

# Distinctive effect of maleic acid and fumaric acid on structural transitions in cationic micellar solution

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**Abstract** Isomeric additives, maleic and fumaric acids (MA and FA) showed a distinctive influence on the structural transition induced by n-octanol in aqueous cetyltrimethylammonium bromide (CTAB) solution. With MA, significant increase in viscosity was observed on successive addition of n-octanol. Samples with high n-octanol concentration showed viscoelasticity. However, no such dramatic change was observed with FA. Rheological studies revealed the existence of entangled threadlike micelles in CTAB/MA/n-octanol system. Newtonian flow behaviour exhibited by the FA-containing samples indicated the presence of spherical micelles. The existence of threadlike micelles in MA containing samples was further confirmed by cryogenic transmission electron microscopy and small-angle neutron scattering studies. The favourable geometry and better acidic strength of MA are regarded as the factors synergistically facilitating unidimensional micellar growth in the presence of n-octanol. In contrast, the stronger hydrophobicity of FA resulting from trans geometry and feeble ionization, modifies the solvent properties and retards micellar growth.

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## Introduction

Surfactants are well known for their ability to micellize into diverse morphologies in aqueous medium. Self-assembly of ionic surfactants is highly sensitive to the presence of additives [1–3]. Slight changes in the additive structure may dramatically modify the features of aggregated structures. Recently, there is an increased interest in designing tunable fluids by exploiting the distinctive effect of structural isomers on micellar association. Many studies have revealed that cis and trans isomers of an organic moiety can influence micellar growth in entirely different ways owing to the differences in their hydrophobicity and orientation in surfactant solutions [4–6]. Additive-induced morphological transitions and consequent fluidity changes are greatly dependent on the nature of amphiphile–additive interaction and locus of additive solubilization. Trans isomers of aromatic acids, being less polar, are found to be very effective in bringing uniaxial growth and viscoelasticity to simple micelles. On the other hand, better aqueous solubility of cis isomers hinder their strong binding to micelles and disqualify them from inducing micellar growth. However, the effect of aliphatic isomeric dicarboxylic acids on micellar morphologies has not been addressed in the literature.

The effect of medium- or long-chain alcohols to get adsorbed onto the micelle palisade layer and to modify the viscosity of cationic micelles is well studied [7–9]. The insertion of alcohol molecules between the charged surfactant head groups reduces the surface charge density and facilitates the formation of alcohol–surfactant mixed micelles. The effect of alcohols becomes prominent in the presence of inorganic salts

or strongly binding aromatic acids [10, 11]. However, the influence of the simultaneous presence of an aliphatic hydrocarbon and alcohol has shown micellar disintegration. Studies with other organic additive combinations are obscure.

Herein, we report the differential effect of the aliphatic isomeric dicarboxylic acids, namely maleic acid (MA) and fumaric acid (FA) in the simultaneous presence of a cosurfactant to alter the aggregation properties of the classical cationic surfactant cetyltrimethylammonium bromide (CTAB). The cosurfactant used is *n*-octanol. Here, in contrast to the trend of aromatic acids, the presence of *cis* isomer is found to be more effective in bringing micellar growth in the surfactant–cosurfactant system. In the absence of octanol, both MA and FA showed similar behaviour in aqueous CTAB system, i.e. got dissolved into the micellar solution without modifying the viscosity significantly. This hints the inability of the acids to strongly bind to the micelle palisade layer and to screen effectively the head group charges. But some contrasting effects were seen with the introduction of octanol. A considerable increase in viscosity was observed with the successive addition of octanol to CTAB–maleic acid system. Also, the rheological response of the system with sufficiently high octanol concentration showed a Maxwell-type viscoelastic behaviour which indicates the presence of entangled wormlike micelles, alias threadlike micelles (TLMs) in the system [12]. In contrast, the viscosity of CTAB–fumaric acid system showed no considerable increase on addition of octanol. The rheological response resembled that of a normal Newtonian fluid which suggests the presence of spherical micelles [13].

