

Article

Role of Particle Size and Mono-to-Polyester Ratio on Gelation Behavior of Sucrose Ester Dispersions

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Abstract

Commercial nonionic sucrose ester surfactants (SEs) contain varying ratios of monoesters and polyesters. In our previous study, we found that when the mono-to-polyester (MP) ratio is close to 1, SE dispersions can form hydrogels at very low surfactant and electrolyte concentrations. In the current study, we systematically investigate how the MP ratio and particle size affect the salt-induced gelation process. We reveal that SE dispersions form hydrogels only within a certain MP range. At low MP ratios (<0.4), micrometer-sized particles form and sediment, preventing gel formation, whereas at high MP ratios (≥ 3), particle concentration decreases, confining gelation to a very narrow electrolyte region. Sonication significantly reduces particle size across all dispersions, expanding the gelation domain down to $MP \approx 0.3$. The critical salt concentration required for hydrogel formation exhibits a maximum as a function of MP ratio at $MP \approx 0.43$, which is explained with the highest measured zeta potential for these particles. The obtained results support the hypothesis that increasing the monoester content enhances surface mobility, suppresses hydroxide ion adsorption, and reduces particle charge, thereby lowering the threshold electrolyte concentration. Finally, particle size reduction enhances overall gel strength and lowers the minimum surfactant concentration required for gelation. These findings enable the rational design of simple, biodegradable hydrogels with tunable properties for future applications in food, pharmaceutical, and cosmetic formulations.

Keywords: biodegradable surfactant; phase behavior; hydrogel; sol–gel; rheology; surface charge; hydrophobic attraction



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1. Introduction

Sucrose esters (SEs) are a versatile class of nonionic surfactants, composed of a hydrophilic sucrose moiety esterified with one or more lipophilic fatty acid chains [1–3]. This allows SEs to be produced entirely from renewable natural resources—sucrose and fatty acids derived from vegetable oils [1–5]. Sucrose esters are of great interest to the industry, not only because of their sustainable origin, but also due to their excellent safety profile. They exhibit very low toxicity and have been proven as non-irritants to both the skin and eyes, making them one of the mildest surfactants available [2,3,6]. Their lack of odor and taste further enhances their high compatibility, making them widely used also in the food industry as additives (E473) [5,7].

The manufacture of SEs, however, presents several challenges [1,2,4,5,8]. Sucrose is a nonreducing disaccharide that contains three primary and five secondary hydroxyl groups. The presence of these eight reactive hydroxyls results in the very low selectivity of the esterification process, yielding complex mixtures of mono-, di-, and higher esters, rather than a single well-defined product [5]. The resulting mono-to-polyester ratio is a key parameter determining the hydrophilic–lipophilic balance (HLB) of the surfactant mixture. Consequently, the wide range of attainable HLB values, combined with the favorable physicochemical properties of the SEs, makes them useful in a broad range of applications. They are widely utilized in cosmetic and pharmaceutical formulations due to their low toxicity and antimicrobial, antioxidant, and potential antitumor properties, as well as permeation enhancers [3,9–13], and in the food industry as effective emulsifiers and foaming agents [14–22].

In a recent study [23], we uncovered a highly unexpected gelation phenomenon in diluted aqueous dispersions of the commercial SE S970 (50% monoesters and 50% di-, tri-, and other polyesters). Upon addition of small amounts of electrolyte, initially freely flowing, low-viscosity liquids transformed into non-flowing, gel-like materials (e.g., 2 wt. % S970 + 9 mM NaCl). This behavior was explained with the interplay between repulsive electrostatic interactions among the in situ formed nanoparticles and the attractive forces acting between them [23,24]. The particles, composed primarily of the polyester molecules, were found to carry a negative charge under native conditions (e.g., after S970 dissolution in deionized water), despite the nonionic nature of the sucrose ester surfactant. This surface charging was attributed to the adsorption of hydroxide anions at the particle surface, an interpretation directly supported by electrokinetic measurements: the magnitude of the negative zeta potential decreased upon addition of electrolyte or a decrease in the pH of the dispersion [23]. In turn, both increasing the electrolyte concentration or lowering the pH reduced the repulsive electrostatic interactions between the particles. Once the electrostatic repulsion became comparable in magnitude to the attractive interparticle interactions (incl. van der Waals forces, hydrophobic interactions, and H-bonding), the particles formed a percolated network, transforming the freely flowing dispersion into a non-flowing, gel-like material. The critical electrolyte concentration required for gelation (C.C.G.) was found to scale with ion valence as $C.C.G. \propto z^{-2.7}$, in good agreement with Debye–Hückel theory for systems with a low surface charge density [25]. Further screening of the particle charge eventually led to collapse of the gel network and phase separation.

This initial study focused on a single sucrose ester containing approximately equal amounts of monoester and polyester molecules [23]. Commercial sucrose ester surfactants, however, are synthesized with a wide range of hydrophilic–lipophilic balance (HLB) values, arising from variations in both the mono-to-polyester ratio and the hydrophobic chain length [3]. The objective of the present study is to elucidate the influence of surfactant molecular composition on the gel formation process and to identify the sucrose esters for which this spontaneous gelation phenomenon can occur. Given that sucrose stearates are commercially available across a broad spectrum of mono-to-polyester compositions, we chose them to perform this study.

2. Results and Discussion

2.1. Characteristics of Nanoparticles Formed from SEs with Different Mono-to-Polyester (MP) Ratios

The sucrose stearates in the studied series differ in their contents of monoesters, diesters, and other polyesters (PEs). This is expected to influence their gelation behavior as the increase in the monoester content is expected to decrease the number of nanometer-sized particles (under otherwise equivalent parameter). These particles serve as the main

structural units for network formation and lead to the significant viscosity change when their charges are regulated, as previously observed for S970 [23].

Before presenting the results about the gelation characteristics of the various SE dispersions, first we discuss the properties of the dispersions to reveal the impact of the MP ratio over the particles sizes and their zeta potential.

Figure 1a presents the average hydrodynamic diameters of the particles measured in the different SEs studied. The particle sizes in S770, S970, and S1170 dispersions were comparable, where average $d \approx 200$ nm. The decrease in the PEs in the S1570 also led to a decrease in the particle size to ca. 150 ± 25 nm. However, larger particles were found in the dispersions of more hydrophobic S570 with average diameter of ca. 300 ± 50 nm. Furthermore, the polyesters in the most hydrophobic SE systematically studied, S470 (75% PEs), formed micrometer size aggregates when dispersed in water using magnetic stirring only; see Figure S1 in the Supplementary Materials. These dispersions appeared relatively viscous even without any addition of salt; thus, they were not investigated further in this state.

