A Small-Angle Neutron Scattering Study of a Shear-Induced Vesicle to Micelle Transition in Surfactant Mixtures

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Aqueous dispersions of cetyltrimethylammonium 3-hydroxynaphthalene-2-carboxylate (CTAHNC) present vesicles at low temperature. An increase in temperature and/or the addition of cetyltrimethylammonium bromide (CTAB) induces a vesicle to micelle transition. Using small-angle neutron scattering (SANS) we investigate the vesicle to micelle transition that seems also to be induced by shear in those systems. Pure CTAHNC and mixtures of CTAHNC and CTAB were considered. At low temperature and in the absence of CTAB, the scattering at small angles present, in a large scattering vector range, the characteristic $\sim q^{-2}$ dependence, due to the scattering of almost flat surfaces (vesicles). When the system is subjected to shear, the scattered intensity decreases in both directions, i.e. parallel *and* perpendicular to the shear flow, while a maximum at a finite scattering vector develops in the perpendicular direction. It is suggested that the intensity decrease in both directions with respect to the shear is due to the disruption of the vesicles while the maximum is associated with the correlation between cylindrical micelles which are formed by the shear. In the presence of small quantities of CTAB, the system is composed of a mixture of vesicles and cylindrical micelles. When the system is subjected to shear, the maximum position displaces toward higher values of the scattering vector in the direction perpendicular to the flow. The dependence of the maximum position as a function of the shear rate, that is, the vesicle to micelle conversion ratio, is determined.

1. Introduction

Several experimental studies have shown that mixed systems containing phospholipids and surfactants[1,2] or mixtures of anionic and cationic surfactants[3] undergo a phase transition from vesicle to cylindrical micelles when the composition of the system is varied. The transition is of first order with the presence of a two-phase region consisting of coexisting bilayer vesicles and micelles.[2] Recently, the formation of vesicles has been reported in solutions of cetyltrimethylammonium 3-hydroxynaphthalene-2-carboxylate (CTAHNC) obtained by mixing equimolar quantities of sodium 3-hydroxynaphthalene-2-carboxylate (SHNC) and cetyltrimethylammonium bromide (CTAB) and washing out the sodium bromide.[4,5] At ambient temperatures, a vesicular phase is found in a rather broad concentration range of CTAHNC as optical micrograph studies have shown.[6] As observed on the microscope, vesicles gradually disappear as the temperature is increased and/or a small amount of CTAB is added.[5,6] The resulting solution is much more viscous, and its rheological features are very similar to that obtained for other charged worm-like micellar solutions.[6] Parallel investigations on the same system using fluorescence anisotropy and NMR[4,5] can also be interpreted on the same basis. Using small-angle neutron scattering (SANS), some of the present authors have presented preliminary results suggesting that a vesicle to micelle transition in CTAHNC can also be induced by shear.[7] The shear-induced transition presents some similarity to those induced by temperature increase or by addition of an ionic surfactant. In the present paper, we report on the effect of shear on the three regions of the phase diagram concerning this transition: (i) the vesicle phase, (ii) the coexisting vesicle–micelle phase, as well as at (iii) the supposed worm-like micellar phase. A detailed scattering study of the vesicle to micelle transition induced by shear is presented for pure CTAHNC and CTAHNC + CTAB mixtures.

2. Experimental Section

CTAHNC was prepared by mixing equimolar proportions of cetyltrimethylammonium bromide (CTAB) and sodium 3-hydroxynaphthalene-2-carboxylate (SHNC) and by removing the counter ions (Na$^+$ and Br$^-$) by a solvent extraction technique described elsewhere.[5] The product was purified by recrystallization. CTAB was purchased from Sigma chemicals and SHNC from Atul products, Bombay, and both were used without further purification.

