Structural Viscosity Induced by Depletion Effect in Stable Vesicle Dispersion

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Abstract: Producing structural viscosity in colloidal dispersions, such as vesicles and capsules, prevents separation of dispersed particles by increasing the viscosity between them, which is advantageous in terms of usability. So far, the separation behavior of various particles has been studied; however, there are very few examples wherein a stable dispersion state was constructed and controlled. In this study, we produced stable dispersions induced by the depletion effect in mixtures of vesicles of cationic surfactant derived from triethanolamine-based esterquat (TEQ) and a specific dextrin derivative (SDD) as a non-adsorptive polymer. In the composition region, where 8 to 16% of TEQ vesicles and 1.2% or less of SDDs were mixed, the viscosity increased proportionally with the particle concentration, and it was observed that stable dispersions were produced by structural viscosity. Furthermore, the effects of TEQ and SDD concentrations, and SDD size on the structural viscosity and cohesive energy were investigated, which were similar to the depletion effect in the Asakura–Oosawa (AO) theory. From the results, it was suggested that the structural viscosity of the mixed dispersions (TEQ vesicles and SDDs) was produced by the aggregated TEQ vesicle networks induced by the depletion flocculation.

Key words: cationic vesicle, nonionic polymer, structural viscosity, depletion effect

1 Introduction

Viscosity is an important factor for the texture and quality of cosmetics and liquid products. In particular, stability during storage and usability of these products is greatly influenced by viscosity. Recently, addition of functional particles (e.g. fragrance capsules) and changing flow patterns with shear have been implemented to achieve a higher performance in liquid products. It is advantageous that the dispersion flow patterns change reversibly from the stable and steady state to the flow state with the use of shear. For the realization of these characteristics, structural viscosity should be rendered to dispersions, which consist of flow patterns in which the viscosity decreases with increasing shear rate. However, it is difficult to control the reversible nature of dispersion flow patterns.

Generally, polymers and surfactants are used to control viscosity. An effective polymer used for increasing viscosity strongly binds to the water molecules and has an excluded volume in aqueous solution. When the polymer concentration exceeds the threshold, the excluded volume of the polymer begins to overlap and interpenetrate each other. Thus, polymers increase the viscosity three-dimensionally in the whole aqueous solution.

Moreover, surfactants form micelles in the solution. When the surfactant concentration increases, the viscosity of the aqueous solution increases with increasing number of micelles. Furthermore, viscosity can also be increased by changing the shape of a micellar from spherical to a rod or string shape by selecting a molecular structure with surfactant and co-surfactants, adding electrolytes, and changing the temperature. Overall, extensive research and efforts are required to tune structural viscosity, and to obtain the desired flow characteristics using polymers and surfactants.

It is especially difficult to grant structural viscosity to dispersions that contain relatively large, submicron, or more particles, for instance, vesicle dispersion applied to a softener. It is difficult for vesicles to maintain a stable dispersed state, because vesicles are spherical particles dispersed lamellar liquid crystal, and have a non-equilibrium system. The separation of vesicle dispersion is promoted according to the conditions such as temperature, concentration, and specific weight of particle, where it is known that the depletion effect plays a role in the interparticle interactions.

Muñoz et al. prepared vesicle dispersions by using a cat-

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ionic surfactant, bis(tallowcarboxyethyl) (2-hydroxyethyl) methylammonium methosulfate, and reported the effect of cationic surfactant concentration on the rheological behavior in the vesicle dispersion. The plateau modulus at a low shear stress in the relaxation spectra increased with an increase in the cationic surfactant concentration. This suggested that the vesicles aggregated in networks like a lamellar phase by strengthening the interparticle interaction. Thus, the viscosity of the vesicle dispersion increased with increasing cationic surfactant concentration; however, controlling the stability and structural viscosity in a vesicle dispersion had not been studied.