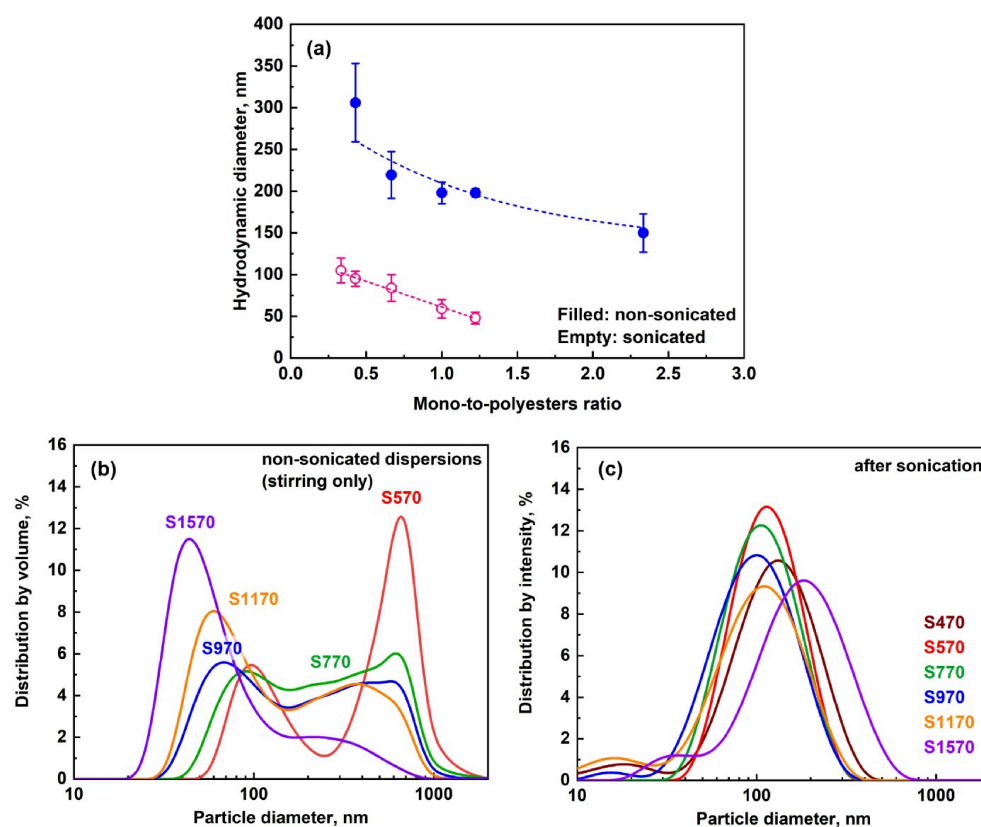


Figure 1. (a) Average hydrodynamic diameter of the polyester particles observed in the studied SE dispersions depending on the MP ratio. Measurements are performed at 90° scattering angle with the original dispersions obtained after magnetic stirring homogenization (blue symbols) or after sonication (empty pink symbols). The error bars represent the standard deviations calculated from three independent measurements performed using independently prepared samples. (b) Particle size distribution measured by volume. Measurements are performed at 173° scattering angle with the original dispersions prepared by stirring only. (c) Particle size distribution measured by intensity for the sonicated samples. Measurements are performed at 173° scattering angle.

The polyester particles formed in the SE dispersions, however, were not monodisperse but rather showed quite polydisperse distributions as seen in Figure 1b. The average polydispersity index (PDI) for the S770 to S1570 samples was 0.40 ± 0.06 , whereas for the S570 dispersion, the PDI was slightly larger, 0.55 ± 0.08 . The fraction of the 600–700 nm

particles decreases upon decrease in the polyester content. Therefore, even though the PE content in the samples decreases in the order S570 > S770 > S970 > S1170 > S1570, the actual number of the particles in each dispersion will not decrease in the same way considering that the volume of the particle is proportional to the third power of its size, $v \propto d^3$; thus, the bigger particles contain significantly higher amounts of the material. A rough estimate of the number of particles in the various dispersions showed that for 2 wt. % 100 g dispersions, the number of particles in the S570 dispersion (70% PEs) is approximately 3 times lower compared to that in the more hydrophilic S1570 dispersion, despite the latter containing only 30% PEs. For this estimate, we assumed that the particles are composed of polyesters only and as an average size, we took the average hydrodynamic diameter determined from the DLS measurements. Therefore, the PE content per se cannot be reliably used to predict the gelation phase behavior of different SEs.

To reduce the significant variation in particle sizes observed in the initial SE dispersions, we sonicated the samples. This led to a significant decrease in the particle sizes, as seen from the empty pink symbols shown in Figure 1a. The PDI for the S570-S970 samples decreased to 0.25 ± 0.04 , whereas for the more hydrophilic SEs, it remained relatively higher, 0.52 ± 0.14 . Furthermore, the size of the biggest particles, which is best characterized by the measured particle distributions by intensity, were found to be comparable among the different dispersions; see Figure 1c. Note that the different SEs contain between 75 and 30% PEs; thus, the number of the particles will be significantly different once their size becomes relatively similar. Thus, in the more hydrophilic SEs, the fraction of the micelles will be higher, which leads to an overall decrease in the mean hydrodynamic diameter (Figure 1a), although the nanometer-sized particles are of comparable size. This also explains the higher PDI observed in these samples.

Another important characteristic determining the gelation behavior of SE dispersions upon addition of electrolyte is their zeta potential. The regulation of the electrostatic interactions between the negatively charged polyester particles was found to be responsible for the creation of gel-like materials with S970 [23]. For that reason, we determined the zeta potential for the particles formed by the various SE dispersions.

The results of the zeta potential measurements of the SE particles in different dispersions in the presence of 5 mM NaCl (to ensure a well-defined position of the slipping plane) are presented in Figure 2a. The zeta potential was observed to decrease (in absolute value) when the monoester content increased for both the original (blue filled circles) and sonicated (empty pink circles) samples. The decrease was relatively linear, excluding the result obtained for S1170 (MP ratio = 1.22) for the original particles and S470 (MP ratio = 0.33) and S1570 (MP ratio = 2.33) for the sonicated samples. The reason for this is that the 5 mM NaCl concentration turns out to be around or above the critical NaCl concentration required for gel formation for these samples, which partially compromises the accuracy of the zeta potential measurements as the particles start to aggregate; thus, these data points were excluded from the linear analysis. The aggregation behavior is further discussed in the next section.

The results in Figure 2a demonstrate further that the zeta potential of the sonicated samples is lower in absolute value compared to this for the same samples before sonication. This difference is especially significant for the S770 and S970 particles, where $|\Delta\zeta| \approx 15$ to 20 mV. This is partially explained with the fact that the pH of the sonicated SE samples was found to decrease by ca. 0.5 pH units: from 7.3 ± 0.4 before sonication to 6.8 ± 0.2 after it. However, such a pH change could be responsible for no more than ca. 5 mV zeta potential change as previously demonstrated from the zeta potential dependence on pH for the S970 particles (see Figure 3c in Ref. [23]). Therefore, another more significant process should explain this bigger change.

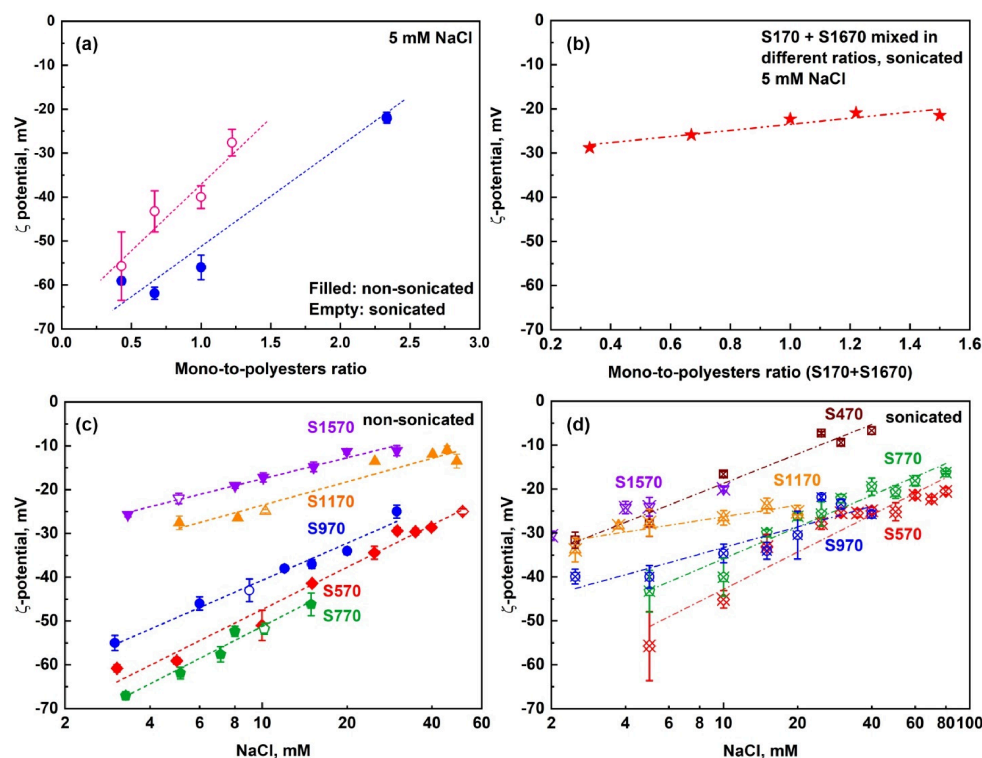


Figure 2. (a,b) Zeta potential of the particles measured in presence of 5 mM NaCl. (a) SE particles prepared with different SEs (i.e., from S470 to S1570). Filled blue symbols show the results for the original samples prepared with magnetic stirring, whereas the empty pink symbols show the results after ultrasonication. (b) Zeta potentials of particles prepared with different mixing ratios of S170 + S1670 surfactants, resulting in varying MP ratios. All dispersions were prepared using magnetic stirring and sonication. (c,d) Zeta potential of particles measured as a function of NaCl concentration added. (c) Original samples and (d) sonicated samples. The error bars in the graphs represent the standard deviations among the results obtained from at least three independently prepared samples studied under the same experimental protocols.