Solutions of pure CTAHNC in deuterated water were prepared 5 days before the experiment. At room temperature,

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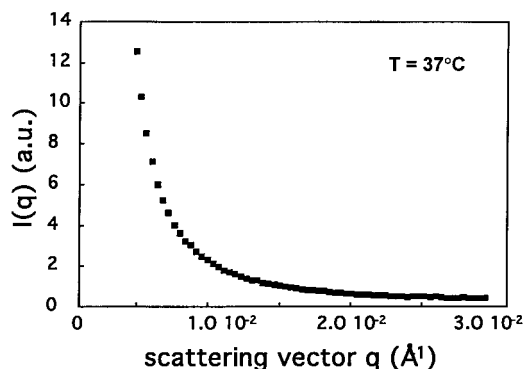**Figure 1.** Scattered intensity (au) as a function of the scattering vector, q, from a solution of 12 mM CTAHNC at $T = 37$ °C.

Figure 2. Scattering intensity (au) in a log scale as a function of the scattering vector, q, for a solution of 12 mM CTAHNC at 37 and 55 °C.

the samples were turbid. Before filling the neutron scattering cells, the samples were heated by a hot air flow until they became transparent. The neutron scattering cells were filled with the transparent (and more viscous) solution, and then they were thermostated for at least 15 min in the spectrometer sample holder at the desired temperature. The same procedure was applied to the preparation of CTAHNC + CTAB solutions. This procedure is possible since the vesicle to micelle transition in those systems is thermally reversible.[5]

Neutron scattering experiments were carried out on the PAXY spectrometer at Laboratoire Léon Brillouin, Saclay, France. Different spectrometer configurations were used: (1) sample–detector distance = 6.5 m and incident wavelength = 12 Å, (2) sample–detector distance = 4 m and incident wavelength = 10 Å. The data were recorded using a bidimensional detector containing 128 × 128 square cells of 5 mm length. Anisotropic data were regrouped in parallel and perpendicular direction with respect to the flow field using circular sectors of 10°. Raw data were normalized by the flat incoherent scattering of water, and the incoherent scattering from the sample was neglected since it is much smaller than the coherent signal. The neutron scattering curves are thus presented in arbitrary scattering units.

3. Results and Discussion

Consider first the pure 12 mM CTAHNC at 37 °C and at rest. As reported in ref 6, micrographs show the presence of large polydisperse vesicles in the system at this temperature. In Figure 1, the scattering intensity from this solution is plotted as a function of the scattering vector. A strong intensity increase at small angles is observed. Such a "central scattering" presents a slope close to −2 when plotted in a log–log scale (Figure 2). This observation is consistent with the predominant presence of vesicles, as observed by microscopy,[6] of a size too large to be measured as the data lie out of the Guinier diffusion regime. The slope of −2 observed for the data in this representation is characteristic for the scattering of a flat surface. In Figure 2, the scattering from a solution of 12 mM CTAHNC at 55 °C is also displayed. The curve at 55 °C, which develops a scattering shoulder, is shifted down for clarity. The straight lines with slopes of −2 and −1 are also represented for comparison. The slope of −1 corresponds to the scattering of a rigid rod without structure. At 55 °C, the viscosity of the solution is much higher than that observed at 37 °C,[6] and one can argue that the shoulder observed in the scattering arises from the correlation between micelles. The curve for 55 °C presents an "average slope" that is smaller than 2 (in absolute value). This shoulder is probably the result of an enhancement of correlation between cylindrical micelles that are formed upon increasing the temperature[7] since
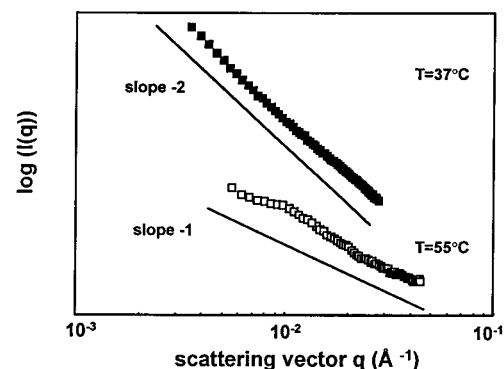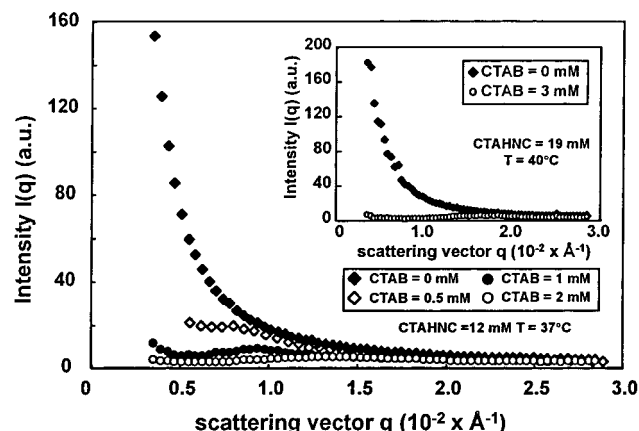

