Solute Induced Chaotic Motion of Self-Propelled Droplets

Prateek Dwivedi, Dipin Pillai and Rahul Mangal

ABSTRACT: The active transport of micron sized 4'-pentyl-4-biphenylcarbonitrile (5CB) liquid crystal droplets propelled through an aqueous solution of tetradecyltrimethylammonium bromide (TTAB) as surfactant and glycerol as a solute, is investigated. On addition of glycerol, it was observed that the motion of active 5CB droplets exhibited a transition from smooth to a jittery chaotic motion. The motion was further found to be independent of the droplet size and the nematic state of 5CB. Upon conducting analogous experiments with Polyacrylamide (PAAM) as the solute, it was confirmed that a mere increase in viscosity cannot explain the transition. We propose the physicochemical interactions of glycerol with TTAB and 5CB, as the main cause responsible for the observed jittery motion. Presence of glycerol significantly enhances the rate of solubilization of the 5CB droplets resulting in a quicker re-distribution of the adsorbed TTAB molecules on the interface causing the droplet to momentarily stop and then restart in an independent direction. This hypothesis is supported by the time evolution of droplets size and interfacial velocity measurements in the presence and absence of glycerol. Overall, our results provide fundamental insights into the scheme of complex interactions emerging due to the presence of a non-reactive solute such as glycerol.

INTRODUCTION

Thermal fluctuation induced Brownian motion offers poor control over the motion of colloidal (10nm-1000nm) particles. Therefore, at these small length scales, where viscous forces dominate inertia (Re <1), some unique propulsion strategies, different from the mechanism used by macro-organisms, are required. Biological microorganisms such as bacteria and unicellular protozoa, utilize appendages attached to their molecular motors which are driven by the chemical energy extracted from the surrounding medium resulting in their net mechanical motion.1-3 This unique ability of the microorganisms to "self-propel" themselves has intrigued the scientific community over decades and in an attempt to fundamentally understand their motion, numerous simulation and theoretical studies have been undertaken.3-9 Lately, researchers have also started exploring artificial model systems known as “artificial active matter” or “artificial micro-swimmers”, which mimic the life-like motion of the micro-organisms.10-12 Unlike equilibrium Brownian motion, these artificial active systems exhibit significantly different transport characteristics. Upon carefully tailoring the design, these artificial systems can transport a cargo, perform an intricate task in microscopic domains and also tune the bulk material properties. Therefore, apart from providing fundamental insights into this out-of-equilibrium motion, these systems contribute to attract tremendous interest due to their potential application in diverse fields such as medicine, material science and environmental science.13-17

These artificial micro-machines do not rely on any external force for their propulsion. Instead, they use a local (particle level) force generated by the asymmetric interactions with the surrounding medium. One way, the desired asymmetry can be invoked is via incorporating an intrinsic asymmetry (shape or composition) in the particle itself. Janus colloids, in which two half sides of the surface of the particles are of different chemical compositions are widely used for self-propulsion. Their chemical inhomogeneity generates an asymmetric interaction with the surroundings, which drives the particle by a mechanism known as self-diffusiophoresis.12,18,19 Another such class of artificial active matter is “active emulsions”10,20-23, where droplets of one fluid perform self-propelled motion while dispersed in another immiscible fluid. The most commonly explored system is of oil/water droplets in surfactant filled water/oil medium. In these active emulsions, symmetry is ‘spontaneously’ broken in an otherwise isotropic droplet, by rendering the surfactant concentration along the interface non-uniform via some mechanism. Asymmetric coverage of the surfactant at the interface creates a gradient in the interfacial tension (γ) which drives the fluid at the interface from high γ towards low γ, which is the well-known Marangoni flow. Since, there is no net external force acting on the system, this interfacial flow propels the droplet towards the region of low interfacial tension. In contrast to solid active Janus particles, these active droplets have the capability to self-deform24,25 while performing robust active motion. Therefore, these systems are considered as model systems to understand microbiological swimmers. In addition, due to their ability to exhibit chemotaxis21 and their bio-compatibility, these droplets are compelling segments for active matter engineering including drug delivery and other bio-medical applications.17