We note that the observed pH decrease upon sonication is an effect known in the literature [26]. It has been shown that the primary cause for it is the production of hydrogen ions and related formation of nitrate and nitrite acids [27]. Furthermore, the increased CO₂ dissolution in water upon sonication also contributes to the observed pH decrease, but its effect is minor [27].

Next, we evaluated the change in the zeta potential for the non-sonicated and sonicated particles upon varying the salt concentration in the solution. The obtained results are presented in Figures 2c and 2d, respectively. The magnitude of the zeta potential was found to decrease linearly with the logarithm of NaCl concentration; see Table 1 for the parameters of the linear fits $\zeta(\log c_{\text{NaCl}})$. Notably, the slope of these fits became smaller with increasing monoester content. Furthermore, the increase in the monoester fraction led to a decrease in the absolute zeta potential estimated for low NaCl concentrations (see the data for intercepts, which shows the extrapolated zeta potential for 1 mM NaCl).

A comparison between the data for sonicated and non-sonicated samples shows that sonication significantly affects both the ζ -potential at very low ionic strength (intercepts) and the sensitivity of the ζ -potential to increasing NaCl concentration, as reflected by the slopes. Specifically, the sonicated samples exhibited lower absolute zeta potential values and smaller slopes compared to the non-sonicated particles. Given that an increase in monoester content is associated with a decrease in the absolute value of the zeta potential (Figure 2a), these observations suggest that sonication alters the surface composition of the

particles, leading to an enrichment of monoester groups at the particle surface. This change in surface composition could explain the significant difference between the zeta potentials measured for sonicated and non-sonicated particles prepared from the same surfactant dispersions at the same ionic strength.

Table 1. Slopes and intercepts ($=\zeta$ -potential at 1 mM NaCl) of the linear fits of ζ vs. $\log c_{\text{NaCl}}$ for different SE dispersions studied with and without applying sonication.

	MP Ratio	Characteristics of the $\zeta(\log c_{\text{NaCl}})$ Dependence			
		Non-Sonicated Particles		Sonicated Particles	
		Slope	Intercept	Slope	Intercept
S470	0.33	-	-	22.2	-41
S570	0.43	32.1	-79	28.1	-71
S770	0.67	33.0	-84	23.9	-60
S970	1.00	28.1	-69	15.6	-49
S1170	1.22	17.8	-41	8.7	-35
S1570	2.33	16.0	-34	15.0	-34

To further test this hypothesis, we prepared SE particles with different MP ratios using mixtures of two commercially available sucrose esters with markedly different hydrophilicities: a highly hydrophobic SE S170 (monoester content = 1% according to the manufacturer), and a highly hydrophilic SE, S1670 (monoester content = 75%). By varying the mixing ratio of these two surfactants, we were able to systematically alter the mono-to-polyester ratio, while maintaining the same types of surfactant molecules in all samples. It should be noted that this last condition is not fulfilled for the commercially available SEs with varying monoester contents, as these surfactants are synthesized independently. Consequently, changes in the MP ratio are likely accompanied by changes in the overall molecular composition, making it difficult to isolate the effect of the particle surface structure over the hydroxide anion adsorption and related surface charging.

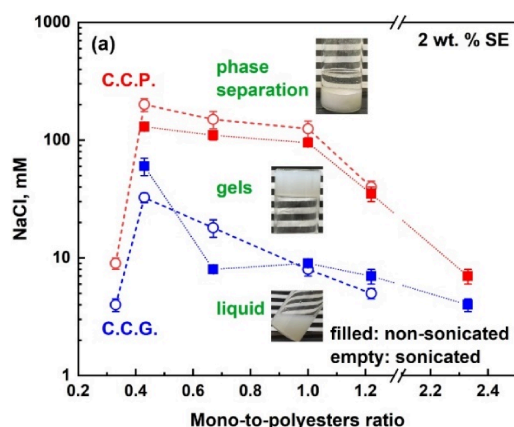
The S170 + S1670 mixed particles were prepared using sonication, as the dispersion of the S170 surfactant using magnetic stirring only resulted in numerous particles with sizes $>20 \mu\text{m}$ even after heating. The obtained particles after sonication had sizes ca. 150–250 nm, which decreased slightly upon increase in the monoester content. The zeta potentials of the resulting particles were measured at a fixed ionic strength of 5 mM and are presented in Figure 2b. Interestingly, the results revealed that the potential is almost independent of the MP ratio, $\zeta \approx -24 \pm 3 \text{ mV}$. The slight decrease in the absolute values upon increase in the monoester content is probably mainly governed by the slight decrease in the pH values of different dispersions (pH = 7.3 for MP = 0.33 and 6.8 for MP = 1.5).

These results further demonstrate that the MP ratio alone does not determine the surface charge. Instead, the obtained experimental results support the hypothesis that it is governed by the specific molecular composition of the particle surface. Enrichment of the surface with the more mobile sucrose monoesters hinders the adsorption of hydroxide ions, thereby reducing the zeta potential. In contrast, surfaces with a higher fraction of more hydrophobic di- and polyesters exhibit higher zeta potentials. For commercially available SE surfactants with varying mono-to-polyester ratios, the surface composition of the resulting polyester particles upon dispersion of the SEs in water can be altered depending on the particle preparation procedure.

Next, we present our results about the phase behavior of SE dispersions upon addition of NaCl.

2.2. Critical Concentration for Gelation (C.C.G.) and Critical Concentration for Phase Separation (C.C.P.)

To assess the influence of polyester content and particle characteristics on the gel formation, we began by investigating the minimum NaCl concentration (denoted as C.C.G.) required to form gel-like, non-flowing dispersions containing 2 wt. % sucrose esters. Dispersions containing both bigger (obtained after magnetic stirring only) and smaller (obtained after ultrasound treatment of the original dispersions) particles were investigated. The obtained results are presented in Figure 3a with blue symbols.



(b) SE	MP ratio	ζ -potential at C.C.G., mV	
		Non-sonicated	Sonicated
S470	0.33	N.A.	−28
S570	0.43	−23	−28
S770	0.67	−52	−30
S970	1.00	−43	−35
S1170	1.22	−26	−28
S1570	2.33	−24	N.A.

Figure 3. (a) C.C.G. (blue symbols) and C.C.P. (red symbols) determined for 2 wt. % SE dispersions prepared with various SEs (S470 to S1570). Filled points show data for the dispersions containing bigger (non-sonicated) particles, whereas the data for sonicated dispersions is shown with empty symbols. The error bars represent the standard deviations calculated from the evaluation of at least three independently prepared samples. The dashed and dotted lines are a guide for the eye. (b) Zeta potentials for SE dispersions measured at the C.C.G. concentrations. The standard deviations calculated from 3 independent measurements for the presented values are $\approx \pm 3$ mV.

The data for the sonicated samples (empty symbols) shows a non-monotonous dependence of the C.C.G. concentration on the MP ratio. The C.C.G. for S470 (MP = 0.33) was determined to be $\approx 4 \pm 0.5$ mM, which is significantly lower than the C.C.G. for S570 $\approx 32.5 \pm 3$ mM. A further increase in the monoester content in the sample led to a decrease in the C.C.G. Although unexpected, this maximum in the C.C.G. vs. MP ratio dependence is easily explained when considering the zeta potential of the obtained sonicated polyester particles; see Figure 3b. They turn out to be practically the same for all the different SEs when determined at C.C.G., $\zeta_{\text{C.C.G., sonic.}} \approx -30 \pm 3$ mV. Therefore, the different NaCl levels needed to form non-flowing gel-like samples are related to the different surface compositions of the particles, which in turn lead to different responses of the particles toward the addition of NaCl. However, once the zeta potential of the particles decreases to ca. -30 mV, a formation of gel-like non-flowing samples is observed even when just 2 wt. % surfactant is used, owing to the formation of a percolated gel network within the volume of the dispersion; see Figure 4.