The two isomers, maleic acid and fumaric acid, differ only in the position of the carboxyl groups. The *cis* isomer, maleic acid, is a stronger acid compared to its *trans* partner, fumaric acid (pKa1 values 1.92 and 3.02, respectively). So, maleic acid shows better dissociation in an aqueous medium [14]. Conductivity and pH measurements supported this argument. In the present system, since the selected acids do not contain phenyl ring, strong micellar binding, as in the case of aromatic dicarboxylic acids, is not possible [15]. So, the expected interaction of maleic acid or fumaric acid with cationic micelles is dominantly electrostatic which may synergistically assist the binding effect of octanol. The geometry of the acid is found to play a pivotal role towards such synergism. The presence of TLMs in the CTAB/maleic acid/octanol system and spherical micelles in the CTAB/fumaric acid/octanol system were further confirmed by SANS and cryo-TEM analysis.

## Experimental section

Cetyltrimethylammonium bromide (CTAB) was purchased from BDH (England). *n*-Octanol was purchased from Merck (Germany) and maleic acid and fumaric acid from Alfa Aesar (England). All the chemicals were used as received. Samples

were prepared in deionized Milli-Q water and kept in a water bath at 45 °C with stirring for about 1 h for homogeneity. The resulting samples were stored at room temperature for at least 1 day before running experiments. Rheological measurements were performed on an MCR-301 rheometer (Anton Paar, Germany) with a parallel plate measuring system (50 mm diameter). Sample temperature was maintained to the accuracy of  $\pm 0.01$  °C. The viscosities of samples were obtained from steady-shear measurements with a shear rate ranging from 0.001 to 100 s<sup>-1</sup>. Dynamic frequency spectra were obtained in the linear viscoelastic regime of each sample as determined by strain sweep measurements. All the frequency sweep measurements were performed in the angular frequency range of 0.05–100 rad s<sup>-1</sup>.

SANS experiments were carried out using SANS diffractometer at Dhruva Reactor, Bhabha Atomic Research Centre, Trombay. The mean wavelength of the incident neutrons is 5.2 Å, and the angular distribution of the scattered neutrons was recorded using a one-dimensional position sensitive detector. The diffractometer covers the scattering wave vector,  $q$  range of 0.017–0.032 Å<sup>-1</sup>. The sample was loaded in a quartz cell of 0.5-cm path length, and the sample temperature was maintained at an accuracy of  $\pm 1$  °C. The differential scattering cross-section per unit volume,  $I(q)$ , of the sample is determined from the measured scattered neutron intensity as per the procedure described elsewhere [16].

The cryo-TEM work was performed at the Laboratory for cryo-EM of Soft Matter, supported by the Technion Russell Berrie Nanotechnology Institute (RBNI). Vitrified cryo-TEM specimens were prepared in a controlled environment vitrification system (CEVS), at a controlled temperature and fixed relative humidity (100 %). It is followed by quenching into liquid ethane at its freezing point. The specimens, kept below -178 °C, were examined by an FEI T12 G2 transmission electron microscope, operated at 120 kV, using a Gatan 626 cryo-holder system. Images were recorded digitally in the minimal electron dose mode by a Gatan US1000 high-resolution cooled CCD camera with the digital micrograph software package.

## Results and discussion

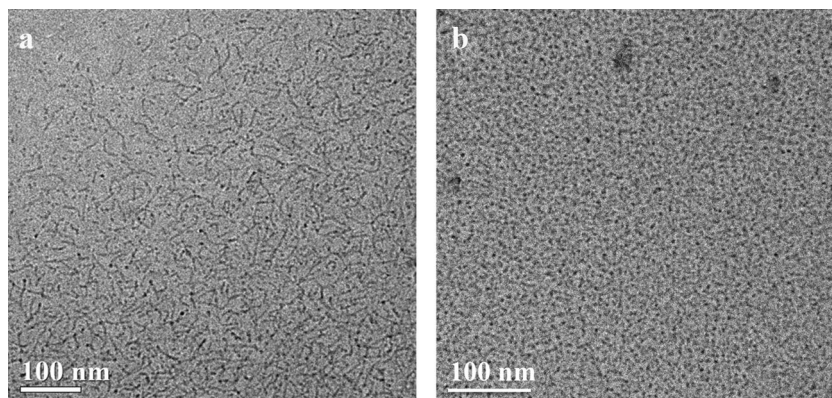
Initially, we studied the effect of varying concentrations of maleic acid (MA) and fumaric acid (FA) on the viscosity behaviour of aqueous CTAB solution. The viscosity of 0.1 M CTAB solution remained almost unaffected by the presence of different concentrations of either MA or FA. CTAB/*x*M MA of 0.1 M and CTAB/*x*M FA of 0.1 M solutions exhibited Newtonian flow behaviour with water-like viscosities, suggesting the presence of spherical or short rod-like micelles. The cryo-TEM image of 0.1 M CTAB/0.04 M MA solution revealed the presence of both spheroidal and short cylindrical