Furthermore, Furst et al. reported the mixing effect of cationic polymer, poly-diallyldimethyl ammoniumchloride (polyDADMAC) on the cationic vesicle dispersion of ditalloveyethylester dimethyl ammonium chloride (DDAC). The DDAC vesicle dispersions, with volume fractions were 0.05–0.3, was separated immediately after preparation, and the addition of polyDADMAC promoted the separation of vesicle particles. It was considered that this separation behavior was not a conventional phase separation, and was affected by the depletion effect explained by the Asakura–Oosawa (AO) theory. However, thickening the DDAC vesicle dispersions and granting structural viscosity without separating them had not been achieved.

Thus, the depletion effect in a vesicle dispersion affects the cohesive power between the vesicle particles and the dispersed state significantly. To realize both stability and structural viscosity in the vesicle dispersion system, it is necessary to control the dispersed state of the vesicle particles by making good use of the depletion effect.

In this study, we aimed at producing a stable vesicle dispersion, which had structural viscosity arising from the depletion effect on adding a polymer to the vesicle dispersions. The vesicles of a cationic surfactant derived from triethanolamine-based esterquat (TEQ), and a specific dextrin derivative (SDD) as a non-adsorbable colloidal polymer were mixed, and their dispersed state was examined. The structural viscosity of dispersions was confirmed by rheology measurement, the cohesive energy was calculated from the obtained rheological parameters, and the participation of the depletion effect was considered.

2 Experimental Procedures
2.1 Materials

Triethanolamine-based esterquat (TEQ), as an ingredient that can form cationic vesicles, was provided from Lion Specialty Chemicals Co., Ltd. (Tokyo, Japan). The main component of TEQ is a double-chained cationic surfactant, di(alkyl fatty ester) quaternary ammonium methosulfate, \( \langle \text{RCOOCH}_2\text{CH}_3 \rangle_\text{2}\cdot \text{N}^+\cdot (\text{CH}_2\cdot \text{CH}_2\text{OH}) \cdot (\text{CH}_3) \cdot \text{CH}_3\text{SO}_4^- \). Polyoxyethylene (50) lauryl ether (C\text{12}EO\text{50}) as a nonionic surfactant was purchased from Nihon Emulsion Co., Ltd. (Tokyo, Japan). Specific dextrin derivative (SDD) as a nonionic polymer was provided from Glico Nutrition Co., Ltd. (Osaka, Japan). Due to the high specificity of branching enzyme, three SDDs had a narrower molecular weight distributions and diameters, which are M. W. = 159 kDa and 15 nm, M. W. = 300 kDa and 20 nm, and M. W. = 437 kDa and 25 nm, respectively.

2.2 Preparation of TEQ vesicles

The TEQ vesicle dispersions were prepared by the liquid crystal phase inversion emulsification method. TEQ cationic surfactant and C\text{12}EO\text{50} were added to a container of a vacuum emulsifier (Primix Corp.) and dissolved homogeneously. The prescribed water was added in two parts into the stirred oil phase. In this process, the TEQ cationic surfactant formed the liquid crystal phase, and inverted to the aqueous vesicle dispersions. The TEQ vesicle dispersions were mixed with the prescribed SDD. To evaluate the stability, the TEQ vesicle/SDD dispersions were placed in test tubes with caps and were maintained at the room temperature for a long time. TEQ is a mixed cationic surfactant; however, it is confirmed by SAXS measurement that TEQ vesicles have a lamellar structure. Furthermore, it can be considered that the particles behave as hard particles under the measurement conditions in this experiment, because the transition temperature \( T_r \) of the TEQ vesicles is 36°C (discussed in subsection 3.3).

2.3 Rheological behaviors

The rheological measurement was conducted after the TEQ vesicle/SDD dispersions were prepared and maintained at 25°C for overnight. The viscoelastic properties of the vesicle dispersions were measured by the stress-controlled rheometer (MCR301, Anton–Paar), which was installed on a cone plate of 50 mm diameter, at a cone angle of 1%, and 0.15 mm gap. The existence of structural viscosity was examined by the shear rate dependence of viscosity, which is measured by increasing of the shear rate. The viscoelastic behavior was clarified by the frequency and strain sweep measurements, in which the frequency was swept from 0.1 to 100 rad·s\(^{-1}\) at a constant strain \( \gamma = 0.1\% \) and the strain was swept from 0.1 to 100% at a constant stress \( \sigma = 1\ \text{Pa}, \) respectively, at 25°C. Each measurement was performed three times to confirm the reproducibility, and their typical results were shown.

