

## Effect of Arabic Gum and Xanthan Gum on the Stability of Pesticide in Water Emulsion

Xiaoguang Zhang<sup>\*,†</sup> and Jiexiang Liu<sup>‡</sup>

<sup>†</sup>College of Chemistry, Nankai University, Tianjin 300071, People's Republic of China, and

<sup>‡</sup>School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, People's Republic of China

**ABSTRACT:** The effect of arabic gum (AG) and xanthan gum (XG) on the physicochemical properties of 2% pesticide avermectin in water emulsions was systematically investigated by measuring creaming stability, droplet size, zeta potential, and rheology. Addition of AG and XG had significant influence on the physicochemical properties of emulsions. Emulsions showed high stability throughout the storage time in the AG concentration range of 0–0.14%. In contrast, addition of XG induced the apparent creaming of emulsion as the XG concentration increased from 0.011 to 0.15%, which might be well explained by the depletion flocculation of droplets. The droplet diameter increased progressively with increasing AG concentration; however, it sharply grew initially with XG concentration and reached a maximum, followed by a gradual decrease. Zeta potential increased gradually as AG concentration was lower than 0.081%, followed by a slight decrease, whereas it reduced dramatically as XG concentration increased from 0.011 to 0.040% and then remained almost unchanged. In the AG concentration range of 0–0.14%, the emulsion exhibited typical Newtonian flow behavior and the viscosity decreased a little. The XG emulsion exhibited Newtonian flow behavior at low XG concentrations ( $\leq 0.019\%$ ), whereas, non-Newtonian flow behavior was displayed at relatively high XG concentrations ( $>0.019\%$ ), wherein viscosity value and yield value increased gradually as XG concentration increased. In addition, the curves of shear stress versus shear rate for XG emulsion and solution were well fitted by a power law model and the Herschel–Bulkley model; the Herschel–Bulkley model fitted much better. The present study would provide useful information for the reasonable application of AG and XG in making stable pesticide emulsion.

**KEYWORDS:** Emulsion stability, arabic gum, xanthan gum, depletion flocculation, droplet diameter, zeta potential

### INTRODUCTION

An emulsion may be defined as a heterogeneous system, consisting of at least two immiscible liquids or phases, one of which is dispersed in the form of droplets in the other. Emulsions are extensively used in many fields such as petrochemicals, cosmetics, paints, pharmaceuticals, food and agricultural products. They are thermodynamically unstable systems that tend to break down over time due to a variety of physicochemical mechanisms, for example, gravitational separation, creaming, flocculation, and Ostwald ripening.<sup>1</sup> However, kinetically stable emulsions can be achieved by adding emulsifiers and/or polysaccharides to overcome the activation energy of the system. Emulsifiers are mainly surfactants that can be adsorbed to the droplet surfaces, lowering surface tension and preventing the droplets from coming close enough together to aggregate. Polysaccharides are widely used to stabilize oil in water emulsions and to control rheological properties. Arabic gum (AG) and xanthan gum (XG) are two kinds of the most commonly employed polysaccharides. AG consists of six carbohydrate moieties and a small proportion of protein (polypeptide chain). It possesses high water solubility, low solution viscosity, and low interfacial activity.<sup>2</sup> The hydrophobic groups on protein are thought to anchor AG to the surface of emulsion droplets, whereas the hydrophilic carbohydrate branches extend into the solution, providing stability against droplet aggregation through steric and electrostatic repulsion.<sup>2,3</sup> XG is an anionic polysaccharide produced by the bacterium *Xanthomonas campestris*. XG has a cellulose backbone with a

trisaccharide side chain at the C-3 atom. The terminal mannose residues are 4,6-pyruvated, which can chelate prooxidant metal ions to inhibit lipid oxidation. The most important characteristics of XG are high low-shear viscosity and strong shear-thinning character. In addition, XG is a nonadsorbing polysaccharide and does not bind to the droplet surface. As the droplets come closer together due to Brownian motion, the region between emulsion droplets is depleted of XG, leaving only the solvent. This induces a concentration gradient of XG between the interparticle region and the bulk solution hence, produces osmotic pressure. The solvent between droplets tends to diffuse out to reduce the XG concentration gradient, causing droplets to aggregate. This is known as depletion flocculation.<sup>4</sup> The degree of flocculation of emulsion droplets depends mainly on the XG concentration, stabilizers, and oil volume fraction. The stability of the emulsion is markedly improved at the relatively high concentration of XG due to the droplet network structure formed in the continuous phase and/or a very high apparent viscosity of the continuous phase.<sup>5–7</sup> In recent years, Mirhosseini et al.<sup>8,9</sup> have investigated the effect of AG and XG mixture on the physicochemical properties of orange beverage emulsion. The high concentration of AG along with low content of XG led to the highest emulsion

**Received:** September 8, 2010

**Accepted:** December 15, 2010

**Revised:** December 15, 2010

**Published:** January 12, 2011

stability.<sup>9</sup> These reports focused mainly on food emulsions by the addition of AG and XG, wherein the concentration of AG was relatively high due to the low interfacial activity. However, the concentration of AG and XG in the preparation of pesticide emulsion cannot be high due to the expensive AG and low-viscosity requirement for emulsion.