(ellipsoidal) micelles in the system but no TLMs capable of bringing viscoelasticity. In the case of 0.1 M CTAB/0.04 M FA solution, only spheroidal micelles are observed (Fig. 1). Both MA and FA are weak, non-aromatic dicarboxylic acids. The lack of phenyl ring limits their strong binding to micellar interface [17]. The charge screening offered by weakly dissociated FA or MA may not be sufficient to bring the elongation of spheroidal/ellipsoidal micelles and impart high viscosity to CTAB solution. However, the existence of short cylindrical micelles in the presence of MA indicates the better micellar charge screening offered by maleic acid molecules as compared to fumaric acid.

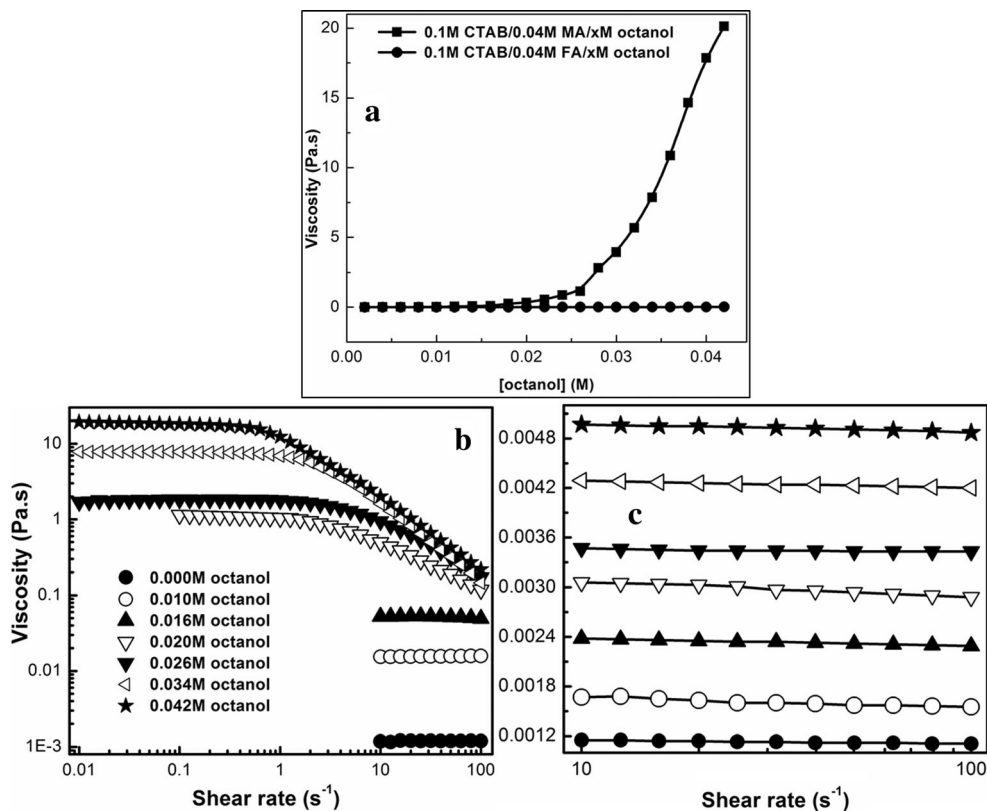
The ability of medium- or long-chain alcohols to bring structural transformations in ionic surfactant solutions are well established [18–20]. We have monitored the effect of four alcohols (hexanol, octanol, decanol and dodecanol) on the morphological transitions in aqueous solution of 0.1 M CTAB in the presence of either maleic acid or fumaric acid (Fig. S1). In all the cases, 0.1 M CTAB/0.04 M MA system showed perceptible increase in viscosity with increasing concentration of alcohol. On the other hand, in 0.1 M CTAB/0.04 M FA system, the viscosity remained almost constant on a progressive addition of different alcohols. Among the selected alcohols, octanol showed highest ability to induce viscosity growth in 0.1 M CTAB/0.04 M MA solution. The location of micellar solubilization of alcohols plays an important role in determining its ability to bring structural growth of globular micelles. Depending on the chain length, alcohols can locate on micellar surface, palisade layer and/or in the hydrophobic micellar core. It is well known that medium chain alcohols ( $n > 4$ ) that get solubilized in the micellar palisade layer exhibit maximum efficiency in promoting micellar growth [21]. Longer alcohols ( $n = 10$  or above) show a tendency to get solubilized in the micellar interior, which cannot bring considerable viscosification of the system [22]. In the present work, since octanol showed the highest efficiency to induce viscosity change in 0.1 M CTAB/0.04 M MA micellar solution, we selected octanol for further studies.

