hat{X}_i) W (X_i - \hat{X}_i)^T + \sum_{i=t-N+1}^t (Y_i - \hat{Y}_i) Q (Y_i - \hat{Y}_i)^T + (X_{t-N} - \hat{X}_{t-N}) P (X_{t-N} - \hat{X}_{t-N})^T \quad (15)$$

where $X = [\phi_n, \phi_{2n}, \dots, \phi_{kn}, \dots, \phi_{mn}]$ are the process states representing the number of WLMs with $k \times n$ aggregates, J is the cost function considered in solving the MHE optimization problem to obtain the state estimates, Y are the measured values of the process output, \hat{Y} are the predicted process outputs, \hat{X} are the predicted values of the process states, W is the weight function corresponding to the process noise, Q is the weight function corresponding to the measurement noise, P is the penalty associated with the arrival cost, and N is the estimation horizon of the MHE. Here, the cost function considered has three components: the process noise weighted by W , the measurement noise weighted by Q , and the arrival cost weighted by P . It is to be noted that the consideration of a quadratic function weighted by P for the arrival cost is able to produce stable error dynamics when an appropriate value of P is considered (Alessandri et al., 2010). Therefore, the constrained optimization problem solved in the MHE can be expressed as follows:

$$\begin{aligned} & \min_{X_{t-N} \dots X_t} J \\ \text{s.t.} \quad & \frac{dX(t)}{dt} = j_p(X, u) - j_{p+n}(X, u) + \dot{N}(X, u) \quad (16) \\ & Y = g(X, u) \\ & \mathbf{0} < \mathbb{I}X < \mathbf{1}\phi_n(t_0) \end{aligned}$$

where j_p denotes the influx due the growth of smaller WLMs, j_{p+n} denotes the loss of WLMs due to the loss of monomers, $\dot{N}(p)$ denotes the flux of WLMs due to their breakage and recombination, Y denotes the process outputs (i.e., the mean length and zero-shear viscosity of the WLM solution), g denotes the nonlinear function relating the process states to the process outputs.

Furthermore, u are the process inputs (i.e., pH, salt concentration, and temperature), $\mathbf{1}$ and $\mathbf{0}$ are the unit and zero vectors of size $(m \times 1)$, where m is the dimension of the nonlinear state-space model, $\phi_n(t_0)$ is the number of smallest self-assembling monomers with size n at time $t = 0$, and \mathbf{I} is the identity matrix of size $(m \times m)$. The bounds considered in the inequality constraint are derived from the process knowledge (Pahari et al., 2021c). Here, N is the prediction horizon over which the MHE optimization problem is solved. This value is chosen by making a trade-off between the computational cost and estimation accuracy.

3. SIMULATION SCHEME

The simulation of the WLM growth model proceeds by introducing the aggregates of size n . The number of ag-

gregates of size n is denoted by $\phi_n(t_0)$. The value of n is obtained as the aggregation number of the smallest micelles which participate as the self-assembling monomers. Its value is obtained from the equation, $p = V/\nu$, where V is the volume of the smallest aggregate, and ν is the volume per unit molecule of amphiphile. The volume of the aggregate is computed by $V = \frac{4}{3}\pi R_s^2 \cdot \left(R_s + (R_s^2 - R_c^2)^{0.5}\right)$,

where R_s is the length of amphiphile and $R_c = 0.76 \times R_s$ (Danov et al., 2020; Nagarajan, 2019). Note that the length of amphiphile is related to the chemical structure of specific amphiphile being considered (Nagarajan, 2019). Specifically, for CTAB, the mean length of WLMs is obtained as 2.550 nm. In addition, the value of ν is obtained as $\nu = 0.5385 \text{ nm}^3$. Subsequently, the value of $\phi_n(t_0)$ is obtained by $\frac{\phi \cdot N_{avg}}{p}$, where ϕ is the number of surfactant molecules added to the solution, and N_{avg} is Avogadro's number. Additionally, the value of pre-factor x is 4.25×10^5 , and the value of the correction factor c_{sa} is considered to be 2.77×10^5 , which is identical to that of ellipsoidal micelles (Jensen et al., 2014). Lastly, for the recombination and breakage, $c_1 = c_2 = k_+$.