Figure 3. Scattering intensity (au) as a function of the scattering vector, q, for samples of 12 mM CTAHNC ($T = 37$ °C) and 19 mM CTAHNC ($T = 40$ °C) for different concentrations of added CTAB.

it was observed that in solutions of 12 mM CTAHNC the transition has a coexistence region of about 15° around 50 °C.[5]

The effect of the addition of CTAB is similar to that of the increase of temperature as can be seen in Figure 3. Here, two CTAHNC concentrations, 12 and 19 mM, are considered. Without any addition of CTAB, the scattering spectra exhibit an enormous increase at small angles, due to the scattering by very big objects, the vesicles. As CTAB is added, the intensity at smaller angles decreases drastically while a maximum develops at a finite scattering vector value q^*.[7] Very small amounts of CTAB are needed to induce the transition at such temperatures. Upon addition of 0.5 mM CTAB to the 12 mM sample, a correlation peak appears at $q^* \sim 0.008$ Å^{-1}. With increasing CTAB concentration, q^* is displaced toward higher q-values and saturates at about 0.014 Å^{-1}. Similar results are observed for the 19 mM sample with the saturation q^* value being 0.018 Å^{-1} (not seen on the scale of the figure). Associating the scattering maximum roughly to the distance between micelles, we can estimate the micellar number density, c, where $c = (q^*/2\pi)^3$. For the 12 mM sample, $c \sim 2.9 \times 10^{15}$ for [CTAB] = 1 mM and $c = 9 \times 10^{15}$ for [CTAB] = 2 mM. Optical micrography studies suggested that the vesicles in a mixture of 12 mM CTAHNC with 2 mM CTAB are probably converted into micelles for temperatures above 40 °C.[6] The present SANS study seems to corroborate this observation.

The temperature effect as well as the effect of addition of CTAB can be described as follows.[5,8] CTAHNC can be looked upon as a complex formed by two oppositely charged surfactants, CTA$^+$ and HNC$^-$. This ion pair effectively acts as a double-chain lipid and has a tendency to form vesicles.
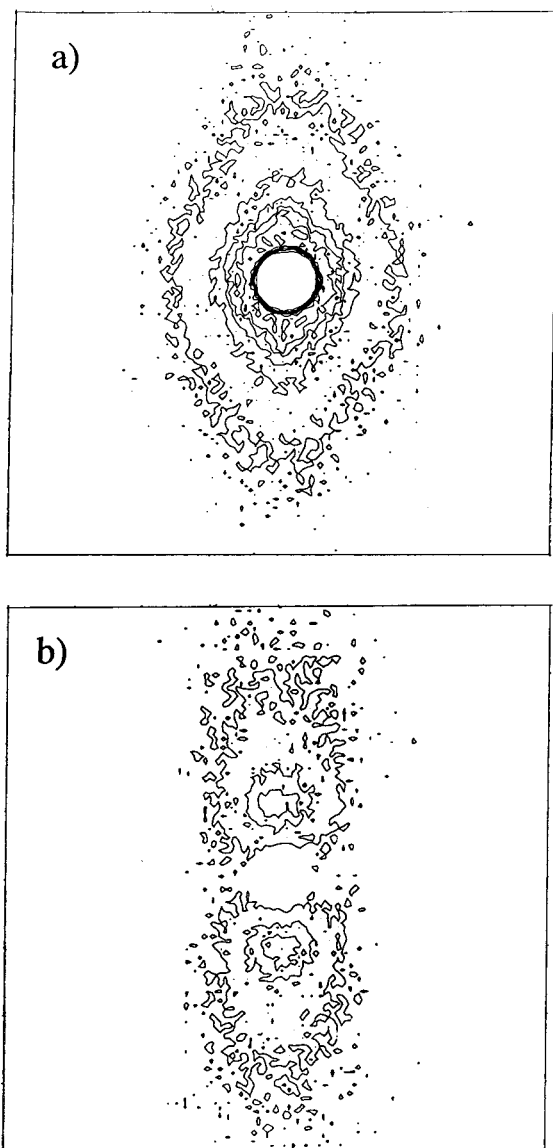
Figure 4. Isointensity curves for (a) 12 mM CTAHNC at $T = 37$ °C with $\dot{\gamma} = 7$ s^{-1} (vesicular phase) and (b) 12 mM CTAHNC with 1 mM added CTAB at $T = 75$ °C with $\dot{\gamma} = 31.5$ s^{-1} (micellar phase).