The effect of octanol concentration on the viscosity behaviour of 0.1 M CTAB/0.04 M MA and 0.1 M CTAB/0.04 M FA solutions are presented in Fig. 2a. As it can be seen, maleic acid-containing micellar system showed perceptible increase in viscosity with increasing concentration of octanol. The steady-shear rheology of 0.1 M CTAB/0.04 M MA/xM octanol samples at selected concentrations of octanol is given in Fig. 2b. Samples with lower octanol content showed shear independent viscosity. But beyond certain concentration (octanol  $> 0.02$  M), the samples exhibited shear-thinning non-Newtonian behaviour and high zero shear viscosity. The shear-thinning nature of micellar solutions hints the presence of long and flexible TLMs in the system. Surprisingly, such drastic growth in viscosity and occurrence of shear-thinning behaviour were not observed in 0.1 M CTAB/0.04 M FA/xM octanol solutions even at relatively high octanol concentration (Fig. 2c). In the presence of fumaric acid, micellar samples showed shear-independent Newtonian behaviour and water-like viscosity even at high octanol concentration. In order to draw better information regarding the viscoelastic properties of the samples, dynamic rheological measurements were carried out. Figure 3a shows the plot of elastic modulus ( $G'$ ) and viscous modulus ( $G''$ ) as a function of oscillatory shear frequency ( $\omega$ ) for some of the high viscosity samples of 0.1 M CTAB/0.04 M MA/xM octanol system. The corresponding plots for 0.1 M CTAB/0.04 M FA/xM octanol samples are given in Fig. 3b. Typical Maxwell-type pattern, exhibiting a viscous nature at low  $\omega$  and an elastic nature at high  $\omega$  with a plateau for  $G'$  and minimum for  $G''$ , can be observed for maleic acid-containing samples. A shift in the cross-over frequency ( $\omega_c$ , frequency at which  $G'$  and  $G''$  cross) to lower frequency region occurs with successive addition of octanol. This signifies an increase in relaxation time ( $\tau_R = 1/\omega_c$ ) which in turn hints the successive elongation of micelles upon increasing the octanol concentration [23]. Unlike maleic acid-containing samples, Maxwell-type viscoelasticity pattern was not followed by 0.1 M CTAB/0.04 M FA/xM octanol system (Fig. 3b). Agreement to Maxwell model can be further confirmed by semi-circular shape of Cole–Cole plot (plot of  $G''$  as