Meanwhile, the rheology model requires four crucial parameters as follows: persistence length (l_p), WLM diameter (d), flexibility ratio (α), and the ratio of breakage time to reptation time (ζ). The variation of these parameters with respect to the reaction conditions such as salt concentration, pH, and temperature can be observed in (Pahari et al., 2021c). Additionally, for the pointer-based algorithm, WLMs with $N_{micelles} = 20,000$ were considered in the simulation domain.

Henceforth, once the stress-relaxation function is obtained it is utilized to calculate the storage and the loss modulus of WLMs (G' and G'') from which the zero-shear viscosity is calculated by $\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega}$. Subsequently, to implement this model to the MHE problem for online estimation of rheological properties of WLMs, simplistic correlation between the mean length of the WLMs and the zero-shear viscosity is determined. For this, it is assumed that other parameters (e.g., diameter, persistence length, entanglement length, and the ratio of reptation time to recombination time) do not significantly vary over the considered input sequences in the given system. Finally, once the relationship is determined, the output equation of the nonlinear state-space model can be constructed.

Specifically, the MHE is implemented to estimate the zero-shear viscosity of the WLM solution. It is observed that the results from the MHE are susceptible to the values of P associated with the arrival cost. The value of P which gives stable and satisfactory error dynamics is obtained as 19.65. Additionally, the weight matrices Q and W are taken to be 0.001 and 0.01, respectively.

To validate the developed framework, a case study of CTAB/NaCl system is employed. Herein, random input sequences of varying pH, salt concentration, and temperature are generated and provided as inputs to the WLM growth model and the rheology model (i.e., when these two models are combined, they are considered as virtual experiments in this work). Given that the mean length of WLMs can be only measured via experiments (i.e., SAXS),

noise is added to the outputs, which are obtained from the virtual experiments, to accurately reflect the reality. Once these measurements are obtained, they are utilized as the inputs of the MHE. Consequently, the MHE can estimate the mean length of the WLMs and the zero-shear viscosity of the solution.

4. RESULTS AND DISCUSSIONS

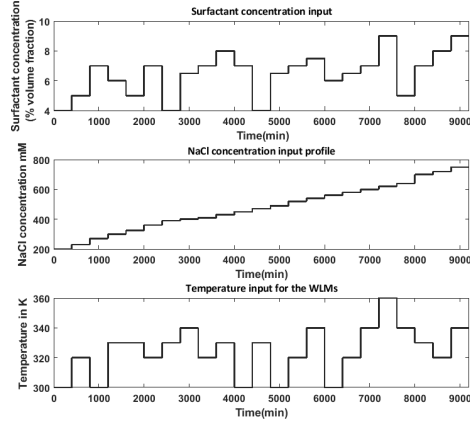
In this section, we highlight the open-loop simulations followed by the discussion on the estimation results of the proposed MHE as a soft sensor to measure the zero-shear viscosity during the synthesis of WLMs.

4.1 WLM growth simulation

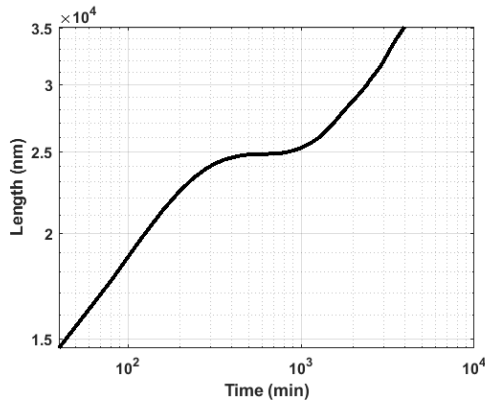
As shown in Fig. 3a, the input sequences of surfactant concentration, pH, and temperature are randomly generated as bounded within the practical operation limits (Pahari et al., 2021a). Thus, the evolution of the mean length with respect to the obtained input sequences is highlighted in Fig. 3b. Subsequently, the stress-relaxation function $\mu(t)$ (Fig. 4a) and the storage-loss modulus (Fig. 4b) for different WLM mean lengths of 4,000 nm and 6,000 nm are evaluated. From those rheology parameters, the zero-shear viscosity is found to be 5.86 Pa · s and 60.76 Pa · s for the mean length of 4,000 nm and 6,000 nm, respectively. Thus, this implies that the proposed model can capture the solution viscosity with varying mean lengths of WLMs. Therefore, multiple simulations were carried out to identify an empirical relationship between inputs (i.e., the mean length of WLMs and surfactant concentration) and output (i.e., zero-shear viscosity) by varying the inputs. Specifically, LASSO regression was performed to identify the relationship between the inputs and the output. The obtained empirical relationship is as follows:

$$\begin{aligned} \eta_0 = & -5.445 \cdot 10^{-17} \cdot \langle L \rangle^5 + 1.185 \cdot 10^{-12} \langle L \rangle^4 - \\ & 9.562 \cdot 10^{-9} \cdot \langle L \rangle^3 + 0.00003494 \cdot \langle L \rangle^2 \cdot c_s - \\ & 0.04625 \cdot \langle L \rangle + 21.02 \end{aligned} \quad (17)$$

where $\langle L \rangle$ is the mean length of the WLMs, and c_s is the concentration of the surfactant added to the solution. As shown in Fig. 6, the predicted values and fitting values of zero-shear viscosity are presented with R_{squared} value of 0.910. Then, this relationship was utilized in the nonlinear model in the MHE to obtain the zero-shear viscosity as an output. Specifically, in this CTAB/NaCl system, the synthesis process continues for two days, and hence, WLMs are likely to grow to substantially long chains, producing products with an extremely high zero-shear viscosity (Pahari et al., 2021c). In other words, operation failures may happen once the zero-shear viscosity exceeds a specific value (e.g., 2,000 Pa · s), which also results in multiple shortcomings. Additionally, the output (i.e., zero-shear viscosity) is highly sensitive to operating conditions, and all operational decisions are based on such output so that the online estimation of the zero-shear viscosity is significant. Moreover, in practice, the measurements of the mean length of WLMs are available in every 40 minutes, which are not sufficient to update the rheological properties of WLMs in real time. Hence, the proposed framework is appropriate to accurately estimate the viscosity during



(a)



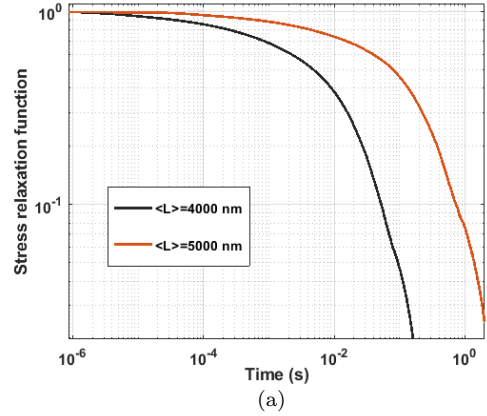
(b)

Figure 3. The results highlighting (a) the input sequence, and (b) mean length evolution of WLMs with respect to time.

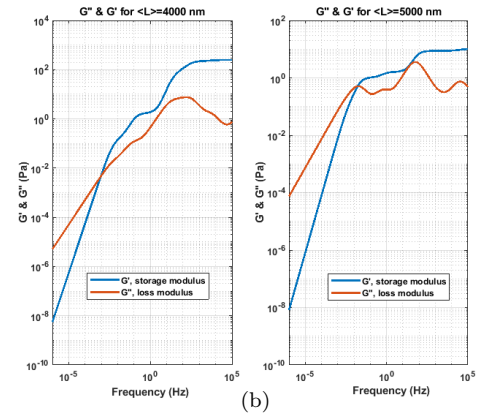
the process even with extremely sparse measurements of process variables such as the mean length of WLMs.

4.2 Moving horizon estimation

Once the nonlinear system is obtained from the input and output relationship, the MHE optimization problem is solved while considering the set of nonlinear equation as a constraint and the set of bounds on the process states. Herein, the set of inputs (Fig. 3a) was fed into the computationally expensive WLM growth model and rheology model (i.e., the virtual experiments) to obtain process measurements (i.e., the mean length and the zero-shear viscosity of WLMs). Note that only the mean length is measured at a sampling period of 40 minutes. Then, white gaussian noise is added to the measurements to include measurement uncertainties. Finally, the MHE estimator utilizes the mean length of WLMs to obtain online estimates of the mean length (Fig. 6) and zero-shear viscosity (Fig. 7) of the solution. As shown in Figs. 6 and 7, the estimates show high accuracies for both mean length and zero-shear viscosity. Here, an optimal set of weight vectors derived via trial and error is employed to obtain such results. For the regimes where measurements are sparse and noisy, it should be noted that the nonlinear model in the estimation problem successfully provides good estimates.