A pesticide in water emulsion is a kind of water-based formulation for crop protection, which is widely viewed as a green and environmentally friendly formulation. Compared to emulsifiable concentrate and microemulsion, the amount of solvent and/or emulsifier used in emulsion is decreased remarkably. However, the destabilization of emulsion restricts badly its quick development. At present, one key problem that needs to be resolved urgently in agrochemical formulation is the improvement of its stability and retention of a long product shelf life. Although many studies on emulsions stabilized by small molecule surfactants<sup>10–12</sup> have already been reported, these emulsion systems are difficult to keep highly stable for long time. To improve pesticide formulation stability, emulsifiers and polysaccharides are often used together in practice. The stability of suspension concentrate (SC) has been enhanced by polysaccharide,<sup>13–15</sup> and viscosity is usually in the range of 500–1000 mPa·s. Stable pesticide emulsions have been also achieved by adding a suitable polysaccharide; however, its viscosity is only several mPa·s. Polysaccharide is predicted to play different roles in emulsions from suspension concentrates. Gamal et al.<sup>16</sup> have reported that the relatively high concentration of XG enhanced the stabilization of the essential oil-based W/O/W multiple emulsions containing Span 80 and Tween 80. To the best of our knowledge, the systematic study of the stabilization of pesticide emulsion containing polysaccharides has been seldom performed up to now, and the stabilization mechanism of emulsion has been not fully cleared up. Avermyctin is an important insecticide that is already used widely in cotton, rice, vegetables, etc. Statistical data reveal that the sales of avermyctin were up to U.S. \$290 million in the global market in 2007. The avermyctin formulation is mainly sold in the form of emulsifiable concentrate. Recently, the emulsion and microcapsule of avermyctin have been also investigated.<sup>7–19</sup> Chen et al.<sup>17</sup> obtained the primary avermyctin emulsion formulation by application of the pseudo ternary phase diagram, and small molecular surfactants were employed to stabilize the emulsion. The long-term stability of emulsion needs to be investigated further. In our previous study,<sup>18</sup> the small droplet diameter and large negative charge of the droplet surface were greatly beneficial to the stability of avermyctin emulsion. In continuation of our previous studies, this study attempted to obtain a much stabler emulsion formulation of avermyctin by the addition of AG and XG to relatively stable emulsions. The aim of this paper is to investigate the influence of AG and XG on creaming stability, droplet size, zeta potential, and rheology and to discuss their roles in stabilizing O/W emulsions. It is further attempted to gain an insight into the stability mechanism of pesticide emulsion.

## MATERIALS AND METHODS

**Materials.** The pesticide avermyctin,  $w(B_1) = 95.2\%$ , was obtained from North China Pharmaceutical Group Aino Co., Ltd. Arabic gum powder was purchased from Sinopharm Chemical Reagent Co., Ltd., and xanthan gum of food grade was purchased from Zibo Cargill Huanghe-long Bioengineering Co., Ltd.. Technical grade surfactants polyoxyethylene (40) castor oil ether (EL-40), polyoxyethylene (20) castor oil ether (EL-20), and octyl phenyl polyoxyethylene phosphonate (OPP) were supplied by Xingtai Lantian Jingxi Chemical Co., Ltd. Xylene and

propylene glycol, of A.R. grade, were purchased from Tianjin Medicine Co. All water used was deionized water or fresh doubly distilled water.

**Emulsion Preparation.** The pesticide avermyctin was dissolved in an appropriate amount of xylene. The surfactant mixtures of EL-40, EL-20, and OPP in appropriate ratio were added to the pesticide solution, which was an oil phase. The appropriate amount of polysaccharide (AG or XG) covering a certain range of concentration was dissolved in deionized water containing the proper amount of propylene glycol and was gently stirred for several hours at room temperature before use, which was as water phase. The emulsion was then prepared by adding slowly the oil phase to the water phase, and after the pre-mix, the mixture was emulsified at 5500 rpm for 20 min at 25 °C. The mass percentages of avermyctin, surfactants, and propylene glycol were 2, 6, and 6%, respectively.

**Stability Measurement.** Approximately 20 mL of freshly prepared emulsion was transferred into a glass tube, then sealed and stored at room temperature. The emulsion volume was read at different times to monitor stability to creaming and coalescence throughout the storage time. The emulsion stability with time was assessed by monitoring the variation of the emulsion volume. Measurement errors were about 2.0%.

**Conductivity Measurement of Emulsion Containing Xanthan Gum.** The emulsion containing XG presented phase separation at 12 h after preparation; at the bottom of the tube was a translucent serum phase and at the top was an emulsion. The emulsion and serum phases were separated first, and then the conductivities were measured with gentle stirring using a DDSJ-308A digital conductometer (Shanghai Precision & Scientific Instrument Co., China) at 25 °C. Measurement errors were about 0.5%.

**Droplet Size Distribution and Zeta Potential Measurements.** The droplet size distribution in the emulsion was determined using BI-90plus (Brookhaven Co.) at 25 °C. Emulsion was prepared and stored at room temperature for 24 h prior to analysis. Measurement was carried out after appropriate dilution of the emulsion with fresh doubly distilled water filtered through a Millipore 0.20 μm membrane filter before use. It was confirmed in advance that the dilution process did not significantly change the droplet size. The measurement errors were <0.5%.

The zeta potential in the emulsion was determined using Zeta PALS (Brookhaven Co.) at 25 °C. An electrophoresis electrode was inserted in the measurement chamber after droplet size measurement. The apparatus first measured the electrophoretic mobility of colloidal particles dispersed in aqueous solution and then automatically calculated the zeta potential using the Smoluchowski equation. The zeta potential was an average value obtained by nine readings per sample. The average deviations of the measurements were <5%.

**Rheological Measurements of Polysaccharides Solution and Emulsion.** The rheology of the polysaccharide solution and emulsion was carried out on a Haake RheoStress RS75 rheometer using double-gap geometry at 25 °C. All measurements were performed before emulsion sample phase separation. Measurement error was <1.0%. In addition, a power law model (eq 1) and the Herschel–Bulkley model (eq 2) were also used to analyze flow curves and estimate the yield stress:

$$\tau = k\dot{\gamma}^n \quad (1)$$

$$\tau = \tau_0 + k\dot{\gamma}^n \quad (2)$$

$\dot{\gamma}$  is shear rate,  $n$  is a flow behavior index,  $\tau_0$  is yield stress, and  $k$  is a consistency index.