The C.C.G. concentration determined for the S170 + S1670 particles prepared with sonication was almost independent of the ratios in which the two surfactants were mixed, C.C.G. $\approx 6 \pm 1$ mM. This result is in excellent agreement with the result showing that the zeta potential of these particles is independent of the MP ratio, $\zeta \approx -24 \pm 3$ mV at 5 mM NaCl (Figure 2b). Therefore, the C.C.G. for dispersions containing ca. 200 nm particles does not depend on the MP ratio, but it is determined by the zeta potential of the particles—once it is decreased to ca. -30 to -25 mV, a gel network can be formed.

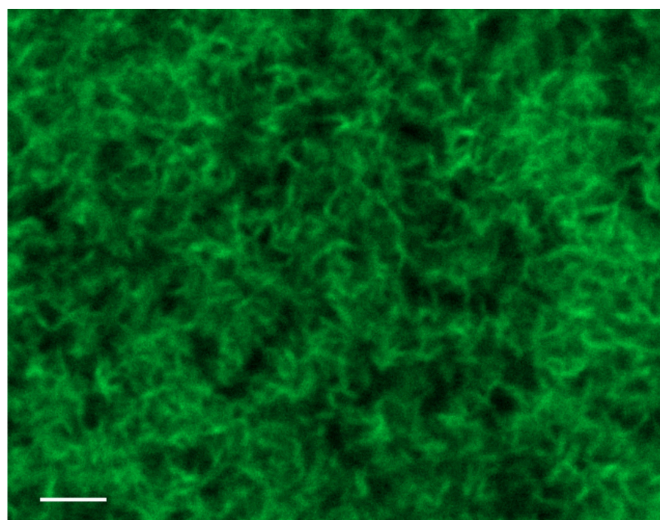


Figure 4. Percolated gel-network observed in a single optical section of a 2 wt. % S570 sonicated dispersion containing 80 mM NaCl; imaged by confocal microscopy. Scale bar = 5 μ m. No such organization is observed in the same dispersions without added salt; see Figure S2 in the Supplementary Materials.

The conclusion that the addition of more hydrophilic molecules into the sucrose ester mixture is able to modify the particle surface and decrease the absolute zeta potential in the absence of NaCl was further supported by the result obtained with particles prepared by mixing S570 + S1670. For this particular experiment, we prepared a mixture of 1.15 wt. % S570 + 0.85 wt. % S1670, so that we obtained 2 wt. % SE final concentration and MP ratio = 1. Using ultrasound, we prepared nanoparticles with sizes ca. 100 nm and ζ -potential = -33 mV (measured at 5 mM NaCl). For this particular sample, we observed complete gel formation upon the addition of 10 mM NaCl only. Note that the C.C.G. for the 2 wt. % S570 sonicated sample is 32.5 ± 3 mM, whereas S1670 is practically not able to form a gel that is able to sustain its own weight due to the very low polyester content. Furthermore, if only the 1.15 wt. % S570 dispersion is prepared in the presence of 10 mM, it maintains low viscosity.

The highest C.C.G. for the non-sonicated samples was determined also for S570, similarly to the sonicated samples. Note that the non-sonicated S470 samples could not be investigated due to the presence of numerous micrometer size aggregates as shown in Figure S1 in the Supplementary Materials. Increasing the percentage of the monoesters in the solution led to a significant decrease in the NaCl concentration needed to induce the gelation; see blue filled squares in Figure 3a. However, while the ζ -potentials at C.C.G. for S570, S1170, and S1570 were near the expected values ($\zeta \approx -25 \pm 2$ mV) where the van der Waals forces are known to be able to overcome the electrostatic repulsion [28–30], the ζ -potentials for the S770 and S970 particles at C.C.G. were significantly higher (in absolute value), $\zeta_{\text{C.C.G.}} \approx -52 \pm 3$ mV for S770 and $\zeta_{\text{C.C.G.}} \approx -43 \pm 3$ mV for S970; see Figure 3b. These measurements were repeated more than 3 times with independently prepared samples, but we always obtained such high values.

To explain the formation of a non-flowing gel network in samples exhibiting such high absolute zeta potentials, an additional attractive interaction must be present between the particles. Combined with the van der Waals attraction, this interaction must be sufficiently strong to overcome the electrostatic repulsion between the particles. We propose that this additional attraction arises from hydrophobic interactions acting between the solid particle surfaces.

To verify this hypothesis, we prepared nanoparticles using S170 and L1695 sucrose esters. Note that L1695 contains C12 fatty acid chains and ca. 87% monoesters, making it

highly hydrophilic. This surfactant has been observed to form ordered spherical micelles in aqueous solutions at concentrations as high as 40 wt. % without any evidence of particle formation [31]. In contrast, S170 contains only 1% monoester and is therefore poorly water-soluble. Therefore, the obtained mixed nanoparticles are expected to consist predominantly of the di- and polyesters of S170, along with the C12-polyesters from the L1695, while the lauric monoesters are anticipated to adsorb at the particle surface and provide their colloidal stabilization.

Furthermore, a significant difference between particles prepared from S170 + L1695 and those from S170 + S1670 is the physical state of the hydrophobic tails of the monoester molecules at 25 °C. The tails of the L1695 surfactant are in a liquid state, whereas the C16-C18 chains of S1670 are in a solid state under these conditions. Consequently, while both types of particles are expected to consist mainly of the polyesters from S170, their surfaces will consist of hydrophilic sucrose headgroups oriented toward the aqueous phase. However, the molecular surface mobility of the S170 + L1695 particles is expected to be significantly higher than that of the S170 + S1670 particles. The surface of the S170 + L1695 particles is expected to be more fluid-like and dynamically mobile, while the S170 + S1670 particles should possess more rigid and less mobile surfaces. Note that hydrophobic attractions are commonly observed between solid hydrophobic surfaces, whereas they might be significantly reduced when the interacting surfaces are fluid and highly mobile because the interfaces can deform and reorganize. Therefore, if the additional attractive force responsible for gel network formation indeed originates from hydrophobic interactions, it should be substantially weaker or absent in the S170 + L1695 system.

According to these considerations, the results obtained with the S170 + L1695 particles showed that gel formation did not occur under conditions where gels readily formed in dispersions containing the S170 + S1670 particles. Despite exhibiting similar characteristics (Z-average particle size ≈ 200 nm, $\zeta \approx -24 \pm 3$ mV for S170 + S1670, and $\zeta \approx -33$ mV for S170 + L1695), the S170 + L1695 dispersions maintained very low viscosities without any evidence of particle structuring or network formation upon NaCl addition. This observation supports the hypothesis that the gelation mechanism involves an additional attractive interaction that is present for particles with rigid surfaces, but is absent when the particle surface is fluid-like and highly mobile.

The C.C.G. of the non-sonicated particles prepared from S770, S970, and S1170 are similar $\approx 8 \pm 1$ mM NaCl. Therefore, we used particles prepared from these three surfactants to study gel formation kinetics under similar conditions, namely at a 10 mM NaCl concentration. The obtained results are presented in Figure 5. Interestingly, although the S770 particles have the highest absolute zeta potential, the gel formation in this sample proceeds in ca. 4 h. Gelation in S970 was considerably slower, with the formation of a completely non-flowing gel requiring about 20 h at the 10 mM NaCl concentration. The slowest kinetics was observed for the S1170 surfactant, for which the gel network developed over ca. 24 h, although the electrostatic repulsion at this ionic strength is the smallest. This result likely originates from the additional hydrophobic attraction present in the S770 and S970 dispersions, where the average particle size is also slightly bigger as compared to the S1170 particles; see Figure 1a,b. We note that the gel formation with the most hydrophilic S1570 surfactant took an even longer time at NaCl concentrations near the C.C.G. (e.g., more than 2–3 days) due to the low particle concentration. In contrast, the gelation of the more hydrophobic S570 particles also required more than 1 day, primarily because of the large particle size, which reduced the particle number concentration. Upon sonication, the time required for the gelation of the S570 dispersions decreased significantly.