(a)



(b)

Figure 4. Figure highlighting (a) Stress-relaxation function for WLMs of mean length $\langle L \rangle = 4000$ nm and $\langle L \rangle = 6000$ nm, and (b) Storage and loss modulus of WLMs for mean lengths 4000 nm and 6000 nm.

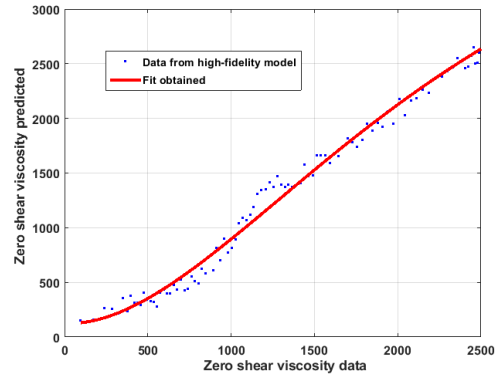


Figure 5. Regression of data obtained from high-fidelity model.

5. CONCLUSION

In this study, an MHE developed with a quadratic arrival cost was utilized as a soft sensor to obtain the estimates of zero-shear viscosity during the production of supercolloidal self-assemblies such as WLMs. A nonlinear state-space model, which includes the population balance of the WLMs, was utilized to obtain the structural evolution of the WLMs during the synthesis process. Subsequently, a pointer-based rheology model was implemented to obtain the zero-shear viscosity of the WLMs. However, the high-fidelity model comprising of the nonlinear state-space

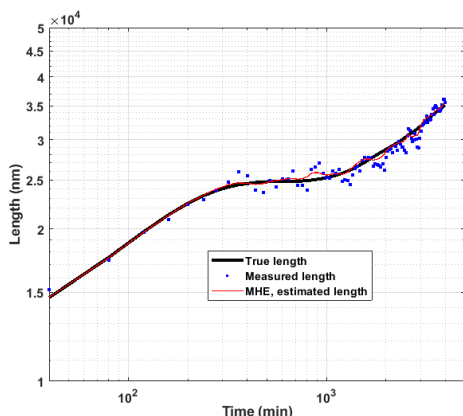


Figure 6. Mean length of WLMs estimated by the MHE.

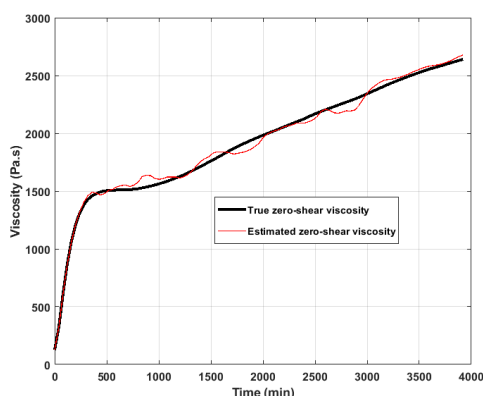


Figure 7. Zero-shear viscosity estimated by the MHE.

model and the pointer based algorithm is computationally expensive. Hence, for utilizing the high-fidelity model in the MHE, a regression model that relates the mean length of WLMs and surfactant concentration to the zero-shear viscosity of the solution was identified. Then, the identified regression model was utilized with the nonlinear state-space model to predict the zero-shear viscosity relatively faster. Utilizing this nonlinear model and regression model as constraints, the MHE optimization problem was solved to obtain online estimates of zero-shear viscosity of the WLM solution. Finally, as a case study, the proposed soft sensor was applied to the system of CTAB and NaCl while considering crucial variables such as pH, temperature, and salt concentration. The results verified that the MHE was able to accurately estimate the mean length and zero-shear viscosity in the presence of noisy and sparse measurements. In the future study, given that no linearization approximation of the system dynamics has been carried out, the performance of MHE can be compared with Extended Kalman Filter (EKF).

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