## RESULTS AND DISCUSSION

**Effect of AG and XG on the Stability of Emulsions.** The appearance of emulsions containing AG and XG at 12 h after preparation is displayed in Figure 1. It is obvious that there are different stabilities in the two kinds of emulsions. In Figure 1a, there is little turbid layer near the surface of the emulsion in the

AG concentration range of 0–0.14%. In contrast, apparent creaming is observed in the emulsion with XG in Figure 1b, and the translucent serum phase is at the bottom of tube, and the emulsion is at the top. Moreover, the emulsion volume decreases gradually as XG concentration increases from 0.011 to 0.15%, whereas the serum volume has a corresponding increase. Here, the serum phase is promoted with the increase of XG concentration. A similar phenomenon has been also observed by other workers<sup>20–22</sup> in emulsions containing polysaccharides. In addition, it is also important to examine the stability of emulsions with storage time. The detailed investigation follows.

Figure 2 shows the stability of emulsions with storage time at different concentrations of AG and XG. For emulsions with AG, the volume fractions of emulsions are almost above 95% in the whole concentrations range studied and remain almost unchanged for about half a year. For emulsions with XG, the emulsion volume fraction decreases gradually over several days initially and then remains almost constant during the storage. It should be pointed out that the emulsion volume fraction reduces markedly with the increase in XG concentration, which means that the stability of the emulsion decreases sharply as XG concentration increases.

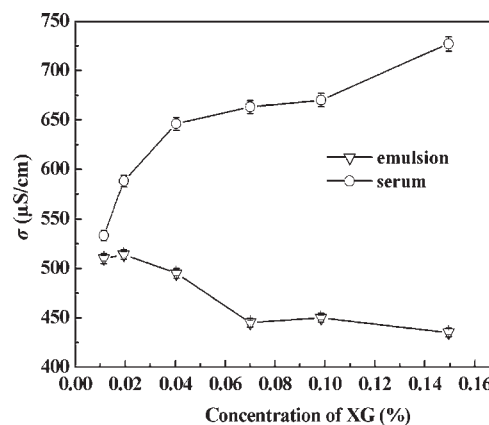
To probe the distribution of XG between emulsion and serum phase, conductivity measurement was carried out and is presented in Figure 3. The conductivity comes mainly from the contribution of XG because XG is in itself a polyelectrolyte. The conductivity of the serum phase rises markedly as XG concentration increases, whereas that of the emulsion reduces gradually. This implies that the greater XG distribution is in the serum phase with the increase of XG concentration, whereas less distribution is in the emulsion. A greater difference of conductivity between emulsion and serum phase indicates that many more XG molecules

transfer from the continuous phase of emulsion to the serum phase with increasing XG concentrations. Conductivity measurement indirectly demonstrates that the appearance of the serum phase is due to the depletion flocculation induced by XG. A similar phenomenon has been also detected by Manoj et al.,<sup>23</sup> who showed that the hydroxyethylcellulose (HEC) concentration in a HEC-rich region was higher than the total HEC concentration due to depletion flocculation. Later, Drakos et al.<sup>24</sup> also proposed that the phase separated into XG-rich and XG-depleted regions at high XG concentration because of depletion flocculation.

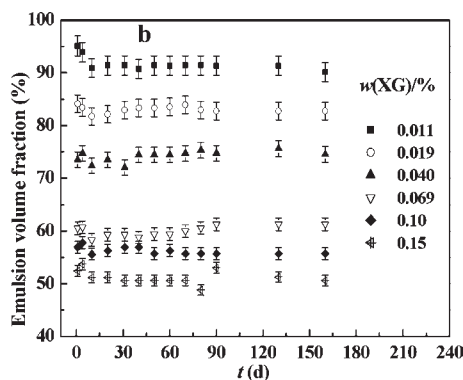
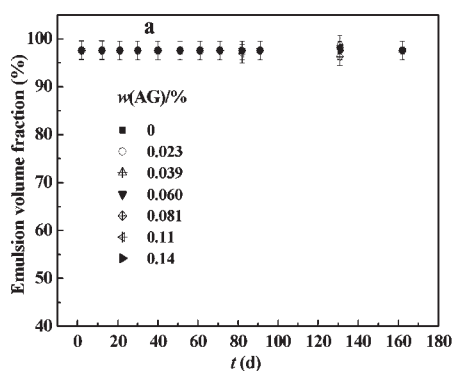
The distinct effect of AG and XG on the stability of emulsions depends closely on the type and concentration of polysaccharide. For the emulsion with AG, the polypeptide chains of AG attach to the droplet surface and produce the net negative charge at the droplet surface, whereas the carbohydrate blocks protrude into the continuous phase and produce the steric (repulsive) effect. The electric charge at the droplet surface enhances gradually with increasing AG concentration, and the steric effect also increases correspondingly. Both electrostatic and steric stabilizations contribute to the emulsion stability; thereto, steric stabilization plays a dominant role.<sup>3,25</sup> Mirhosseini et al.<sup>8</sup> have demonstrated that AG had a negative effect on the emulsion stability at high concentration due to a large excess of nonadsorbed AG that induces depletion flocculation.<sup>26</sup> However, the concentration of AG is relatively low and emulsion remains very stable in our study, which suggests that AG molecules only adsorb onto the droplet surface without lying in continuous phase at low levels of AG addition. The emulsion with XG exhibits extensive creaming