2.4 Characterization of TEQ vesicle dispersions

The \( \zeta \) potential and the hydrodynamic radius of the TEQ vesicles were evaluated at 25°C by electrophoretic light scattering (ELS: Zeta sizer Nanoseries, Malvern) and dynamic light scattering (DLS: ALV-CGS3 system, \( \lambda = 532\ \text{nm}, 45\ \text{mW}, \) scattering angle at 90°), respectively. The TEQ vesicle dispersions were diluted 10 times with ELS.
measurement and 100 times with DLS measurement. The transition temperature of gel to liquid crystals of the TEQ vesicles after mixing SDD was measured differential scanning calorimetry (Nano DSC, TA instrument). The temperature scanning was performed by raising the temperature from 5°C to 60°C, and then lowering it to 5°C continuously, at 1°C/min scan rate. Each measurement was performed three times to confirm the reproducibility, and their typical results were shown.

3 Results and Discussion

3.1 Stability of TEQ vesicle/SDD mixed dispersion

Figure 1a shows the images of the 12% TEQ vesicle dispersions that were mixed with SDDs (0, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, and 3.2 wt%) maintained at 25°C overnight, and centrifuged at 3200 rpm for 6 hours, to observe the effect of adding SDDs quickly. When SDD was not added, a semi-transparent layer appeared in the upper layer and water separated. When 2.4% or more excess SDD was added to the TEQ vesicle dispersion, the SDD-rich aqueous solution was separated in the lower layer. It was suggested that adjusting the concentration of dispersed particles precisely was important to obtain a stable TEQ vesicle/SDD dispersion. Figure 1b shows a dispersed-state diagram with TEQ vesicle and SDD concentrations that were observed after mixing and storing them for a month at room temperature. The 20% or less TEQ vesicle dispersions without SDD gave homogeneous states just after preparation; however, they were slightly separated after they were left for a month at room temperature. When the SDDs was mixed into these TEQ vesicle dispersions, the viscosity increased proportionally with the SDD concentration, and a region appeared, in which the stability and the fluidity were compatible for usage (it is shown as a gray oval region in Fig. 1b). Further increase in the SDD concentration lowered the fluidity of the TEQ vesicle/SDD dispersion, and the surplus addition of SDDs above a threshold promoted the separation again. In the case of 12% TEQ vesicles, the mixture was separated into an upper vesicle-rich layer and a lower SDD-rich layer on adding 2.8% or more SDD. This result was similar to the separation tendency under accelerated conditions shown in Fig. 1a. Furthermore, the viscosity with 20% TEQ vesicle dispersion increased significantly and the separation speed became slow. The effect of adding SDD in these TEQ vesicle dispersions is not clear, and the separation was observed for all SDD concentrations shown in Fig. 1b. It is observed that the surplus concentrations of TEQ vesicles and SDD promoted separation.

3.2 Effect of particle size and concentration on structural viscosity

The rheological properties were evaluated to confirm the presence of structural viscosity and their key factors in the stable TEQ vesicle/SDD dispersion described in subsection 3.1.