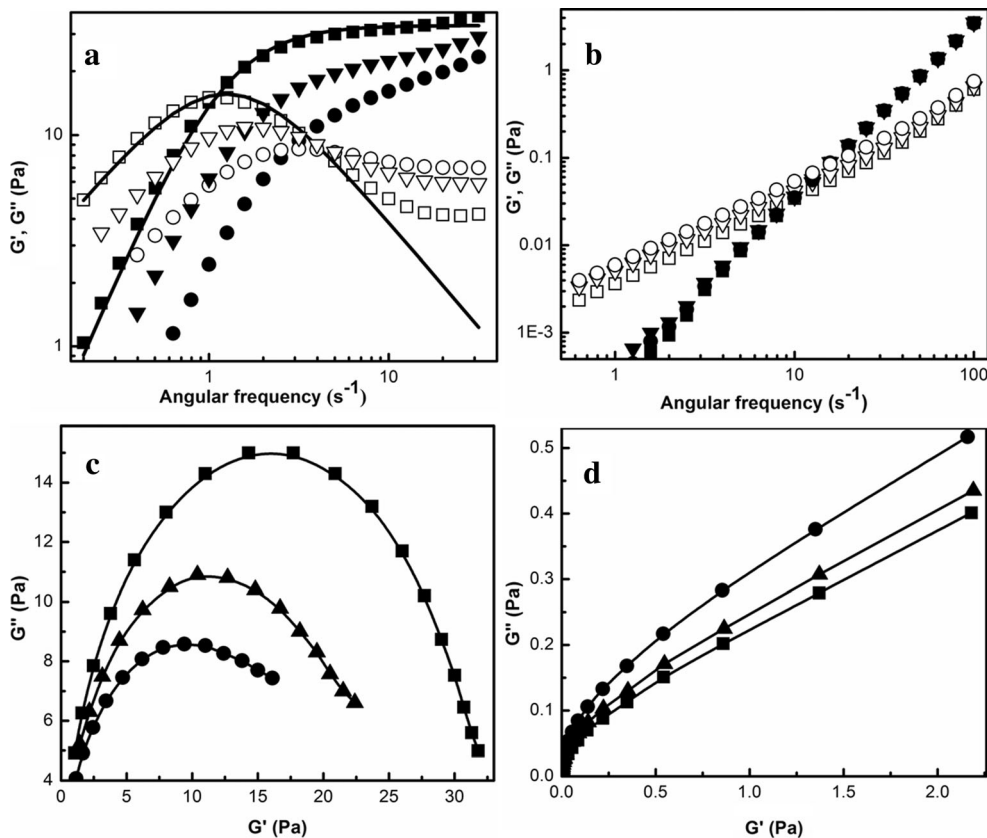
**Fig. 1** Cryo-TEM image of **a** 0.1 M CTAB/0.04 M MA and **b** 0.1 M CTAB/0.04 M FA micellar samples (scale bar 100 nm)



**Fig. 2** **a** Viscosity profile of 0.1 M CTAB/0.04 M MA/xM octanol and 0.1 M CTAB/0.04 M FA/xM octanol systems as a function of octanol concentration. **b** Steady-shear viscosity response of 0.1 M CTAB/0.04 M MA/xM octanol system at different octanol concentrations. **c** Steady-shear viscosity response of 0.1 M CTAB/0.04 M FA/xM octanol system at different octanol concentrations (symbol indication for octanol concentrations are same as **b**)



**Fig. 3** Frequency spectrum of **a** 0.1 M CTAB/0.04 M MA and **b** 0.1 M CTAB/0.04 M FA in the presence of • 0.036 M octanol, ▼ 0.04 M octanol and ■ 0.042 M octanol. Closed symbols represent  $G'$  and open symbols represent  $G''$  (solid lines in **a** represent fit to Maxwell model). **c** Cole–Cole plot for 0.1 M CTAB/0.04 M MA/xM octanol and **d** Cole–Cole plot for 0.1 M CTAB/0.04 M FA/xM octanol samples (symbol indications for octanol concentrations are same as above)