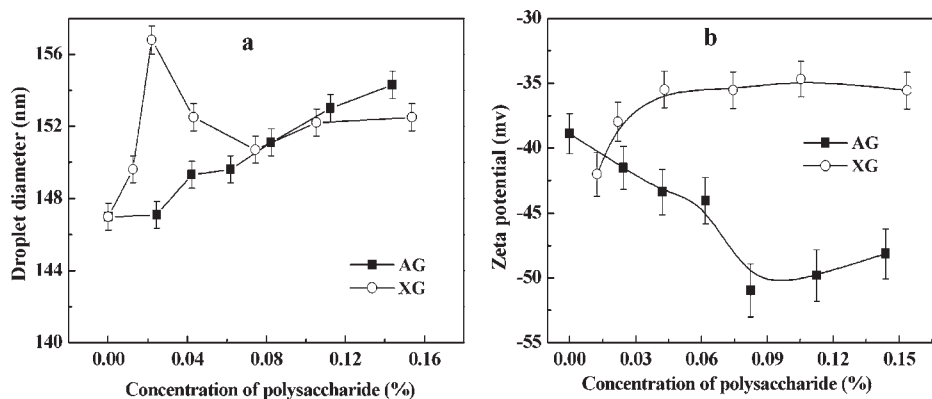
**Figure 1.** Photographs of emulsions prepared with AG (a) and XG (b) after preparation for 12 h at room temperature: (a) concentration of AG in the sequence 0, 0.023, 0.039, 0.060, 0.081, 0.11, and 0.14% from left to right; (b) concentration of XG in the sequence 0.011, 0.019, 0.040, 0.069, 0.10, and 0.15% from left to right.



**Figure 3.** Variation of conductivity in emulsion and serum phase with XG concentration.



**Figure 2.** Variation of volume fraction for emulsion containing AG (a) and XG (b) with storage time.



**Figure 4.** Dependence of droplet diameter (a) and zeta potential (b) on the concentration of polysaccharides.

with increasing XG concentration, which may be attributed to depletion flocculation of the emulsion droplets.<sup>27–29</sup> When XG is added to the emulsion, the flocculation of droplets occurs via the depletion mechanism. As a polyelectrolyte polymer, XG molecules do not adsorb at the interfaces; rather, there is electrostatic repulsion between XG molecules and emulsion droplets because both of them have net negative charges. XG molecules are excluded from the region between droplets at close separation. Hence, the concentration of XG in the region between the droplets is lower than in the bulk phase. Thereby an osmotic pressure is formed, which prompts the solvent of the region between the droplets to flow out. This process may enhance the drainage and decrease the viscosity of the continuous phase between the droplets. As a consequence, the volume of this region between the droplets decreases, the droplets approach further, and the serum phase volume rises.<sup>27</sup> In addition, electrostatic repulsion between droplets may be reduced due to electrostatic screening of XG that resembles electrolyte (such as NaCl). The screening of the electrostatic interactions reduces the height of the energy barrier, and the electrostatic attraction between droplets increases. As the XG concentration increases, the attractive forces (osmotic attraction and van der Waals) become great enough to overcome the repulsive forces, and the droplets tend to flocculate into a secondary minimum; thus, droplets aggregate and induce the depletion flocculation. Ye et al.<sup>27</sup> have also used it to explain the flocculation phenomenon induced by XG.

**Effect of Polysaccharides on the Droplet Diameter and Zeta Potential.** The effect of polysaccharides on droplet diameter and zeta potential is investigated and presented in Figure 4. In Figure 4a, the droplet diameter of AG emulsion enhances gradually with increasing AG concentration. By contrast, the droplet diameter of XG emulsion increases initially with the increase of XG concentration and reaches a maximum, followed by a sharp decrease at high concentration, and finally remains almost unchanged. Ye et al.<sup>27</sup> have also observed a similar phenomenon in O/W emulsions containing hydrolyzed whey protein and XG. For the AG emulsion, droplet diameter depends mainly on the adsorption of AG. As AG concentration increases, more AG molecules adsorb on the droplet surface, and the interface layer becomes thicker; thus, droplet diameter increases. Moreover, steric stabilization enhances with the increase of AG molecules adsorbed, which would improve the stability of emulsion. In the XG emulsion, XG molecules locate in the continuous phase of emulsion and the serum phase. At low XG concentrations, the weak flocculation of droplets takes place, which makes droplets aggregate, and droplet diameter increases suddenly. This has been also used by Ye et al.<sup>27</sup> to explain that the droplet

diameter increased at low XG concentrations. They thought that the creaming rate was lowered due to the high viscosity of the aqueous phase at XG concentrations >0.2%, which resulted in the decrease of droplet diameter. However, the electrostatic screening of XG may play an important role in the XG emulsion in our work. As the concentration of XG increases gradually, the screening of the electrostatic interactions increases and the solvent of the region between the droplets diffuses out, which compresses the electrical double layer and reduces the distance of electrostatic repulsion; therefore, the droplet diameter decreases. As the addition of XG continues to increase, the depletion flocculation becomes much stronger. Here, XG concentration in serum phase increases, whereas that in continuous phase may remain constant, which makes the screening of the electrostatic interactions remain unchanged, and hence droplet diameter remains almost constant.

In Figure 4b, it is found that the zeta potentials for all emulsions are negative. For the AG emulsion, the zeta potential value increases sharply when the concentration is increased from 0 to 0.09% and then reduces a little. For the XG emulsion, the zeta potential value reduces suddenly when the concentration is <0.04%, and then it remains nearly unchanged. For the AG emulsion, the zeta potential is closely dependent on AG adsorption on the droplet surface. The adsorbed AG amount on the droplet surface increases with the increase of AG concentration; thus, droplet charge enhances correspondingly. As the concentration of AG is >0.081%, droplet volume increases due to the increase of droplet diameter, which may cause the slight decrease in charge density; hence, the zeta potential decreases a little. The increase in droplet charge would strengthen the electrostatic repulsion among the droplets and prevent droplet aggregation. In addition, the zeta potential values of AG emulsions are found to be higher than  $-37.5$  mv, which can prevent particle contact and produce a stable system.<sup>30</sup> For the XG emulsion, it is interesting to find that the trend of zeta potential value with the XG concentration is well consistent with that of the conductivity of XG in emulsion mentioned in the former. Initially, a reduction in zeta potential value is due to apparent compression of the electrical double layer in the presence of XG. Zeta potential values remain almost constant at high XG concentration, which indicates that a few XG molecules exist in continuous phase and many XG molecules are in the serum phase. The trend of zeta potential values agrees well with that of conductivity of XG in emulsion, which confirms again that XG induces the depletion flocculation.