Figure 5. Scattered intensity (au) in the direction perpendicular to the flow as a function of the scattering vector, q, for the sample of 12 mM CTAHNC with 1 mM CTAB at 75 °C.

However, at a given temperature, a certain fraction of the complex dissociates and is in equilibrium with single ions, which act as single-chain detergents giving the system a tendency to form micelles. An increase in temperature is therefore equivalent to the addition of single-chain surfactants, shifting the system toward the micellar phase.

Consider now the effect of shear on CTAHNC dispersions. Figure 4 shows two isointensity curves taken as examples. In Figure 4a, the scattering from a solution of 12 mM CTAHNC without any added CTAB ($T = 37$ °C) under shear is displayed. Mostly vesicles are present in the system. The shear rate is $\dot{\gamma} = 7$ s^{-1}. The shape of the isointensity curves is close to an ellipse with a long axis aligned perpendicular to the flow direction. This alignment of isointensity curve is a feature of anisotropic objects that align along the flow direction. This suggests deformation and alignment of vesicles with shear. The shape of these isointensity curves is, in principle, related to the aspect ratio of the vesicles under shear flow. However, as shown by the micrographs of ref 6, the polydispersity in vesicle size is very high and their shape is not always spherical. Therefore, in the present case, any attempt to obtain a
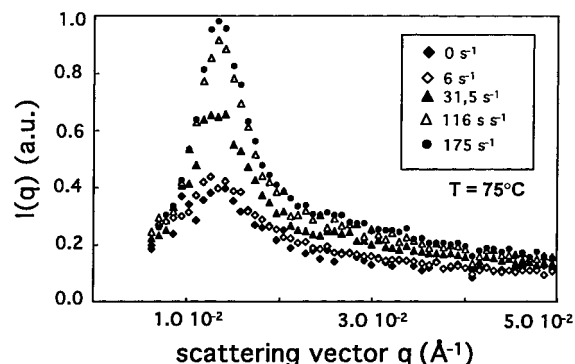
dependence of the aspect ratio of vesicles with shear rate would lack precision.

In Figure 4b, the other extreme of the phase diagram is considered. The sample subjected to shear is 12 mM CTAHNC with 1 mM CTAB at 75 °C. At this temperature and CTAB concentration no vesicles are observed on the microscope, and the rheological response of the system is that of a worm-like micelle phase.[6] Indeed, under shear, the isointensity curves present the typical signature of the scattering of cylindrical micelles aligned along the flow:[9] when the system is subjected to shear, the maximum ring on a bidimensional detector, corresponding to the correlation between micelles, transforms into two spots placed perpendicular to the flow. This is a consequence of the alignment of cylindrical micelles in the flow direction. In Figure 5, the scattered intensity in perpendicular direction with respect to the flow is plotted as a function of the scattering vector for a solution of 12 mM CTAHNC with 1 mM CTAB at 75 °C. The classical picture of cylindrical micelles subject to shear[9] is found in this case: for all employed shear rates, including zero shear, the position of the scattering maximum remains at the same finite value ($\sim$0.013 Å^{-1}). The overall behavior of the system at this temperature is the typical behavior of a worm-like micelle solution under shear. Rheological results of ref 6 together with the above results strongly suggest that at high temperatures CTAHNC solutions present mostly worm-like micelles.