Over the years, different approaches to invoke spontaneous asymmetry in isotropic droplets with uniform surfactant coverage, have been reported. One approach is to use localized targeted chemical reactions such as hydrolysis26,27 and bromination22,28 of surfactant molecules which alter their surface activity. Numerous experimental reports have
utilized a similar approach of interfacial chemical reaction to achieve self-propulsion of droplets.21,29,30 Another popular approach is to utilize the adsorption-depletion of surfactants triggered by micellar solubilization.21,31–33 Although the exact mechanistic details remain elusive, here we briefly discuss the widely accepted hypothesis. For bulk surfactant concentration above its critical micellar concentration (CMC), emulsion droplets disintegrate into smaller nanosized droplets/filled-micelles through the process of “micellar solubilization”.10,20,34 During solubilization, nano-droplets are released by incorporating the surfactant molecules from the interface of the parent droplet and from the free surfactant molecules present in the continuous phase. As a result, the droplet interface gets depleted of surfactant molecules, which is replenished by the breakup of free micelles approaching the moving droplet. Due to the active motion, the front edge of the droplet gets more supply of free micelles compared to the trailing edge. Therefore, as a result of the two simultaneous processes the apex of the droplet always maintains high surfactant concentration in comparison to the trailing edge which further propels the droplet in the same direction. It is believed that at sufficiently high surfactant concentration, minor fluctuations in droplets position and surfactant coverage can trigger the active motion. Theoretically, it has been shown that above a critical Peclet number a stationary isotropic Brownian droplet can become unstable, leading to an autonomous sustained active motion.32,33

Different combinations of oil droplets in aqueous ionic surfactant solutions10,20–27,35 and inverse oil in water emulsions36 have been reported to display self-propelled motion through this micellar solubilization. Actively moving, nemat liquid crystal (LC) droplets, are known to help in visualization of the flow-field inside the droplets. Experimentally, 4-pentyl-4’-cyanobiphenyl (5CB) a thermotropic liquid crystal in aqueous solution of ionic tetradecyltrimethylammonium bromide (TTAB) surfactant has been mostly studied.21,34,37,38 Using 5CB in TTAB aqueous solution as the model system, so far researchers have investigated a few fundamental aspects of the locomotion of the droplets including the effect of the surfactant concentration and size of the droplet.37 Kruger et al. demonstrated that the nematic phase of the droplet causes the droplet to adopt a novel curling mode of motion.38 These droplets have also been demonstrated to exhibit chemotaxis and negative autochemotaxis, certifying them to be the most ideal to study of biological microorganisms and cellular motion.

An extensive literature survey suggests that previous studies typically have overlooked the presence of non-reactive molecular solutes in the continuous phase. Addition of such solute is expected to alter various properties of the system including viscosity, pH, interfacial tension etc., which can have a profound effect on the self-propelled motion. Furthermore, to realize the goal of using these artificial model active droplets in performing intricate tasks, it is critical to understand the effect of these additional solutes. In this experimental study, to the best of our knowledge for the first time, we have explored the effect of the addition of glycerol as a solute on the active motion of 5CB oil droplets. Properties of being thermally stable, its good miscibility with water and poor miscibility with 5CB39, made glycerol an ideal candidate.

### EXPERIMENTAL SECTION

**Figure 1:** Schematic representation of the experimental setup. The scale bar in the optical micrograph corresponds to 40 µm.

We dispersed thermotropic liquid crystal 4-pentyl-4’-cyanobiphenyl (5CB, Sigma Aldrich) droplets in aqueous solution of 6wt% trimethyl ammonium bromide (TTAB, Loba chemicals). Glycerol (Loba Chemicals) and polyacrylamide (PAAM, molecular weight ~ 600 kDa, Polysciences Inc.) were separately used as molecular solutes. 5CB droplets of size ~20µm-100µm were produced by vortexing the mixture. Low concentration of 5CB ~ 0.15 v/v% was used to ensure low number density of droplets to avoid droplet-droplet interaction.

The emulsion was injected into a custom-made optical cell with vertical height of 100 µm. Motion of isolated 5CB droplets was observed using upright polarized optical microscope Olympus BX53. An Olympus LC30 camera with 2048 x 1532 pixels resolution was used to record the motion of the droplets. A thermal stage was mounted on the microscope to maintain a constant temperature during the measurements. Droplet tracking was performed with ImageJ using an image correlation-based approach to obtain particle trajectories (X(µm), Y(µm) vs. Δt).

Interfacial tension of 5CB in aqueous surfactant solution with varying TTAB concentration (cTTAB) with the addition of different solutes, was measured at 25 °C using pendant drop contact angle meter (Data Physics OCA 35). A droplet of 5CB was produced in the aqueous phase and the contour
shape of the hanging LC droplet was fitted using Young-La-place equation equation. A Rheometer (TA Instruments DHR3) with a couette assembly was used to measure the viscosity of the aqueous PAAM and glycerol solutions.