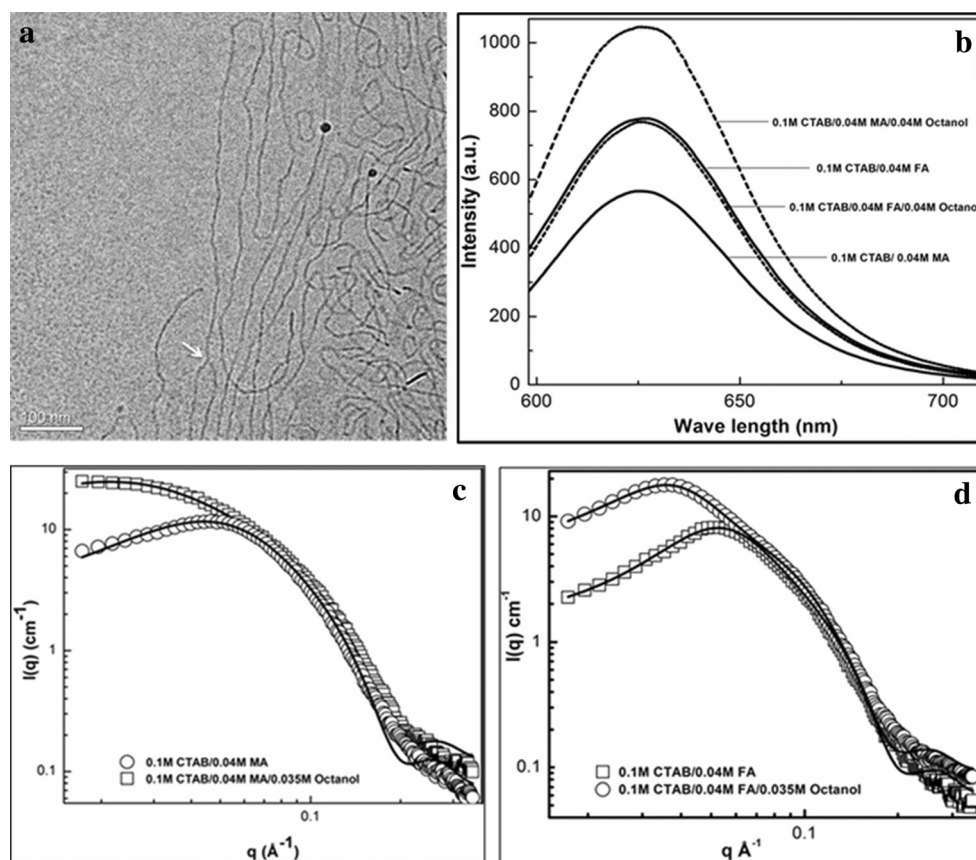


a function of  $G'$ ) [24]. Maleic acid-containing samples closely followed a semi-circular pattern in the Cole–Cole plot, whereas fumaric acid-containing samples deviated considerably from the semi-circle shape (Fig. 3c, d). Oscillatory shear response of 0.1 M CTAB/0.04 M MA/xM octanol samples together with the high viscosity values observed in the steady-shear rheology suggests the existence of entangled TLMs in the system at sufficiently high octanol concentration. The cryo-TEM image obtained for 0.1 M CTAB/0.04 M MA/0.04 M octanol sample (Fig. 4a) confirms the presence of long and entangled TLMs responsible for the high viscosity and viscoelasticity of the system [25].

The first pKa values of maleic acid and fumaric acid (1.92 and 3.02, respectively) indicate that maleic acid is a stronger acid compared to its trans isomer, fumaric acid. Conductivity and pH measurements carried out on 0.1 M CTAB/xM MA and 0.1 M CTAB/xM FA solutions also supported the better acidic strength of maleic acid (Fig. S2). In maleic acid, the close proximity of two carboxylic acid groups quickens the first dissociation as it is favourable for the subsequent hydrogen bond formation. Such a possibility of hydrogen bonding stabilization is absent in the trans isomer and is relatively weak in dissociation [26]. Hence, the charge screening offered by MA to CTAB micelles could be greater as compared to that offered by FA. The adjacent positions of two carboxyl groups