3.2.1 Effect of SDD concentration

Figure 2 shows the shear rate dependence of viscosity η with 12% TEQ vesicle dispersions. When the SDDs, which were 20 nm, were added to the 12% TEQ vesicle dispersion, the viscosity increased in the low shear rate region and decreased with an increase in the shear rate. The viscosity in the low shear rate region and decreased with an increase in the shear rate. The viscosity in the low shear rate region increased with the increase in SDD concentration up to 1.2%. Moreover, the viscosity of the 1.2% SDD solution was uniformly low within the whole shear rate range, indicating that the structural viscosity was developed by the addition of SDD. Further, the viscoelastic behavior was evaluated in these mixed dispersions. Figure 3 shows the viscoelastic parameters, storage
modulus ($G'$), and loss modulus ($G''$) within the frequency range of $0.1–100$ rad $\cdot$ s$^{-1}$ at $\dot{\gamma} = 0.1$% with TEQ vesicle/ SDD dispersions. The values of $G'$ and $G''$ increased with an increase in the SDD concentration. The value of $G''$ surpassed that of $G'$ up to 0.8% SDD; however, the value of $G'$ exceeded that of $G''$ within whole frequency range in the case of 1.2% SDD. This means that a stronger network structure among the TEQ vesicles was formed in TEQ vesicle dispersion including 1.2% SDD, and that structural viscosity was promoted by increasing the SDD concentration.

3.2.2 Effect of TEQ concentration

Figures 4a and 4b show the change in rheological behaviors according to the TEQ concentration in the TEQ vesicle dispersions including 1.2% SDD which is 20 nm. As shown in Fig. 4a, with an increase in the TEQ vesicle concentration, the viscosity at a low shear rate increased and the structural viscosity was developed more strongly. Moreover, as shown in Fig. 4b, the $G'$ and $G''$ values were almost the same with 8% and 12% TEQ vesicle concentration; however, the value of $G'$ is greater than that of $G''$ ($G' > G''$) in the whole frequency range with 16% TEQ vesicle concentration. From these results, it was considered that an increase in the TEQ concentration promotes flocculation among vesicle particles and formation of networks. It was observed that TEQ concentration also developed structural viscosity.

3.2.3 Effect of SDD size

Figures 5a and 5b show the change in rheological behaviors according to the SDD size in the 12% TEQ vesicle/0.04 mM SDD dispersion. When the SDD diameter became larger from 15 to 25 nm, the viscosity at the lower shear rate and the $G'$ and $G''$ values in the whole frequency range increased with an increase in the SDD diameter. The $G''$ value surpassed the $G'$ value ($G'' > G'$) in the TEQ vesicle/ SDD dispersions including 1.2% SDD which is 20 nm.
vesicle/SDD dispersion added SDD of 15 nm; however, the $G'$ values became larger than the $G''$ values in the dispersions added with SDDs of 20 and 25 nm. It was confirmed that the SDD size affected the network structure among TEQ vesicles and their flocculation force.

3.3 Dispersed state of TEQ vesicle and SDD

To confirm if TEQ vesicle and SDD each behaved as independent particles in TEQ vesicle/SDD dispersion, the hydrodynamic radius ($R_H$), $\zeta$ potential, and transition temperature with the TEQ vesicle were measured. Figures 6a and 6b show the distribution of hydrodynamic radius ($D_v(R_H)$) measured by DLS with TEQ vesicles and SDD particles before mixing. The TEQ vesicles and SDDs had distributions within 40–110 nm and 5–20 nm, respectively. When both TEQ vesicle and SDDs were mixed (Fig. 6c), their hydrodynamic radii did not change as compared to those before mixing. Furthermore, the $\zeta$ potential of the TEQ vesicles was the same before and after mixing SDD, as shown in Fig. 7a, and also the transition temperature of the TEQ vesicles did not change, as shown in Fig. 7b. It was observed that no interaction occurred between the TEQ vesicles and SDDs, and both particles behaved independently. From these results, it is suggested that the structural viscosity of TEQ vesicle/SDD dispersion was induced by the depletion flocculation effect proposed in the AO theory, which occurs when two types of particles having different sizes coexist.