We consider below the shear effect on mixed systems of vesicles and micelles. The scattering in parallel and perpendicular directions to the flow are displayed in Figures 6 and 7 for 12 mM CTAHNC without any added CTAB at 45 and 55 °C, respectively. The scattering at rest is also represented in both cases. At 45 °C, the isotropic scattering curve at rest shows a strong scattering due to the vesicles that are also observed optically.[6] As the shear rate increases, the scattering at small angles decreases in *both directions*, parallel and perpendicular to the flow, with respect to the isotropic curve. Alignment of any object along the flow direction should decrease the scattering parallel to the flow and increase it in the direction perpendicular to the flow. Decreasing of intensity *in both directions* is a strong indication of the disruption of vesicles upon shearing. At the same time, a maximum in the direction perpendicular to the flow at a finite scattering vector appears for high shear rates. The presence of such a maximum indicates strong alignment of objects along the flow direction, suggesting strongly the formation of micelles under shearing.

The sample at 55 °C already exhibits a small shoulder on the spectrum at rest. This indicates that, in this case, the micellar fraction is larger than that of the sample at 45 °C, if one assumes
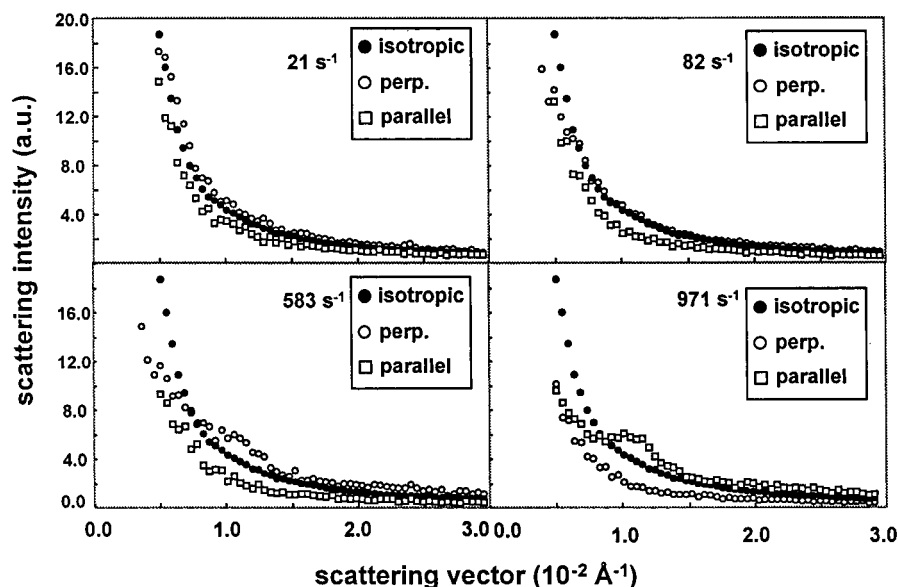
Figure 6. Scattered intensity (au) as a function of the scattering vector, q, in the directions parallel and perpendicular to the flow for a 12 mM CTAHNC solution at 45 °C. Curves for different shear rates are displayed as well as the isotropic scattering curve.