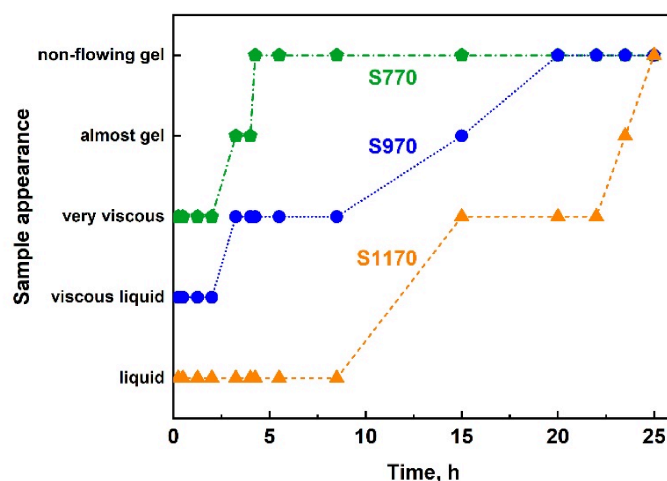


Figure 5. Gel formation kinetics for 2 wt. % dispersions of S770 (green pentagons), S970 (blue circles), and S1170 (orange triangles) in the presence of 10 mM NaCl. The sample appearance description is shown as observed by the naked eye. The lines are a guide to the eye only.

Next, the critical concentration for phase separation (C.C.P.) was analyzed as a function of the MP ratio and particle size. The obtained results are shown with red symbols in Figure 3a. Similarly to the C.C.G., the C.C.P. starts from relatively low values for the S470 particles, increases significantly for the SEs with intermediate MP ratios, and again decreases for the more hydrophilic S1170 and S1570. The observed trend is in good agreement with the zeta potential values determined for different dispersions: the widest NaCl concentration interval for gel formation with the original non-sonicated particles is found for the S770 sample, where the gel formation is also observed to start at the highest (in absolute value) zeta potential. In contrast, the interval is the narrowest for S1570, where the zeta potential at low ionic strengths is also the lowest (i.e., the particles are least charged). These observations are easily explained when considering that the gel collapse proceeds once the electrostatic repulsion becomes insufficient to counteract the attraction between the particles. This happens once the absolute zeta potential decreases below ca. 10–15 mV. However, the exact value could not be precisely determined as severe aggregation between the nanometer particles was observed at NaCl concentrations exceeding the C.C.G even for very diluted dispersions; see Figure S3 in the Supplementary Materials. Therefore, the zeta potential measurements at concentrations exceeding C.C.G. are likely reflecting the zeta potential of the particles which are still slightly charged and remain as individual entities within the solution, whereas another significant part of the particle may have already formed aggregates.

The comparison between C.C.P. for the original non-sonicated dispersions and the sonicated ones shows a slight increase in C.C.P. for the dispersions containing smaller particles. However, the general trends with respect to the MP ratio are preserved. This result is likely related to the slower rate of zeta potential decrease upon increase in the NaCl concentration observed for the sonicated particles as compared to the non-sonicated (see the data for the slopes presented in Table 1). As discussed, this should be related to the increased content of monoester molecules on the particle surface upon sonication, which also governs the lower absolute zeta potential at low electrolyte concentration.

We note that in the present paper, only gels obtained upon addition of NaCl were systematically investigated. However, our previous work on gel formation with S970 has shown that $C.C.G. \propto z^{-2.7}$ (where z is the cation charge), while the properties of the resulting gels are relatively independent of the specific electrolyte when compared at equivalent relative positions with respect to the C.C.G. and C.C.P. boundaries [23]. Consistent with

these findings, additional experiments performed in the present study (results not included) showed no significant differences among the tested monovalent salts for different SEs, whereas the C.C.G. for MgCl_2 and S770 was approximately 1.25 mM, which is in agreement with the predicted valence dependence.

2.3. Effect of SE Concentration on Gel Formation

All results presented in the previous section were obtained using 2 wt. % SE dispersion. Here, we examine the effect of SE concentration on gel formation. Two aspects were investigated: the C.C.G. at SE concentration of 4 wt. % and the minimum SE concentration required for gel formation at a fixed NaCl concentration.

The results obtained for the C.C.G. in 4 wt. % SE dispersions (prepared without sonication) are presented in Figure 6a. As shown in the figure, the C.C.G. for 2 and 4 wt. % SE dispersions were practically the same for all studied SEs, with the exception of S570 ($\text{MP} = 0.43$). In this case, a substantial decrease in the NaCl concentration required to induce gel formation was observed upon increase in the SE concentration. Specifically, gel formation occurred at ca. 30 mM NaCl for the 4 wt. % S570 dispersion, compared to about 60 mM NaCl for the corresponding 2 wt. % S570 dispersions. Interestingly, this decrease is comparable to that observed for the 2 wt. % S570 dispersions after sonication, for which the C.C.G. was also reduced significantly to approximately 32.5 mM.

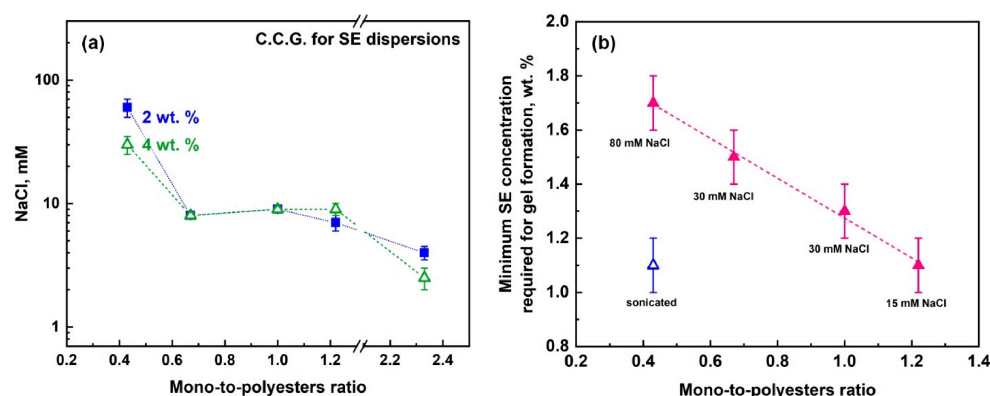


Figure 6. (a) Phase diagram showing the critical NaCl concentrations required to form non-flowing gel-like samples dependent on the MP ratio for 2 wt. % SE dispersions (blue filled squares) and 4 wt. % dispersions (empty green triangles). The lines are guides to the eye only. (b) Minimum SE concentration required for gel formation as a function of MP ratio. The SE concentrations are determined at the NaCl concentrations denoted on the graphs, which correspond to ca. 25% of the gelation interval determined for 2 wt. % SE dispersions. Filled pink points: original, non-sonicated dispersions; empty blue point: sonicated dispersion. The error bars represent the standard deviations calculated from the evaluation of at least three independently prepared samples.

To understand the origin of this pronounced decrease, we further investigated the properties of the 4 wt. % S570 dispersions. The mean hydrodynamic diameter of the particles prepared from 5 wt. % and 2.5 wt. % SE dispersions (used to obtain final SE concentrations of 4 and 2 wt. %, respectively, after NaCl addition) were practically the same. The measured zeta potentials also showed no significant differences. It should be noted, however, that zeta potential measurements were performed after dilution of the dispersions to 0.2 wt. % SE concentrations in order to ensure reliable measurements. Therefore, even if some differences were present in the concentrated samples, they may have been diminished or eliminated upon dilution.

One notable difference between the 2 and 4 wt. % S570 dispersions was their pH. The pH of the 4 wt. % samples was ca. 0.6 pH units lower than that of the 2 wt. %

samples. Such a decrease in pH is expected to reduce the surface charge of the particles, which is consistent with the lower NaCl concentration needed for gel formation in more concentrated dispersions.