RESULTS AND DISCUSSION

To validate our experimental protocol, we first explored the motion of 5CB liquid crystal droplets in aqueous TTAB surfactant (6wt%) solution at constant temperature of 25°C (see supporting videos S1-S3). Since, it is known that micelles play a key role in the propulsion mechanism, maintaining the bulk surfactant concentration >> CMC is considered to be a critical requirement.10,20,21 CMC for TTAB in water ~ 0.13wt% which ensured that C_{TTAB} (=6wt%) >> CMC. Since, the height of the optical cell is comparable to the droplet size, their motion remains mostly constrained in 2D (X-Y). In figure 2(a), we show few representative X-Y trajectories of different sizes of active 5CB droplets for a duration of 100 s. Absence of any overall anisotropy in the trajectories confirm the absence of any noticeable bulk convection. Using the center of mass position of the droplets at different time intervals, 2D mean square displacement (MSD) vs $\Delta t$ was calculated, figure 2(b). Parabolic nature of the MSD confirms the active motion. Displacements of the active droplets are observed to be much larger compared to the typical Brownian MSD values (=4D$\Delta t$) for the droplets of similar size. Here, $D = \frac{k_BT}{6\pi\eta R}$ is the Brownian Diffusivity obtained using classical Stokes-Einstein equation. Here $k_B$ is the Boltzman constant, $T$ is the absolute temperature, $\eta$ is the viscosity of the continuous phase and $R$ is the size of the droplet. The trajectories also indicate a size-dependent droplet locomotion, with larger droplets (50µm-70µm) performing random active motion, moderate size (20 µm-50 µm) droplets showing spiral trajectories (curling motion) and smaller droplets (<20 µm) displaying relatively linear motion. This observed change in the mode of active transport with droplet size, is attributed to the viscous forces deforming the director field of the nematic 5CB droplets. Increasing droplet size results in higher magnitude of the MSD values for same $\Delta t$, which suggests higher propulsion speed for larger size of the droplets. These observations of the control experiments are in agreement with the previous reports.37,38

Next, to investigate the effect of the addition of molecular solute on the motion of active 5CB droplets, we repeated these measurements with the addition of 80wt% glycerol to the surfactant-laden aqueous phase (see supporting videos S4-S6). Again to ensure self-propulsion, through the measurement of interfacial tension $\gamma$ w.r.t. $c_{TTAB}$ (see figure 1S) we confirmed that with 80wt% glycerol CMC(=0.45wt%)<<$c_{TTAB}$ (6wt%). The corresponding X-Y trajectories (~100 s) of active 5CB droplets, shown in figure 3(a), indicate an anomalous jittery behavior. Additionally, the fluctuations in the motion were observed for different size of droplets. In figure 3(b), we show the corresponding 2D MSD data. Clearly, the MSD values in presence of 80wt% glycerol is significantly lower compared to the MSD obtained in the absence of glycerol. This suggests that glycerol significantly lowers the average speed, which is consistent with an expected slowing down due to the increased viscosity ($\eta_{80wt\%glycerol-water}$ ~40 Pa-s and $\eta_{water}$ ~ 1Pa-s). We also notice, that in presence of 80wt% glycerol, there is no significant variation in MSD values at different times for different size of droplets, indicating that the average propulsion speed is not size dependent. The Brownian fluctuations $\sqrt{4D\Delta t}$ for these droplets of similar size for $\Delta t=100$s were ~0.16-0.28 µm, which are significantly smaller than the observed fluctuations (~10 µm), confirming that the Brownian motion is not responsible for increased randomness in the motion. For active colloids, it is well known that the change in direction of motion is influenced by the Brownian
rotational diffusivity $D_r = \frac{k_BT}{8\pi \eta a^2}$. In active droplets, other mechanisms such as interfacial instability etc., may also contribute to the change in direction of active transport. Nonetheless, the onset of this peculiar chaotic motion on the addition of glycerol to the aqueous phase, is in complete contrast to the theoretical expectations of reduced rotation in more viscous media. Through additional experiments, figure 3(c), we also observed that the fluctuations in an otherwise smooth active trajectory, increases continuously with an increase in concentration of glycerol in the aqueous phase. The above observations clearly suggest that the chaotic fluctuations are non-Brownian in nature and the underlying mechanism is solute induced, which we shall expand upon later.