Figure 7. Scattered intensity (au) as a function of the scattering vector, q, in the directions parallel and perpendicular to the flow for a 12 mM CTAHNC solution at 55 °C. Curves for different shear rates are displayed as well as the isotropic scattering curve.
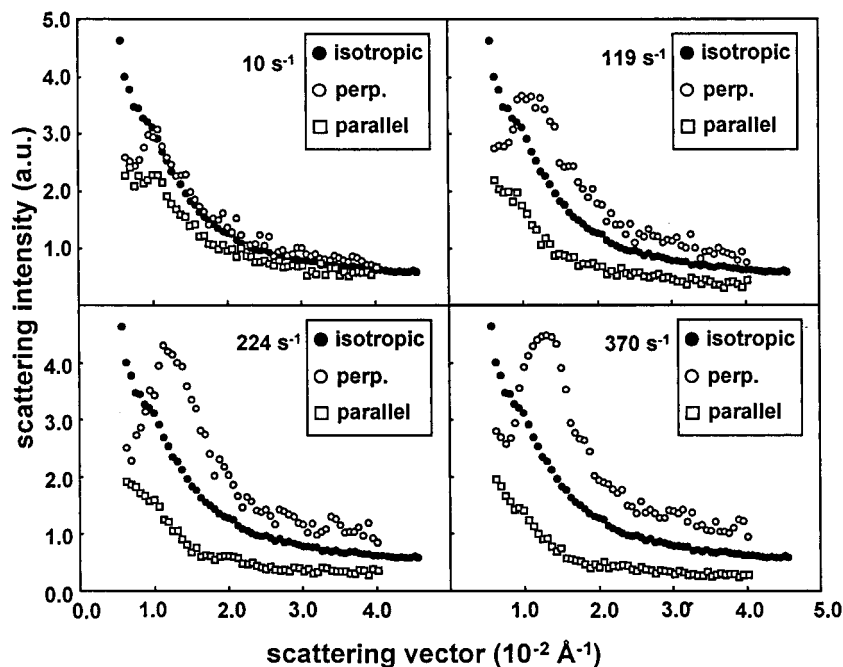
that the correlation shoulder comes from the scattering of micelles. It also exhibits appearance and displacement of a maximum toward higher values of the scattering vector at smaller shear rates than that needed for the sample at 45 °C. Also, the scattering maximum observed for $T = 55$ °C at 370 s^{-1} is much more pronounced than that observed for the 45 °C sample at a much higher shear rate (971 s^{-1}). It is also placed at higher q-values, indicating a shorter correlation distance between micelles. One can argue that because of a higher temperature, the sample at 55 °C contains a higher population of micelles than that at 45 °C. It is therefore much easier to observe, at low shear rates, the development and displacement of the correlation maximum in the perpendicular direction to the flow than what is probably due to the vesicle to micelle conversion. Note also that the scattering upturn at very small angles due to the presence of the vesicles is much more

pronounced in the sample at 45 °C than at 55 °C (the units of both figures are the same). As in the case of 45 °C, while a scattering maximum at a finite scattering vector appears with shear, the scattering intensity in *both directions* at very small angles decreases, strongly suggesting a vesicle to micelle transition induced by shear.

In order to elucidate the shift of the correlation maximum toward higher scattering vectors, and hence the increase in micelle number density with shear rate, a suitable choice of the concentration and temperature has to be made. The strong upturn at small angles due to the scattering from vesicles has the tendency to mask the scattering correlation peak. Also, as suggested by the curves discussed above, the smaller the scattering upturn due to the presence the vesicles, the smaller the shear rate needed to observe the correlation maximum. We therefore chose a sample of 12 mM CTAHNC with 0.5 mM
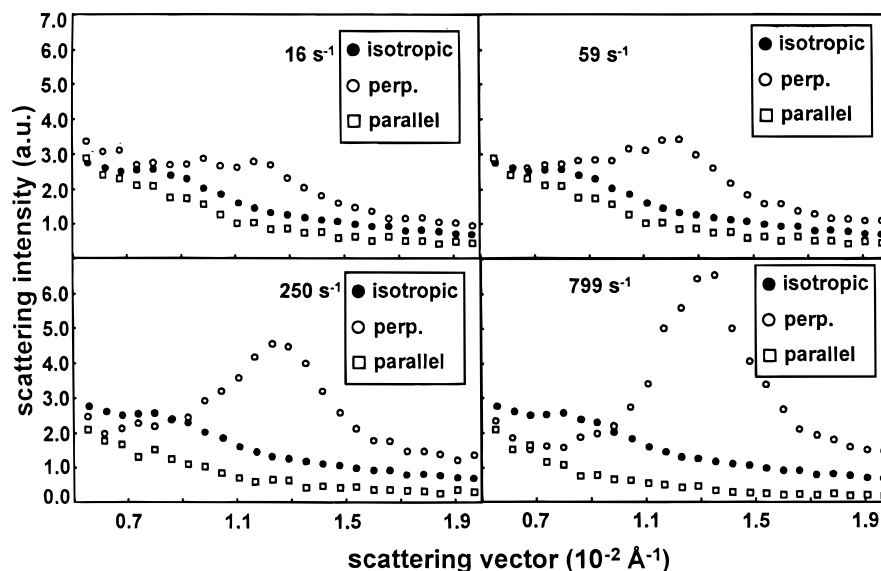
Figure 8. Scattered intensity (au) as a function of the scattering vector, q, in the directions parallel and perpendicular to the flow for a solution of 12 mM CTAHNC with 0.5 mM CTAB at 37 °C. Curves for different shear rates are displayed as well as the isotropic scattering curve.
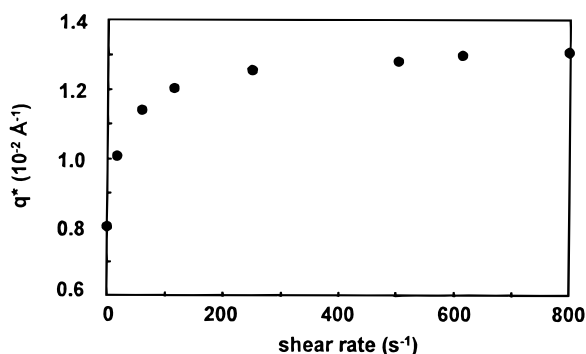