**Rheology Measurements of Solution and Emulsion Containing Polysaccharides.** To further elucidate the effect of polysaccharides

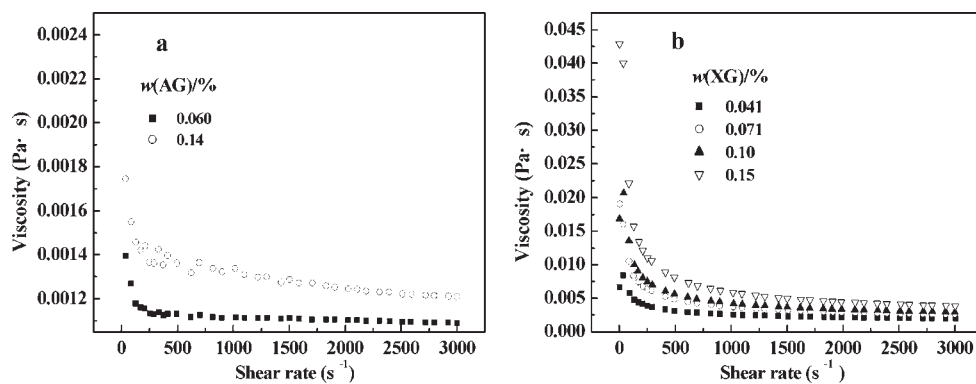


Figure 5. Viscosities of solutions as a function of shear rate at various concentrations of AG (a) and XG (b).

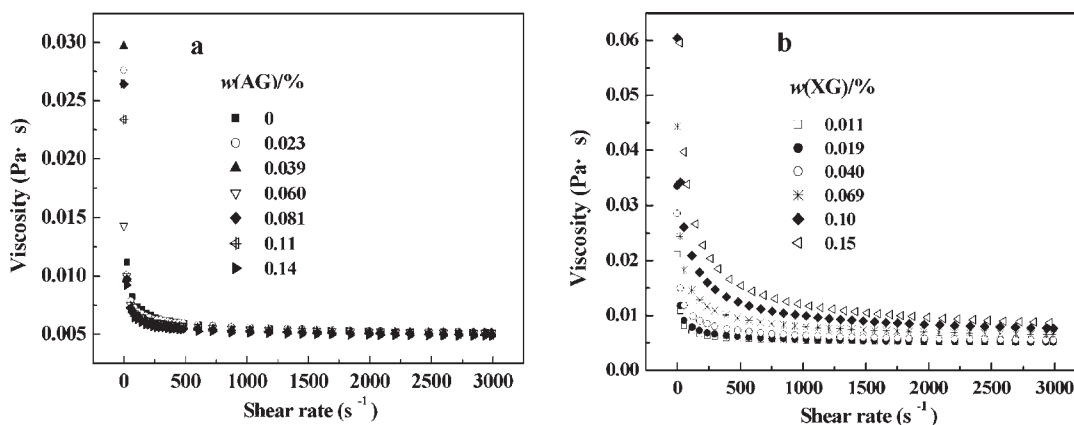


Figure 6. Viscosities of emulsions as a function of shear rate at various concentrations of AG (a) and XG (b).

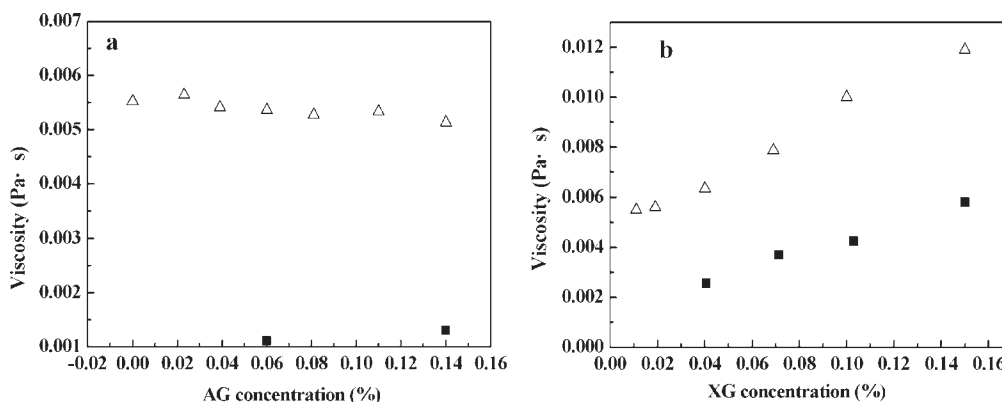
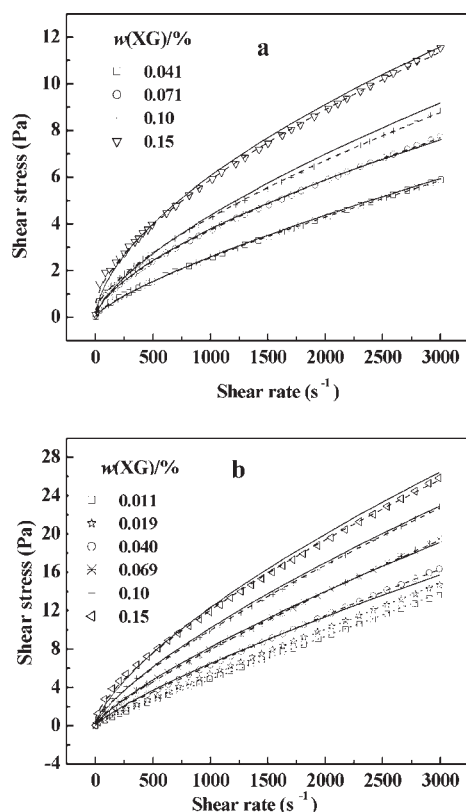


Figure 7. Viscosities of solution (■) and emulsion (Δ) as a function of AG (a) and XG (b) concentrations at a shear rate of 1000 s<sup>-1</sup>.