3.4 Depletion effect and cohesive energy in TEQ vesicle/SDD dispersions

The interparticle potential energy ($V_{dep}$) caused by the depletion flocculation is defined by Equation (1), which was proposed in AO theory,$^{22,30}$ where $P_{osm}$ is the osmotic pressure, $D$ and $d$ are the diameters with larger and smaller particles, respectively, and $a$ is the center-to-center distance. Here, in the case of larger $a$ than $D$ and smaller $a$ than $D + d$, the depletion flocculation effect appears. The driving force of depletion flocculation ($P_{osm}$) is defined by Equation (2),$^{30}$ where $n$ is the mole number of small particles, $V$ is the bulk volume, $N_A$ is the Avogadro constant, $k_B$ is the Boltzmann constant, and $T$ is the temperature.

$$V_{dep} = -\frac{\pi}{12} P_{osm} (D + d - a)^2 (2D + 2d + a)$$
The TEQ vesicle and SDD discussed in subsection 3.2 act as large and small particles, respectively. Thus, the TEQ and SDD concentrations and the SDD size affected the depletion effect through Equations (1) and (2), respectively. Accordingly, it was considered that these three factors induced depletion flocculation in TEQ vesicle/SDD dispersions. Therefore, the networks among the TEQ vesicle particles were formed and structural viscosity that stabilizes the dispersed particles appeared.

To thoroughly understand the aggregation behavior of the TEQ vesicle/SDD dispersions mentioned in subsections 3.1 and 3.2, the cohesive energy density ($E_c$) was estimated. The cohesive energy density ($E_c$) is the energy that is required to collapse the aggregated networks among particles, and is defined by Equation (3) [2].

$$E_c = \frac{1}{2} G' \gamma_{cr}$$

(3)

where $G'$ is the storage modulus and $\gamma_{cr}$ is the inflection point, which is a critical point at which the constant $G'$ in the low strain range decreases with increasing strain. Further, $G'$ shifts from the linear region to the non-linear region on the strain-sweep curve. Figure 8 shows the strain sweep curves of $G'$ that were presented in the TEQ vesicle/SDD dispersions shown in Figs. 2 and 3. The $G'$ value of dispersions including 12% TEQ vesicles increased with an increase in the SDD concentration. In any case, the $G'$ value was constant in the low strain range and lowered in the large strain range. Table 1 presents the $E_c$’s that were estimated from $G'$ and $\gamma_{cr}$ shown by arrows in Fig. 8. The $\gamma_{cr}$ values decreased and $E_c$ values increased with an increase in the SDD concentration. This result suggests that the decrease in the interparticle potential energy by the AO theory was promoted by the increase in SDD concentration as small particles, and that the structural viscosity was produced into the dispersions by the interparticle networks. Tables 2 and 3 present the effects of TEQ vesicle concentration and SDD size on the values of $E_c$, which were estimated with the TEQ vesicle/SDD dispersions shown in Figs. 4 and 5, respectively. Here, their strain sweep curves of $G'$ were not shown; however, the values of $E_c$ were calculated by the same method presented in Table 1. As presented in Tables 2 and 3, the values of $E_c$ increased with an increase in the TEQ vesicle concentra-
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This indicates that these factors also induced the depletion effect and the networks among particles were controlled by the inter-particle potential energy. The $E_c$ value of the dispersion including 16% TEQ and 1.2% SDD, which was the highest total concentration in the rheological measurement, was the largest. It was considered that an increase in the particle volume fraction decreases $n/V$ of $P_{osm}$ in Equation (2) and the decrease in the interparticle distance of vesicles, thereby enhancing the depletion flocculation.

Previously, Aben et al. reported the depletion flocculation behavior in the dispersions mixed nonionic O/W emulsions-mixed xanthan gum. The storage modulus $G'$, the critical strain $\gamma_c$, and also the cohesive energy $E_c$ increased with increasing xanthan gum concentration. However, the values of $E_c$ and $\gamma_c$ are $1/10$ to $1/1000$, compared with those in our dispersion system. Furthermore, the observed value of $G'$ was several Pa at 0.1% or less xanthan gum, which was comparable to that for our vesicle dispersions; thus, it is inferred that the structural viscosity in their system was produced dominantly by the thickening xanthan gum. Consequently, it is insisted again that our TEQ vesicle/SDD dispersions had a solution structure, in which the strong cohesive power was induced by the depletion effect, and promoted formation of networks among vesicle particles. Furthermore, $\gamma_c$ presented in Table 1 decreased with an increase in the SDD concentration. The value of $\gamma_c$ decreased when the TEQ concentration increased from 12% to 16%, as presented in Table 2; thus, it is suggested that the cationic charge repulsion between the TEQ vesicle particles of the network structure SDD was accumulated, and consequently, the elastic structure was weakened.