Figure 9. Maximum position $q*$ as a function of the shear rate for the solution of 12 mM CTAHNC with 0.5 mM CTAB at 37 °C.

CTAB at 37 °C for this study. As shown in Figure 3, in the absence of shear this sample provides a spectrum at small angles with a soft maximum at a finite scattering vector. In Figure 8, the SANS intensity curves for this sample at various shear rates in the directions parallel and perpendicular to the flow are displayed. The isotropic curve, the same as that of Figure 3, is also represented. For clarity, only the q-range around the maximum position is displayed. At zero shear rate, a small peak is observed at a q-value of 0.008 Å^{-1} as the sample contains a small fraction of micelles coexisting with vesicles at this temperature. As the shear rate is increased, the scattering peak observed in the perpendicular direction to the flow moves to higher q-values as its intensity increases. The shift of the correlation maximum towards high q-values suggests an increase in micellar volume fraction in the solution, and the increase in the maximum intensity corresponds to strong alignment of micelles in the flow direction.[9−12] For high shear rates (>500 s^{-1}) there is no significant displacement of the scattering peak, which suggests that most of the vesicles are converted into micelles. In Figure 9, the peak position, $q*$, is plotted versus shear rate. The final peak position reached by shearing in this sample is identical to that reached in pure 12 mM CTAHNC at 55 °C (see Figure 6); although in the latter case, an increase at small angles in both directions is still observable, suggesting that not all vesicles were, in that case, transformed into micelles. The dependence of the peak position on shear rate can be easily described by a model of spontaneous curvature where a coupling between the average curvature and shear has been considered.[13]

Finally, note that for data of Figure 8, as in the other above curves, the intensity at very small angles in both directions is smaller than that of the isotropic signal. The mechanism of alignment of vesicles with the shear flow cannot be responsible for this observation. When objects align with shear, the intensity scattered at small angles increases in the perpendicular direction to the flow while it *increases* in parallel direction. In the present case, the intensity at very small angles decreases in *both* directions. This is a strong indication that the population of vesicles decreases with increasing shear rate, that is, vesicles are, at least partially, disrupted by the flow.

4. Conclusions

The SANS results reported here support strongly the idea that a vesicle to micelle transition in cationic and anionic surfactant mixtures can be induced by shear. The transition, which can be also induced by an increase in temperature or by addition of CTAB, presents a large coexistence region. The effect of shear on suspensions containing vesicles only, as well as that on the coexistence phase, has been investigated. In both cases, the effect of shear on the scattering spectra was to produce (i) a strong decrease in the scattering at very small angles *in both directions* with respect to the shear and (ii) the development of a scattering maximum at a finite scattering vector. Feature i was attributed to the disruption of vesicles under shear while feature ii has been associated mostly to the correlations between cylindrical micelles that are suggested to develop under shear. The shift of the scattering maximum to higher scattering vectors with increasing shear rate has been ascribed to the increase in the fraction of micelles produced by the shear. The results presented here are in qualitative agreement with rheological experiments monitored by optical microscopy observations[6] carried out on the vesicle to micelle transition on the same system.

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