To confirm that the lowered pH influences the decreased NaCl allowing gel formation in 4 wt. % dispersions, we conducted an experiment in which the pH of the 2 wt. % dispersion, obtained by dilution of initial 5 wt. % stock dispersion, was adjusted to the same level as that in the 4 wt. % S570 dispersions. For this sample, we observed gel formation using 50 mM NaCl (instead of 60 mM NaCl as required for the same sample without pH adjustment). However, gels were not formed at lower NaCl concentrations as in the case of 4 wt. % S570 solution, demonstrating also the important role of the number of particles present within the dispersion.

Next, the minimum SE concentration required for gel formation was investigated. For this series of experiments, the NaCl concentration was fixed at a value corresponding to approximately 25% of the gelation interval determined for the 2 wt. % dispersions, i.e., $c_{\text{NaCl}} \approx 0.25 \times (\text{C.C.P.-C.C.G.}) + \text{C.C.G.}$. The specific NaCl concentrations which we selected were 80 mM for S570, 30 mM for S770 and S970, and 15 mM for S1170 dispersions. S1570 dispersions were not investigated because their concentration region for gel formation was rather narrow, and gel formation was found to be very slow even at 2 wt. % concentrations, requiring several days for completion.

At these fixed salt concentrations, the minimum SE concentration required for gel formation was found to decrease linearly as the monoester content increased over the investigated range of MP ratios (0.43 and 1.22); see Figure 6b.

The relatively high SE concentration required for gelation of the S570 dispersions was attributed to the larger particle size in the original non-sonicated samples compared to those prepared from the other SEs. The larger particle size results in a decreased number of individual particles, despite the higher polyester content. Since gelation proceeds through the formation of a percolated network spanning through the entire dispersion volume, the nanometer-sized polyester particles act as nodes within the attractive network, while their electrostatic interactions are regulated by electrolyte addition. Consequently, a sufficient number of particles is needed to establish a continuous gel structure.

To verify this hypothesis, the experiment was repeated using the sonicated S570 sample. In this case, the minimum SE concentration for gelation decreased from 1.7 ± 0.1 wt. % for non-sonicated sample to 1.1 ± 0.1 wt. % for the sonicated sample, which is comparable to the concentration found to be needed for gel formation in the non-sonicated S1170 dispersion.

2.4. Rheological Properties of the Gels

Next, we compared the viscoelastic properties of the gels prepared with various SE dispersions. The results are summarized in Figure 7. Similarly to the experiments determining the minimum SE concentration required for gel formation at a given NaCl concentration (Figure 6b), the NaCl concentration in the gel-like samples prepared for rheological measurements was fixed to ca. 25% of the gelation interval determined for the 2 wt. % dispersions.

It should be noted that, although the samples capable of supporting their own weight are referred to as “gels”, they do not satisfy the strict rheological definition of a gel, according to which a gel should exhibit a pronounced plateau in the storage and loss moduli as a function of frequency [32]. The loss moduli of the currently investigated samples were relatively independent of the applied oscillation frequency, whereas the storage moduli increased slightly with increasing frequency; see Figure S4 in the Supplementary Materials. Nevertheless, in all strain sweep experiments, we always observed that the storage modulus G' was about one order of magnitude higher than the loss modulus G'' at strains up to at least 50%, suggesting a strongly connected elastic network. Furthermore, the very low particle

weight fraction at which these non-flowing gel-like materials are obtained (i.e., <2 wt. %) suggests the formation of a relatively open water-rich network, rather than compact three-dimensional aggregates. Therefore, following the established terminology for systems with similar rheological characteristics [33], we refer to these gel-like materials as gels or hydrogels.

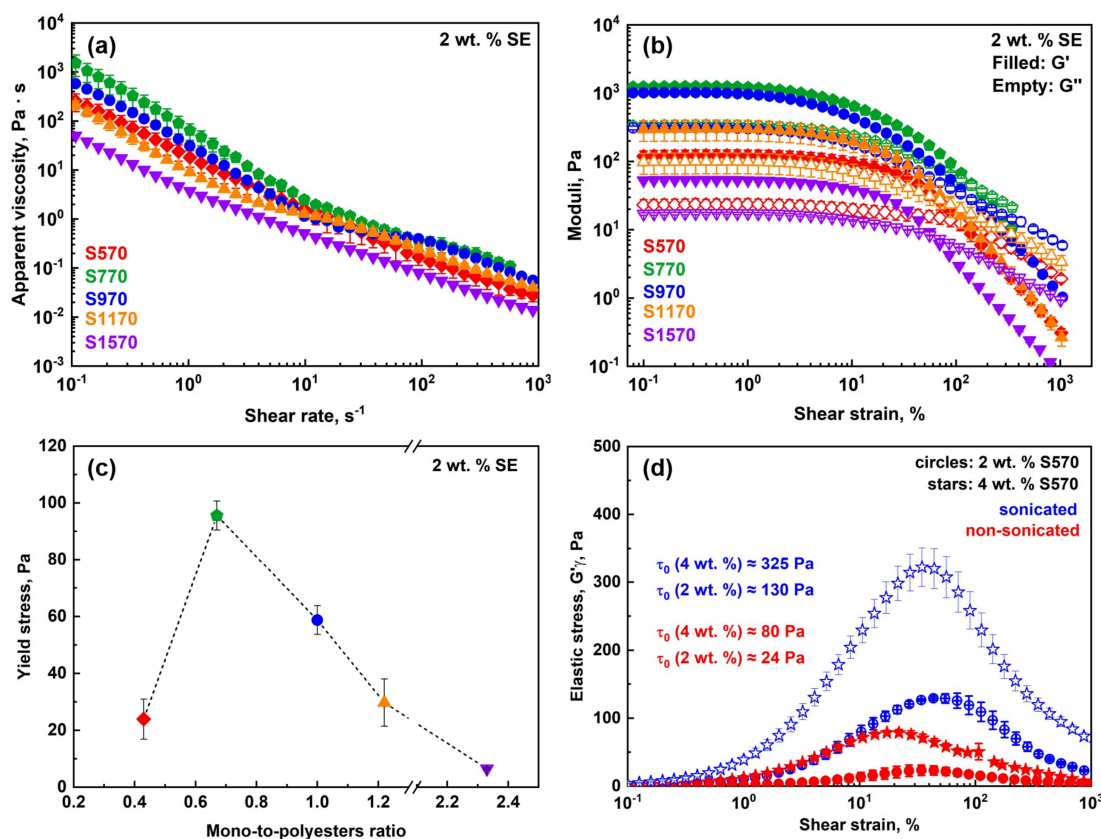


Figure 7. (a) Apparent viscosity as a function of shear rate for 2 wt. % SE gels. (b) Storage (filled symbols) and loss (empty symbols) moduli for 2 wt. % SE gels. (c) Yield stresses for the gels shown in (b). The same colors as in (a) and (b) have been used to denote the different SEs. (a–c) The results are obtained with the following NaCl concentrations: 80 mM for S570; 30 mM for S770 and S970; 15 mM for S1170; and 5.75 mM for S1570. Non-sonicated samples were used. (d) Comparison between the viscoelastic properties of 4 wt. % (stars) and 2 wt. % (circles) S570 gels prepared with 80 mM NaCl with (empty blue points) or without (red points) sonication of the initial dispersion. The error bars represent the standard deviations calculated from at least three independent measurements performed using independently prepared samples. Note that for some of the data points, the error bars are smaller than the symbols and are therefore not visible.

The results from the viscosity measurements and shear strain variation experiments at a fixed oscillation frequency of 1 Hz showed that the strongest gels are obtained with S770 dispersions, followed by S970 dispersions; see Figure 7a,b. The storage and loss moduli and the yield stress determined for S1170 gels were slightly higher compared to those for S570 gels, whereas the S1570 gels had the smallest yield stress and the lowest apparent viscosity under the studied NaCl level (Figure 7c).

These results are in good agreement with the finding that the gels with S770 and S970 start to form at significantly higher zeta potential compared to the other SEs studied, which was explained by additional hydrophobic attraction.