favour the proper orientation of maleic acid molecules on the micelle surface and support the compact association of octanol molecules into the micellar palisade layer. The trans positioning of polar groups in fumaric acid may not be supportive for a convenient arrangement on the micelle surface. Also, the trans geometry of fumaric acid makes it less hydrophilic compared to maleic acid. The changes in hydrophobic environment of micellar samples can be monitored by studying the fluorescence intensity of Nile Red entrapped in the micelles. Nile Red is a lipophilic dye, the fluorescence intensity of which varies depending on the hydrophobicity of the environment [27]. The fluorescence spectra of Nile Red obtained in different micellar solutions are presented in Fig. 4b. Nile Red showed better fluorescence intensity in 0.1 M CTAB/0.04 M FA sample as compared to 0.1 M CTAB/0.04 M MA sample, suggesting the higher hydrophobicity of the fumaric acid-containing system. But a noticeable increase in the fluorescence intensity of Nile Red can be observed in 0.1 M CTAB/0.04 M MA/0.04 M octanol solution, while the intensity was not much influenced by the presence of octanol in 0.1 M CTAB/0.04 M FA solution. Increase in Nile Red fluorescence intensity in the CTAB/MA/octanol solution suggests that there is an expansion in the hydrophobic core volume of the micelles into which the stain is encapsulated. Elongated micelles are characterized by higher packing parameter ( $p = v/a_0l$ , where  $v$  is the

**Fig. 4** **a** cryo-TEM image of 0.1 M CTAB/0.04 M MA/0.04 M octanol sample (scale bar 100 nm). **b** Fluorescence emission spectra of Nile Red (2.5  $\mu$ M) in different micellar solutions. **c** SANS profile for maleic acid-containing micellar samples and **d** SANS profile for fumaric acid-containing micellar samples. Solid lines in **c** and **d** represent fit to ellipsoidal model



volume of hydrocarbon tail with a maximum effective length  $l$  and  $a_0$  is the cross-sectional area of the head group at the interface) as compared to spherical micelles [28]. Hydrophobic core volume is more in the case of long TLMs as compared to small globular micelles. So, the higher fluorescence intensity of Nile Red in 0.1 M CTAB/0.04 M MA/0.04 M octanol supported the existence of elongated micelles. The insignificant changes in the fluorescence intensity in the fumaric acid system hint that the micelles are not grown considerably after the addition of octanol.

An important factor determining the effectiveness of alcohols to induce micellar growth is the partitioning of alcohol molecules between micellar phase and bulk water phase [29]. Octanol when added to ionic micellar solution, owing to its negligible aqueous solubility, prefer to be in the micelle palisade layer than in the bulk water phase, thereby acting as a spacer reducing the electrostatic repulsion between charged surfactant heads and facilitating micellar growth [30]. But any modification in the solvency of the medium may alter the expected partitioning trend of alcohols. Certain additives can make water a better solvent for surfactant monomers or bound cosurfactants, leading to micellar disintegration [29, 31]. L. R. Harutyunyan and co-workers have recently showed the efficiency of ascorbic acid to act as a structure-breaking solutes and co-solvent, causing reduction in surfactant aggregation number in ionic micellar solution [32]. The presence relatively hydrophobic fumaric acid in aqueous medium may favour better dissolution of either or both octanol and the surfactant monomers, persuading them to leach out to the bulk water phase. In order to verify this point, we monitored the effect of concentration of FA or MA on the viscosity behaviour of surfactant–alcohol (0.1 M CTAB/0.042 M octanol) micellar sample (Fig. S3). An increase in viscosity with the progressive addition of MA was observed which is consistent with the proposed view of synergistic assistance offered by MA to octanol in prompting micellar elongation. However, at higher MA concentrations, a decrease in viscosity was observed. This could be due to the branching of TLMs, offering a faster mechanism for relaxation [33]. A few branch points can be seen in the cryo-TEM image of 0.1 M CTAB/0.04 M MA/0.04 M octanol sample (indicated by arrow head in Fig. 4a). Hence, the increased number of branch points can be expected at higher MA concentrations, which contribute towards viscosity reduction. Contradictory to the effect of MA, a continuous decrease in viscosity was observed on progressive addition of FA to 0.1 M CTAB/0.042 M octanol micellar sample. The initial viscosity itself was comparatively low hinting the presence of small aggregates. Further reduction in viscosity with increase in FA concentration suggests the possibility of leaching out of micelle components into the bulk phase and consequent decrease in micelle size [34]. So, from the above discussion, one can view the cis isomer maleic acid as a charge-screening additive synergistically assisting

the binding effect of octanol and favouring the formation of TLMs, whereas the trans isomer, fumaric acid, as a co-solvent which modifies solvent properties and retards micellar growth.