(AG and XG) on the stability of emulsion, the rheological behaviors of solutions and emulsions containing polysaccharides are investigated and compared. The viscosities of polysaccharide solutions and emulsions as a function of shear rate are shown in Figures 5 and 6, respectively. In Figure 5a, AG solutions behave like a Newtonian liquid (i.e., viscosity essentially independent of shear rate) with low apparent viscosity, which is well in agreement with the results of Islam et al.<sup>2</sup> In Figure 5b, solutions containing XG exhibit shear-thinning behavior with low-shear viscosity increasing with XG concentration, which are identified as non-Newtonian liquids.

In Figure 6a, the AG emulsion shows typical Newtonian flow behavior in the concentration range of 0–0.14%, and the viscosity decreases slightly with concentration. In Figure 6b, emulsions show typical Newtonian flow behavior at low XG concentrations ( $\leq 0.019\%$ ), whereas non-Newtonian flow behavior is detected at relatively high XG concentrations ( $\geq 0.040\%$ ), and their viscosity values at a given shear rate increase progressively with increasing XG concentration. This similar phenomenon has been also observed by Sun et al.<sup>6</sup> As the shear rate sufficiently increases to overcome the Brownian motion, the droplet–droplet interaction is deformed and eventually disrupted,<sup>31</sup> and the emulsion

droplets become more ordered along the flow field and offer less resistance to flow; thus, viscosity decreases.<sup>32,33</sup> It is also found that the shapes of the viscosity–shear rate profiles for the XG emulsions (Figure 6b) are similar to those for the XG solutions (Figure 5b). The non-Newtonian flow behavior displayed in XG emulsions is closely correlated with the extent of flocculation. Although emulsion droplets appear partially flocculated at low



**Figure 8.** Shear stress as a function of shear rate for solution (a) and emulsion (b) containing XG and the curves fitted by the power law model (—), Herschel–Bulkley model (---), and linear model (···).

XG concentration ( $\leq 0.019\%$ ), they still display Newtonian flow behavior. With increasing XG concentration from 0.040 to 0.15%, the extent of flocculation increases progressively, and the effective volume fraction of the flocs increases;<sup>34</sup> hence, non-Newtonian flow behavior is more apparent.

The viscosities of solutions and emulsions at a shear rate of  $1000\text{ s}^{-1}$  are plotted as a function of polysaccharide concentration in Figure 7. In Figure 7a, the viscosity value of the AG emulsion decreases slightly with increasing AG concentration, which is much higher than that of AG solution. Addition of AG has little effect on the viscosity of the emulsion. This may be because the rigidity of the interface layer increases a little with the increase of adsorbed amount of AG molecules on the droplet surface. In Figure 7b, the apparent viscosity values of both emulsion and solution increase markedly with XG concentration increasing from 0.011 to 0.15%, and the viscosity value of emulsion is distinctly higher than that of solution at the same XG concentration, which indicates that XG concentration plays a dominant role in influencing viscosity value. The viscosity enhancement of emulsion may be attributed to the higher effective volume fraction of the flocculated structure, and weak gels could form in emulsions at XG concentrations of  $>0.040\%$ .<sup>35</sup>

The dependence of shear stress on shear rate for solution and emulsion of XG is shown in Figure 8. In Figure 8a, the shear stress of a solution increases sharply as shear rate increases, followed by a linear increase. In Figure 8b, it can clearly be observed that there is a linear relationship between shear stress and shear rate at low XG concentrations of 0.011 and 0.019%. The curves of shear stress versus shear rate for XG emulsions are similar to those for solutions at XG concentrations of  $>0.040\%$ . In addition, the power law model and the Herschel–Bulkley model are also used to fit curves of shear stress versus shear rate at XG concentrations  $>0.040\%$ , and the curves fitted with line and dash type are also plotted in Figure 8. Table 1 also appends the fitted results of yield stress ( $\tau_0$ ), flow behavior index ( $n$ ), consistency index ( $k$ ), and correlation coefficient ( $R^2$ ). It is found that the curves of shear stress versus shear rate for XG emulsion and solution are fitted well by the power law model and Herschel–Bulkley model; especially the Herschel–Bulkley model is much better.  $k$  is a reflection of apparent viscosity, and it increases

**Table 1.** Results of Shear Stress as a Function of Shear Rate for Solution and Emulsion Containing XG Fitted by the Power Law Model, Herschel–Bulkley Model, and Linear Model

$w(\text{XG})/\%$	power law model $\tau = k\dot{\gamma}^n$			Herschel–Bulkley model $\tau = \tau_0 + k\dot{\gamma}^n$			
	$k/\text{Pas}^n$	$n$	$R^2$	$k/\text{Pas}^n$	$n$	$\tau_0$	$R^2$
Emulsions							
0.011	0.0046 <sup>a</sup>	1	0.9975				
0.019	0.0051 <sup>a</sup>	1	0.9955				
0.040	0.0249	0.81	0.9995	0.0145	0.88	0.179	0.9995
0.069	0.0393	0.77	0.9985	0.0250	0.83	0.289	0.9996
0.10	0.0627	0.74	0.9967	0.0465	0.77	0.420	0.9995
0.15	0.102	0.69	0.9912	0.0810	0.72	0.670	0.9995
Solutions							
0.041	0.0144	0.75	0.9905	0.0115	0.78	0.107	0.9995
0.071	0.0415	0.67	0.9950	0.0324	0.68	0.180	0.9994
0.10	0.0475	0.63	0.9754	0.0355	0.67	0.280	0.9996
0.15	0.103	0.59	0.9755	0.0646	0.64	0.519	0.9997

<sup>a</sup>The results are fitted by linear model of  $\tau = k\dot{\gamma}$ .

with the increase in XG concentration, which is well in agreement with the results of viscosity measurement. The  $n$  values of solutions and emulsions are less than unity and decrease as XG concentration increases from 0.040 to 0.15%, which suggests that the shear thinning behavior becomes more pronounced with increasing XG concentration. This is due to the formation of stiff rod molecules stabilized by their side chains, which consist of mannoses and glucuronic acids.<sup>36</sup> The  $\tau_0$  of solutions and emulsions are in the ranges of 0.107–0.519 and 0.179–0.670 Pa, respectively, and it increases with XG concentration from 0.040 to 0.15%. In addition, the curves of shear stress versus shear rate at XG concentrations of 0.011 and 0.019% can also be well fitted by the linear relationship  $\tau = k\dot{\gamma}$  seen from the dotted curve in Figure 8b and  $R^2$  values in Table 1, which confirm their typical Newtonian flow behavior again.