Figure 7d shows a comparison between the viscoelastic properties obtained with 2 and 4 wt. % S570 dispersions with or without sonication. Note that the sonication was

shown to significantly reduce the particle sizes, thus leading to an increase in the number of particles. As particles serve as nodes in the gel network, the increase in their number under otherwise equivalent conditions should lead to an increase in the gel network strength. Indeed, the moduli and the yield stress determined for 4 wt. % non-sonicated S570 samples were significantly higher compared to those of 2 wt. % S570 gel at the same NaCl level; viz. yield stress increased from ca. 24 Pa to about 80 Pa when the SE concentration was raised from 2 to 4 wt. %. The application of sonication further improved the gel strength, and the measured yield stress for the 2 and 4 wt. % samples increased to 130 Pa for the 2 wt. % dispersion and about 325 Pa for the 4 wt. %, which is ca. 4–5 times higher compared to that of the respective non-sonicated samples.

In addition, it should be noted that the gels obtained in the present study are thermo-responsive, as the solubility and molecular organization of the polyester molecules in similar SE mixtures, and consequently, the presence of the dispersed particles, have been shown to depend strongly on temperature [24]. Upon heating above the melting temperature of the polyesters, the molecular arrangement is disrupted and the particles disappear, leading to the loss of the junctions within the percolated network. As a result, the gel network breaks down and the sample returns to a low-viscosity, freely flowing state; see Figure 8. Upon subsequent cooling, the gel network is restored, and the sample once again exhibits gel-like behavior, demonstrating that the gels are not only thermo-responsive, but also thermo-reversible. The applied heating–cooling cycles were performed four consecutive times on the same sample, consistently yielding identical behavior and demonstrating the excellent robustness and reproducibility of the process.

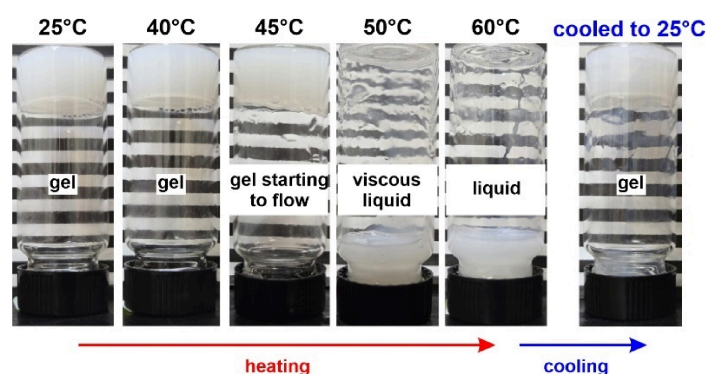


Figure 8. Thermo-responsive behavior of the prepared gels. Macroscopic appearance of the 4 wt. % S570 gel prepared from a sonicated dispersion with 80 mM NaCl at different temperatures, as indicated in the pictures. The gel-like behavior is lost upon heating above the melting temperature of the polyesters (to ca. 50 °C), but is restored when the dispersion is subsequently cooled to 25 °C. The heating–cooling cycles shown were performed four consecutive times, always yielding the same result, demonstrating the excellent reproducibility of the thermo-responsive properties of the prepared gel.

3. Conclusions

In the present study, we investigated how variations in the mono-to-polyester content in commercial sucrose stearates with different HLB values affect the formation of water-rich, particle-based elastic three-dimensional networks, which transform initially freely flowing dispersion into gel-like materials capable of retaining their structure under gravity. For simplicity, these materials are referred to as gels or hydrogels throughout the paper. The gelation phenomenon has previously been reported for S970 (mono-to-polyester ratio ≈ 1) [23]. To summarize, the polyesters found in commercial sucrose ester (SE) surfactants were found to be insoluble in water and instead formed nanoparticles at 25 °C. These nanoparticles spontaneously acquired a negative charge due to hydroxide anion

adsorption on their surface. Appropriate charge regulation either via electrolyte addition or by pH decrease led to the formation of a space-spanning attractive percolated network. This transformed the freely flowing sucrose ester dispersions into completely non-flowing gels when the attractive van der Waals forces became comparable in magnitude to the electrostatic repulsion. However, complete screening of the particle charges led to their aggregation and phase separation occurred [23].

The newly obtained results demonstrated that the specific properties of the nanometer polyester particles and the minimal salt concentration required for gel formation do not depend on the mono-to-polyester ratio of the molecules in the dispersion when their type is fixed. Instead, the gels started to form when the zeta potential of the in situ formed solid nanoparticles was decreased to ca. -25 mV, which is consistent with the commonly reported threshold for colloidal stability in classical suspensions [28–30]. However, this conclusion does not apply to the commercial sucrose esters with various HLBs as the change in the HLB is also related to the change in the composition of the molecules within the sucrose ester surfactant mixture. In this case, based on the obtained experimental results, it was suggested that the increase in the monoester fraction on the particle surface leads to increased surface mobility which suppresses the hydroxide anion adsorption, lowering the surface charge of the particles. In turn, the lower surface charge required a lower electrolyte concentration to decrease the zeta potential to ca. -30 or -25 mV and allow gel formation. In contrast, particles containing shorter chain C12 molecules, whose fatty acid chains are in a liquid state under the studied conditions, did not form gel networks despite having similar zeta potentials.

Interestingly, for SEs with approximately equal fractions of mono- and polyesters (S770, MP ratio = 0.67 and S970, MP ratio = 1), we found that the gel formation starts at substantially higher zeta potentials ≈ -40 to -55 mV. Such high electrostatic repulsion could not be overcome by van der Waals attraction alone, suggesting the presence of an additional attractive interaction. This was attributed to the presence of hydrophobic attraction acting between these particles. When this additional attraction was present, the gel formation at NaCl concentration near the minimum salt concentration was the fastest.

Additionally, experiments with dispersions prepared with and without sonication demonstrated that sonication alters the surface composition of the polyester particles. The sonicated particles exhibited a lower zeta potential than the original particles, suggesting surface enrichment with monoesters, consistent with the similar trend observed upon increasing the monoester content in the SE mixture. Sonication also resulted in the formation of smaller nanoparticles, which enhanced the gel network strength and reduced the minimum surfactant concentration required for gel formation, particularly for the more hydrophobic SE mixtures that initially contained considerably larger particles. The lowest SE concentration found to induce hydrogel formation was ca. 1.1 wt. %.

These findings reveal that electrolyte-induced gelation in SE dispersions is governed by a subtle interplay between surface composition and mobility, electrostatic charge regulation, and hydrophobic interactions. This understanding provides a basis for the rational design of thermo-responsive hydrogels with tailored properties, which may be of interest for future applications in the food, pharmaceutical, and cosmetic formulations.

4. Materials and Methods

4.1. Materials

In the present study we investigated a series of sucrose fatty acid esters (denoted as SE), kindly provided by Mitsubishi Chemical Group Corporation, Tokyo, Japan. The esters with trade names S470, S570, S770, S970, S1170, S1570, and S1670 were systematically investigated and used as received. All of these esters contain ca. 70% C₁₈-chains and 30%

C₁₆-chains, while their mono-to-polyester ratio (denoted as MP throughout the text) varied between 0.33 and 3.00, as shown in Table 2. Furthermore, SE S170 (sucrose stearate with 1% monoester content) and the lauric chain L1695 (monoester content = 87%), products of Mitsubishi Chemical Corporation, were also utilized in some model experiments.

Table 2. The monoester content and mono-to-polyester (MP) ratio for the sucrose esters investigated in this study.

Sucrose Ester	Monoester Content, %	MP Ratio
S170	1	0.01
S470	25	0.33
S570	30	0.43
S770	40	0.67
S970	50	1.00
S1170	55	1.22
S1570	70	2.33
S1670	75	3.00

The phase behavior of aqueous dispersions of these esters was studied in the presence of varying concentrations of sodium chloride (NaCl) with purity $\geq 99\%$, product of Sigma-Aldrich. The deionized water used for the preparation of all dispersions was purified by Elix 3 Module, MilliporeSigma, Burlington, MA, USA.

4.2. Methods

4.2.1. Dispersion Preparation and Flow Behavior Evaluation

Sucrose stearate dispersions were prepared following the procedure described in our previous study [23]. Briefly, the dry SE powder was mixed with water and homogenized by stirring at a temperature of 77 °C for approximately 30 min. Then, the solution was cooled down to 25 °C and used for further investigations. When studying the phase behavior of dispersions prepared with two mixed sucrose esters, the dry SE powders were mixed initially and then the mixed dispersion was prepared following the same procedure.