SANS analysis was performed on different micellar samples in order to further elucidate the microstructural features responsible for the differences in flow properties of maleic acid and fumaric acid-containing micellar systems. Samples were made in  $D_2O$  to get the required contrast between micellar structures and solvent. SANS spectra of micellar solutions in the absence and presence of octanol are presented in Fig. 4. The scattering profile of 0.1 M CTAB/0.04 M MA (Fig. 4c) shows a broad correlation peak in the low  $q$  region which is an indication of repulsive interaction between charged micellar heads. The peak occurs at  $q_m \sim 2\pi/d$ , where  $d$  is the average distance between micelles and  $q_m$  is the value of  $q$  at the peak position [35]. Significant increase in the scattering intensity and disappearance of correlation peak can be seen for 0.1 M CTAB/0.04 M MA/0.035 M octanol sample implying an increase in the micellar dimension and decrease of effective charge per micelle. These observations strongly suggest scattering from elongated micelles in the octanol added sample [36]. Model fitting of experimental values is appeared to be in good agreement with the data (solid lines in Fig. 4c). The values of semi minor axis ( $b=21 \text{ \AA}$ ) and semi major axis ( $a=51 \text{ \AA}$ ) obtained from large  $q$  data analysis of the SANS spectrum of 0.1 M CTAB/0.04 M MA sample support the presence of ellipsoidal micelles in the system (details of SANS analysis is provided in the supporting information). A considerably high value of semi major axis ( $a \approx 111 \text{ \AA}$ ) was obtained for 0.1 M CTAB/0.04 M MA/0.035 M octanol sample. But the semi minor axis ( $b=21 \text{ \AA}$ ) remained unaltered which hits the uniaxial elongation of micelles. Unlike maleic acid-containing samples, the SANS spectra of both 0.1 M CTAB/0.04 M FA and 0.1 M CTAB/0.04 M FA/0.035 octanol samples (Fig. 4d) show correlation peaks in the low  $q$  region, which indicates poor charge screening of CTAB micelles in the fumaric acid-containing samples even in the presence of octanol. The results obtained from SANS analysis are in good agreement with the rheology data, confirming the presence of small micelles in the CTAB/FA system before and after octanol addition whereas a transition from spheroidal or ellipsoidal micelles to elongated TLMs in the CTAB/MA solution upon adding octanol.

The micellar structures responsible for the distinctive flow properties of CTAB/MA/octanol and CTAB/FA/octanol solutions are identified with the support of rheology, cryo-TEM, SANS and fluorescence studies. The transition from watery liquid to viscoelastic, gel-like fluid observed in the CTAB/MA system on progressive addition of octanol is ascribed to the morphological changes occurring in the system from short micelles to entangled TLMs. The structural transitions induced by the palisade layer solubilization of octanol are well

assisted by the favourable cis geometry of maleic acid molecules. The retention of water-like flow properties by CTAB/FA/octanol system suggests that fumaric acid with trans geometry fails to synergistically assist the octanol molecules in inducing morphological changes to CTAB micelles. Instead of assisting micellar growth, fumaric acid modifies the solvent properties causing the dissolution of micellar components into the bulk phase. The contrasting effect of the two isomeric acids on the flow properties of CTAB/octanol solution can be effectively utilized for the designing of tunable fluids.

## Conclusion

The distinctive effect of two simple isomeric acids on the aggregation properties of surfactant micelles has been demonstrated. The cis isomer maleic acid is found to be very effective in synergistically assisting n-octanol to induce structural transitions in CTAB solution. Very high viscosity and viscoelasticity are shown by CTAB solution containing maleic acid and certain concentrations of octanol. But the trans isomer fumaric acid under identical conditions is incapable of inducing such high viscosity and viscoelasticity to the CTAB/octanol micellar solution. Rheological studies, SANS analysis and cryo-TEM images helped to confirm the presence of long TLMs in the high viscosity samples containing maleic acid. The dissimilar effect of the geometrically isomeric acids on the aggregation properties of ionic micelles may open up a facile route to design stimuli-responsive fluids.

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