In conclusion, the emulsion stability depends mainly on the type and concentration of polysaccharides. The emulsion remains highly stable throughout the storage time at AG concentrations of 0–0.14% at room temperature. However, the emulsion exhibits apparent creaming at XG concentrations of 0.011–0.15%, and the emulsion volume decreases gradually with increasing XG concentration. The creaming is due to the flocculation of emulsion droplets induced by XG via a depletion mechanism. In addition, pesticide emulsions must also remain stable for 7 days at low temperature ( $-5\text{ }^\circ\text{C}$ ) and even for a few days at extreme conditions ( $< -10\text{ }^\circ\text{C}$ ). It is interesting to find that the emulsion with AG can remain stable for 7 days even at  $-10\text{ }^\circ\text{C}$ . This may have a close correlation with AG adsorption at the droplet surface. We intend to examine in detail the effect of AG on the stability of emulsions at low temperature in the future. From a technological perspective, AG addition would be highly advantageous to the stabilization of pesticide emulsions. However, the addition of XG has a negative effect on the stability of pesticide emulsion among the XG concentrations studied. If XG concentration continues to increase to high levels, the emulsion stability may be improved due to the high viscosity. However, high viscosity will bring a series of severe problems to emulsion production, such as high power consumption, long production times, difficulty in pouring, etc. Therefore, it is necessary to select a proper XG concentration in making pesticide emulsions.

## AUTHOR INFORMATION

### Corresponding Author

\*Phone: +86-22-23499474; e-mail: xgzhang@nankai.edu.cn.

### Funding Sources

We are grateful for financial support from the Natural Science Foundation of Tianjin, China (08JCYBJC00700).

## REFERENCES

- (1) Robins, M. M.; Hibberd, D. J. Emulsion flocculation and creaming. In *Modern Aspects of Emulsion Science*; Binks, B. P., Ed.; The Royal Society of Chemistry: London, U.K., 1998; pp 115–144.
- (2) Islam, A. M.; Phillips, G. O.; Slijivo, A.; Snowden, M. J.; Williams, P. A. A review of recent developments on the regulatory, structural and functional aspects of gum arabic. *Food Hydrocolloids* **1997**, *11*, 493–505.
- (3) Jayme, M. L.; Dunstan, D. E.; Gee, M. L. Zeta potentials of gum arabic stabilised oil in water emulsions. *Food Hydrocolloids* **1999**, *13*, 459–465.
- (4) Radford, S. J.; Dickinson, E. Depletion flocculation of caseinate-stabilised emulsions: what is the optimum size of the nonadsorbed protein nano-particles?. *Colloids Surf., A* **2004**, *238*, 71–81.