To evaluate the effect of the initial particle size, part of the originally prepared SE dispersions was subjected to ultrasonication. Ultrasound treatment was performed using a SYCLON ultrasonic cell crusher (SKL-1500, Ningbo Sklon Lab Instruments Co., Ltd., Ningbo, China), operated at 60% power (900 W) for a total duration of 8 min, using 5 s on/5 s off pulse cycles. A sonotrode with a diameter of 2.5 cm was immersed approximately 1 cm into a 50 g sample contained in a glass bottle with a diameter of 4.5 cm. During the ultrasonication, the sample temperature was raised to ca. 77 ± 3 °C, which is identical to the temperature used during dispersion preparation. After completion of the sonication, the dispersions were transferred to a water bath with temperature ca. 15 °C and allowed to cool to 25 °C. Within the text, we refer to these samples as “sonicated”, whereas the dispersions obtained by magnetic stirring only at high temperature are referred to as either “original” or “non-sonicated” samples.

The samples containing electrolyte were prepared at 25 °C by diluting concentrated sucrose stearate dispersions with concentrated salt solutions to achieve the desired final concentrations. A 5 wt. % SE stock dispersion was used for samples diluted to 4 wt. %, while a 2.5 wt. % dispersion was used for 2 wt. % or lower final concentrations. The samples were prepared in 6 g quantities in vials with a diameter of 2.5 cm. The vials were stored at 25 °C and monitored for at least 1 week, and typically for more than 1 month. The

critical concentration for gelation (C.C.G.) was defined as the minimum salt concentration at which the initially freely flowing samples formed a gel-like material, which was able to sustain its own weight when the vial was turned upside down. The critical concentration for phase separation (C.C.P.) was defined as the lowest NaCl concentration at which the formation of bulk liquid phase was observed concomitantly with the presence of a gelled phase, or alternatively as the minimum NaCl concentration at which the gelled samples started to flow. The C.C.G. and C.C.P. concentrations were evaluated after 1 week of storage to ensure that the internal particle arrangement had reached a stable state. At least three independently performed samples were used to ensure reproducibility.

4.2.2. Rheological Measurements

Rheological measurements were performed using a rotational rheometer DHR-3, TA Instruments, New Castle, DE, USA, equipped with a parallel plate geometry (40 mm diameter of the upper plate, gap 500 μm). Sandpaper (grade P100) was attached to both the upper and lower plates before the measurements to prevent a possible wall-slip between the sample and the plates during the measurements. Viscoelastic properties were characterized by oscillatory amplitude sweep experiments, where the strain amplitude was varied from 0.01% to 100% at a fixed frequency of 1 Hz. The yield stress of a given sample was determined as the maximum of the elastic stress (equal to elastic modulus, G' , multiplied by the absolute oscillation strain γ) plotted against the oscillation strain (γ) [34]. Additionally, oscillatory frequency sweep experiments were performed at a fixed deformation of 0.5% for selected samples and the viscosities were measured using flow ramp experiments with the shear rate logarithmically increased from 0.01 to 1000 s^{-1} . All measurements were performed at 25 $^{\circ}\text{C}$ and at least three independently prepared samples were measured to ensure reproducibility of the obtained results. The measurements were performed using samples that had been allowed to gel for 24–48 h, except for the S1570 samples, which were stored for 8 days prior to measurement.

4.2.3. Zeta Potential Measurements

Zeta potential measurements of the studied samples were performed using a Zetasizer Nano ZS (Malvern Panalytical, Malvern, UK). Samples with lower than 9 mM ionic strength were analyzed in disposable folded capillary cells (DTS1070), whereas samples with higher ionic strengths were measured using cell ZEN1010, allowing for measurements at elevated electrolyte concentrations. All experiments were performed at 25 $^{\circ}\text{C}$ with samples which were pre-diluted to SE concentration of 0.2 wt. % with a salt solution to achieve the desired final NaCl concentration. At least three independent measurements were conducted for each sample to ensure reproducibility. Note that the currently determined zeta potentials determined for the 0.2 wt. % S970 dispersions are comparable to those previously measured for 2 wt. % dispersions [23], demonstrating that dilution does not significantly affect the measured values.

The Smoluchowski equation was used to convert the measured electrophoretic mobility, U_e , into a zeta potential, ζ [35]:

$$\zeta = U_e \eta / (\epsilon \epsilon_0) \quad (1)$$

where ϵ is the dielectric constant for water solution 78.5, ϵ_0 is the permeability of vacuum, and η is the viscosity of water, which is 0.8872 mPa·s at 25 $^{\circ}\text{C}$.

4.2.4. pH Measurements

The pH of the studied dispersions was determined using a Fisher brand AB200 bench-top pH/conductivity meter, Thermo Fisher Scientific, Waltham, MA, USA. All measurements were performed at 25 $^{\circ}\text{C}$.

4.2.5. Dynamic Light Scattering (DLS)

The size of the colloidal particles in the original sucrose ester dispersions (prior to salt addition) was studied using a variable multi-angle light scattering instrument (LS-spectrometer, LS instruments AG, Fribourg, Switzerland). The scattering angle was set to 90° for these measurements. To check the sizes of the biggest particles in the dispersions, we also measured the size distributions using Zetasizer Nano ZS (Malvern Panalytical, Malvern, UK), which detects the scattered light at a 173° angle. A refractive index of 1.546 and an absorbance of 0.01 were used for the dispersed material, while the refractive index and viscosity of the dispersant (water) were set to 1.330 and 0.89 Pa·s, respectively. The scattering data were analyzed using Mie theory.

To prevent multiple scattering, all investigated systems were diluted to a concentration of 0.2 wt. % before measurement using deionized water. Note that the dilution does not alter the measured particle sizes, as demonstrated previously by the excellent agreement between the measured sizes and those observed directly (without sample dilution) by cryo-TEM [23]. Furthermore, the dilution was performed at 25 °C, when the tails of the SE molecules are in a frozen state and the particles have already formed.

All experiments were performed at 25 °C and at least three independent measurements were conducted for each sample to ensure reproducibility.

4.2.6. Confocal Microscopy

The gel network structure of selected samples was visualized using a confocal microscope LSM 900 (Carl Zeiss Microscopy GmbH, Oberkochen, Germany) equipped with an AxioImager.Z2m microscope stand. Images were acquired using ×20 objective and processed using Zeiss Zen 3.8 imaging software.

To enable visualization of a fluorescent signal, the already prepared sonicated SE dispersions (without added salt) were heated to 55 °C and labeled with BODIPY fluorescent dye (493/503, product of Sigma-Aldrich, Burlington, MA, USA) by dissolving the dye at 1 mM concentration upon stirring for 5 min at 200 rpm. Note that the used dye concentration is negligible compared to the SE content; thus, it is not expected to affect the structures formed. After dye dissolution, the samples were again cooled to 25 °C and the required amounts of NaCl solution and water were added to obtain the desired final SE and NaCl concentrations. The resulting samples were homogenized by hand shaking and were immediately transferred to Petri dishes, where they were allowed to undergo gelation. The gelled samples were subsequently visualized using the confocal microscope.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/gels12110974/s1>. Figure S1: Optical microscopy images of S470 dispersion in water (without sonication); Figure S2: Confocal microscopy images of 4 wt. % S570 sonicated dispersion without and with 80 mM NaCl; Figure S3: Macroscopic images of 0.2 wt. % S770 dispersions with 5 and 50 mM NaCl; Figure S4: Storage and loss moduli as a function of the oscillation frequency for 4 wt. % S570 gels with 80 mM NaCl.

Author Contributions: Conceptualization, D.C. and S.T.; methodology, D.C. and S.T.; validation, P.B. and D.C.; formal analysis, P.B. and D.C.; investigation, P.B. and D.C.; data curation, P.B. and D.C.; writing—original draft preparation, D.C.; writing—review and editing, D.C. and S.T.; visualization, P.B. and D.C.; supervision, D.C. and S.T.; project administration, S.T.; funding acquisition, P.B. and S.T. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

C.C.G.	Critical Concentration for Gelation
C.C.P.	Critical Concentration for Phase separation
HLB	Hydrophilic-Lipophilic Balance
MP	Mono-to-Polyester ratio
PE	Polyesters
SE	Sucrose Ester

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