

Supporting Information

The Mechanism Difference between CO₂ and pH Stimuli for a Dual Responsive Wormlike Micellar System

Caili Dai, Qianru Yang, Mingwei Gao, Mingwei Zhao*, Jianfeng Jiang*

School of Petroleum Engineering, State Key Laboratory of Heavy Oil Processing,

China University of Petroleum (East China), Qingdao 266580, P. R. China

Caili Dai Email: daicl@upc.edu.cn

Tel: +86-532-86981183 Fax: +86-532-86981161

Mingwei Zhao Email: zhaomingwei@upc.edu.cn

Tel: +86-532-86981183 Fax: +86-532-86981161

For the better understanding of this system, effect of temperature on the system has been done on the rheological properties. The steady shear viscosity curve of this system at different temperatures can be shown from Figure S1 a. The three curves all can be fallen into two parts, which showed the zero steady shear viscosity (η_0) in the low steady shear rate, while shear-thinning behavior was performed in the higher steady shear rate. It is usually regarded as the formation of wormlike micelles^{1,2}. At 35 °C, η_0 reaches the maximum value. This may be due to the tight wormlike micelles and stable network structure at 35 °C.

Besides steady shear measurements, oscillatory shear measurements at different temperatures are shown in Figure S1 b. The systems all showed liquid-like behavior and solid-like behavior at low shear frequencies and high shear frequencies (ω), respectively. The elastic modulus (G') growth rate is greater than viscous modulus (G'') with the increasing shear frequencies, the two curves intersect at the shear rate (ω_c). With the increase of the shear frequencies, G' kept on increasing until a platform modulus value (G_0) while the G'' reached the crest and then decreased. When G'' decreased to the minimum, the value is called G_{min}'' . Overall, these rheological behaviors (steady shear measurements, oscillatory shear measurements) are the typical representation of wormlike micelles, which follow the Maxwell's model³⁻⁵. Thus, the behaviors of the system accords with Maxwell equations:

$$G'(\omega) = G_0 \frac{\omega^2 t_R^2}{1 + \omega^2 t_R^2} \quad (1)$$

$$G''(\omega) = G_0 \frac{\omega t_R}{1 + \omega^2 t_R^2} \quad (2)$$

$$t_R = \frac{1}{\omega^*} \quad (3)$$

$$G_0 = 2G^* \quad (4)$$

Where G_0 and ω are the platform modulus and angular rate, respectively, and t_R is the relaxation time calculated from equation (3). If G_0 cannot reach the platform, G_0 value can be estimated by equation (4).

To further prove how well the system fit with the Maxwell model with the rising of temperature, the Cole-Cole plot is commonly used. Cole-Cole plot is a curve of G' as a function of G'' . The equation is as follows, which is established by equation (1) and (2):

$$G''^2 + \left(G' - \frac{G_0}{2}\right)^2 = \left(\frac{G_0}{2}\right)^2 \quad (5)$$

In Figure S1 c, in the low shear frequencies, the experimental points fit well with the theoretical line reckoned through equation (5) due to Rouse relaxation modes^{6, 7}. While the deviation appears at higher shear frequencies since Rouse relaxation modes⁸. With the rise of temperature, the deviation occurs at smaller shear rate because of different micelle winding degrees.

In addition, as Maxwell model fluid, the average micellar contour length (L) of wormlike micelles can be calculated as follows:

$$L \approx l_c \frac{G_0'}{G_{min}''} \quad (6)$$

Where l_c is the average length between entanglement points, which typical value of 80-150 nm is known from the above reference⁹. G_{min}'' is the minimum of the viscous modulus (G'') in the high shear frequencies.

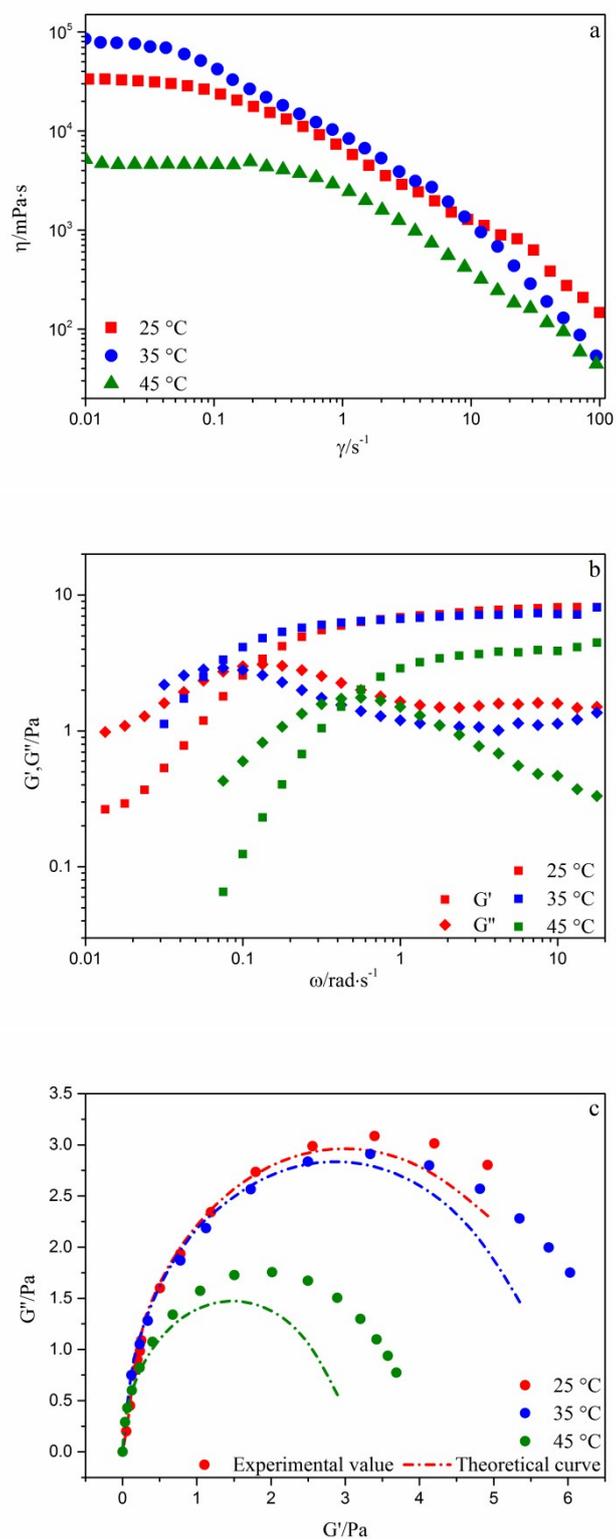


Figure S1. 40 mM NDPD and 60 mM NaSal system at different temperatures: (a) steady shear viscosity curve; (b) G' and G'' versus frequencies; (c) Cole-Cole plots.

References

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