- (5) Parker, A.; Gunning, P. A.; Ng, K.; Robins, M. M. How does xanthan stabilise salad dressing?. *Food Hydrocolloids* **1995**, *9*, 333–342.
- (6) Sun, C. H.; Gunasekaran, S.; Richards, M. P. Effect of xanthan gum on physicochemical properties of whey protein isolate stabilized oil-in-water emulsions. *Food Hydrocolloids* **2007**, *21*, 555–564.
- (7) Hemar, Y.; Tamehana, M.; Munro, P. A.; Singh, H. Influence of xanthan gum on the formation and stability of sodium caseinate oil-in-water emulsions. *Food Hydrocolloids* **2001**, *15*, 513–519.
- (8) Mirhosseini, H.; Tan, C. P.; Hamid, N. S. A.; Yusof, S. Effect of Arabic gum, xanthan gum and orange oil contents on  $\zeta$ -potential, conductivity, stability, size index and pH of orange beverage emulsion. *Colloids Surf., A* **2008**, *315*, 47–56.
- (9) Mirhosseini, H.; Tan, C. P.; Hamid, N. S. A.; Yusof, S.; Chern, B. H. Characterization of the influence of main emulsion components on the physicochemical properties of orange beverage emulsion using response surface methodology. *Food Hydrocolloids* **2009**, *23*, 271–280.
- (10) Waghmare, J. T.; Ware, A. M.; Momin, S. A. Neem oil as pesticide. *J. Dispersion Sci. Technol.* **2007**, *28* (2), 323–328.
- (11) Casanova, H.; Araque, P.; Ortiz, C. Nicotine carboxylate insecticide emulsions: effect of the fatty acid chain length. *J. Agric. Food Chem.* **2005**, *53*, 9949–9953.
- (12) Casanova, H.; Ortiz, C.; Peláez, C.; Vallejo, A.; Moreno, M. E.; Acevedo, M. Insecticide formulations based on nicotine oleate stabilized by sodium caseinate. *J. Agric. Food Chem.* **2002**, *50*, 6389–6394.
- (13) Shen, J.; Huang, Q. L.; Xia, J. B.; Chen, D.; She, D. M.; Li, F. M.; Hu, W. The effects of dispersant and xanthan gum to rheological property of carbendazim suspension. *Chin. J. Pestic. Sci.* **2008**, *10* (3), 354–360.
- (14) Ma, J. K.; Ou, X. M.; Bu, H. Y.; Cai, D. L.; Nie, S. Q.; Liang, J. Application of orthogonal experiment in surfactant screening of formulation indoxacarb 10% SC. *Mod. Agrochem.* **2009**, *8* (3), 15–18.
- (15) Liu, Y. *Study on the Physical Stability of Dichlorbenzuron 20% SC [D]*; Shandong Agricultural University: Taian, China, 2009.
- (16) Elshafei, G. M. S.; El-Said, M. M.; Attia, H. A. E.; Mohammed, T. G. M. Environmentally friendly pesticides: essential oil-based w/o/w multiple emulsions for anti-fungal formulations. *Ind. Crop Prod.* **2010**, *31*, 99–106.
- (17) Chen, D.; Huang, Q. L.; Lü, H. P.; She, D. M.; Li, F. M.; Shen, J.; Xia, J. B. Studies on the application of the pseudo-ternary phase diagram inscreening pesticide emulsion in water. *Mod. Agrochem.* **2008**, *7* (4), 25–28.
- (18) Zhang, X. G.; Liu, J. X.; Wang, H. Y.; Wang, M. Y.; Fan, Z. J. Stability of avermectin emulsion in water. *Acta Phys. Chim. Sin.* **2010**, *26* (3), 617–625.
- (19) Song, Q.; Mei, X. D.; Huang, Q. L.; Wang, Z. Y.; Ning, J. Preparation of abamectin microcapsules by means of emulsion polymerization and its bioactivity. *Chin. J. Pestic. Sci.* **2009**, *11* (3), 392–394.
- (20) Vélez, G.; Fernández, M. A.; Muñoz, J.; Williams, P. A.; English, R. J. Role of hydrocolloids in the creaming of oil in water emulsions. *J. Agric. Food Chem.* **2003**, *51*, 265–269.
- (21) Singh, H.; Tamehana, M.; Hemar, Y.; Munro, P. A. Interfacial compositions, microstructures and properties of oil-in-water emulsions formed with mixtures of milk proteins and  $\kappa$ -carrageenan: 1. Sodium caseinate. *Food Hydrocolloids* **2003**, *17*, 539–548.
- (22) Singh, H.; Tamehana, M.; Hemar, Y.; Munro, P. A. Interfacial compositions, microstructure and stability of oil-in-water emulsions formed with mixtures of milk proteins and  $\kappa$ -carrageenan: 2. Whey protein isolate (WPI). *Food Hydrocolloids* **2003**, *17*, 549–561.
- (23) Manoj, P.; Fillery-Travis, A. J.; Watson, A. D.; Hibberd, D. J.; Robins, M. M. Characterization of a depletion-flocculated polydisperse emulsion I. Creaming behavior. *J. Colloid Interface Sci.* **1998**, *207*, 283–293.
- (24) Drakos, A.; Kiosseoglou, V. Stability of acidic egg white protein emulsions containing xanthan gum. *J. Agric. Food Chem.* **2006**, *54*, 10164–10169.
- (25) Acedo-Carrillo, J. I.; Rosas-Durazo, A.; Herrera-Urbina, R.; Rinaudo, M.; Goycoolea, F. M.; Valdez, M. A. Zeta potential and drop growth of oil in water emulsions stabilized with mesquite gum. *Carbohydr. Polym.* **2006**, *65*, 327–336.

(26) Tan, C. T. Beverage emulsions. In *Food Emulsions*, 2nd ed.; Larsson, K., Friberg, S. E., Eds.; Dekker: New York, 1990; pp 445–478.

(27) Ye, A.; Hemar, Y.; Singh, H. Enhancement of coalescence by xanthan addition to oil-in-water emulsions formed with extensively hydrolysed whey proteins. *Food Hydrocolloids* **2004**, *18*, 737–746.

(28) Gu, Y. S.; Decker, E. A.; McClements, D. J. Influence of pH and *t*-carrageenan concentration on physicochemical properties and stability of  $\beta$ -lactoglobulin-stabilized oil-in-water emulsions. *J. Agric. Food Chem.* **2004**, *52*, 3626–3632.

(29) Ye, A.; Hemar, Y.; Singh, H. Influence of polysaccharides on the rate of coalescence in oil-in-water emulsions formed with highly hydrolyzed whey proteins. *J. Agric. Food Chem.* **2004**, *52*, 5491–5498.

(30) Ingersen, K.; Klein, J.; Pincus, P. Forces between surfaces and adsorbed polymers 3.  $\theta$  solvent. Calculations and comparison with experiment. *Macromolecules* **1990**, *23*, 548–560.

(31) Peamprasart, T.; Chiewchan, N. Effect of fat content and preheat treatment on the apparent viscosity of coconut milk after homogenization. *J. Food Eng.* **2006**, *77*, 653–658.

(32) Song, K. W.; Kim, Y. S.; Chang, G. S. Rheology of concentrated xanthan gum solutions: steady shear flow behavior. *Fiber. Polym.* **2006**, *7* (2), 129–138.

(33) McClements, D. J. Emulsion rheology. In *Food Emulsions—Principles, Practice and Techniques*; McClements, D. J., Ed.; CRC Press: Washington, DC, 1999; pp 235–266.

(34) Manoj, P.; Watson, A. D.; Hibberd, D. J.; Fillery-Travis, A. J.; Robins, M. M. Characterization of a depletion-flocculated polydisperse emulsion II. steady-state rheological investigations. *J. Colloid Interface Sci.* **1998**, *207*, 294–302.

(35) Mandala, I. G.; Savvas, T. P.; Kostaropoulos, A. E. Xanthan and locust bean gum influence on the rheology and structure of a white model-sauce. *J. Food Eng.* **2004**, *64*, 335–342.

(36) Hayati, N. I.; Che Man, B. Y.; Tan, P. C.; Aini, N. I. Droplet characterization and stability of soybean oil/palm kernel olein O/W emulsions with the presence of selected polysaccharides. *Food Hydrocolloids* **2009**, *23*, 233–243.