### Recovery of structural viscosity with TEQ vesicle/SDD dispersion

Figure 9 shows the microscopic images with and without shear in the dispersion, which is a mixture of 12% TEQ vesicles and 1.5% SDDs, and shows structural viscosity. Before a shear was applied, the microscopic image of the TEQ vesicle/SDD dispersion showed that the aggregation domains existed partially (Fig. 9a). These domains also indicate the formation of networks among vesicle particles by depletion flocculation. When a shear was applied, the images showed homogeneous dispersions that appeared as a single phase (Fig. 9b). However, after the shear was cancelled, the structure of the vesicle dispersions returned to its original pattern in a few seconds (Fig. 9c). It was observed that this TEQ vesicle/SDD dispersions, which had structural viscosity, showed excellent structural recovery with a shear.

### Conclusion

In this study, to control the dispersion state by the depletion effect, the TEQ vesicle dispersions, which tend to sep-

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**Table 2** Elastic modulus $G'$, critical strain $\gamma_c$, and cohesive energy density $E_c$ obtained from strain sweep curves as a function of TEQ concentration.

<table>
<thead>
<tr>
<th>TEQ conc. (wt%)</th>
<th>$G'$ (Pa)</th>
<th>$\gamma_c$ (%)</th>
<th>$E_c$ (mJ·m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3.25</td>
<td>2.80</td>
<td>1.27</td>
</tr>
<tr>
<td>16</td>
<td>53.17</td>
<td>1.30</td>
<td>3.90</td>
</tr>
</tbody>
</table>

**Table 3** Elastic modulus $G'$, critical strain $\gamma_c$, and cohesive energy density $E_c$ obtained by strain sweep curves as a function of SDD size.

<table>
<thead>
<tr>
<th>SDD size (nm)</th>
<th>$G'$ (Pa)</th>
<th>$\gamma_c$ (%)</th>
<th>$E_c$ (mJ·m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.20</td>
<td>3.50</td>
<td>0.74</td>
</tr>
<tr>
<td>20</td>
<td>2.28</td>
<td>2.80</td>
<td>1.27</td>
</tr>
<tr>
<td>25</td>
<td>3.56</td>
<td>3.00</td>
<td>1.60</td>
</tr>
</tbody>
</table>

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**Fig. 9** Microscopic images of TEQ vesicle dispersions including 1.5% SDDs. (a) Stationary state before giving shear, (b) collapsed state of network structure after giving shear, and (c) network structure recovery state 3 min after shear removal.

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ardate, were essentially mixed with nonionic polymer SDDs, which do not interact with the TEQ vesicles. In the TEQ/SDD dispersions, the viscosity increased proportionally with TEQ concentration and concentration and size of SDDs, and a stable dispersion region appeared. This rheological behavior of the stable TEQ/SDD dispersions suggested that the vesicles (as large particles) aggregated with SDDs (as small particles) by the depletion effect, and structural viscosity was produced by the vesicle networks. Furthermore, the cohesive energy $E_c$, which was estimated from the storage modulus $G'$, and the critical strain $\gamma_c$ in these stable dispersions became larger with the increase in particle concentration and size. Thus, the cohesive force related to the depletion effect could be controlled by the concentration and size of the dispersed particles. Furthermore, these dispersions demonstrated structural viscosity while settling and exhibited excellent stability in the dispersed state; they also exhibited structure recoverability, that is, the structural viscosity broken by shear could be restored quickly. This structure recoverability is advantageous in terms of usability, such as convenience of pouring and handling, and is expected to have a high utility value in various industries.

References