Using the X-Y data, we then also computed the average instantaneous velocity ($v_{inst}$). As shown in figure 4, in contrast to the average propulsion speed, despite $\eta_{80wt\% \text{glycerol-water}} \sim 40^*\eta_{\text{water}}$, $v_{inst}$ values are comparable to the no glycerol case. This is indeed an unusual

Figure 3: 5CB droplets in 6wt% TTAB aqueous solution with 80wt% Glycerol: (a) Trajectories (~ 100 s) of active with varying droplet size. (b) Mean square displacement (MSD) with time. Lines represent the MSD values for active droplets in just the aqueous solution as shown in figure 2(b). (c) X-Y trajectories of active 5CB droplets (~50 µm) in 6wt% aqueous TTAB solution with varying glycerol concentrations. All Scale bars correspond to 100 µm.

Figure 4: Comparison of average instantaneous speed ($v_{inst}$). Inset shows the comparison of the persistence length ($L_p$), for active 5CB droplets in 6wt% TTAB aqueous solution.
observation, which we will discuss later in the article. Using \( v_{\text{inst}} \), we further calculated the persistence length \( L_p = \tau_R v_{\text{inst}} \) for the active 5CB droplets. Here, \( \tau_R \) is the rotational time scale which is obtained by fitting the velocity autocorrelation \( C(t) = \langle v_{\text{inst}}(t) v_{\text{inst}}(0) \rangle \) using following equation, supporting figure 25:

\[
C(\Delta t) = 4D\delta(\Delta t) + v_{\text{inst}} \cos(\alpha t) \exp(-2\alpha t/\tau_R) \ldots (1)
\]

Figure 5: X-Y trajectory of (a) Isotropic 5CB droplet in 6wt% TTAB aqueous solution (b) Nematic 5CB droplet in 6wt% TTAB aqueous solution with 0.8wt% PAAM. Both scale bars correspond to 100 \( \mu \)m.

Here, \( D \) is the Stokes-Einstein diffusivity, \( \omega \) is the angular velocity of the droplet. Consistent with the previous observations, addition of glycerol significantly lowers \( L_p \) compared to no glycerol case, see inset to figure 4. Overall, we conclude that in the presence of glycerol 5CB droplets were propelled with similar instantaneous velocity with that in the absence of glycerol. However, due to frequent fluctuations and change in direction their net drift and the persistence length was significantly lesser.

Now, we proceed to investigate whether the nematic phase of the 5CB droplet is the cause behind the observed chaotic motion. At 25°C, 5CB droplet is in the nematic phase which has been earlier shown to play a critical role in governing the mode of active transport in surfactant solution.\(^{27,28}\) In presence of TTAB the 5CB molecules align perpendicular to the interface forcing a point defect to form at the core of the droplet. During locomotion in aqueous surfactant solution, it was observed that the defect moves towards the stagnation point at the apex of the droplet. The viscous forces at the leading edge of the droplet try to displace the defect in the angular direction which are countered by the elastic forces of the liquid crystalline phase. For smaller droplets due to high elastic energy the defect remains unmoved, whereas for bigger droplets the defect dislocates to some equilibrium angle forcing the droplets to execute curling motion. On visualizing the 5CB droplet in 80wt% glycerol aqueous solution we noticed that the point defect fluctuated randomly in different directions (supporting video S7), consistent with the jittery motion of the droplet. To investigate the exact role of the nematic liquid crystalline phase of 5CB on its chaotic motion in presence of glycerol, we carried out experiments at T=42°C, which is above the nematic to isotropic transition temperature of 35°C.\(^{40}\) Interestingly, the observed motion (supporting video S8) was similar to the motion at 25°C and the droplet displayed chaotic motion, see figure 5(a). Therefore, it clearly establishes that the nematic structure of the droplet is not responsible in originating the rapid fluctuations in the motion of droplet.

Next, to understand the role of the increased viscosity on the observed chaotic motion, we examined the motion of 5CB droplets in 0.8 wt% aqueous PAAM polymer solution carrying 6wt% TTAB (supporting videos S9-S10). Viscosity of aqueous polymer solution was nearly matched with that of the glycerol aqueous solution (figure 3S). Additionally, rheology measurements confirmed that for the experimental time scales PAAM solution did not display any elastic effects (see figure 3S). Figure 5(b) shows the trajectory of 5CB droplet (~51 \( \mu \)m) in 6wt% TTAB aqueous solution with PAAM. Clearly, the anomalous jittery motion of the droplets was absent, rather, the trajectories resemble the unperturbed motion typically observed in just the aqueous TTAB solution. Therefore, we conclude that the increased viscosity is not the underlying reason behind the anomalous motion of 5CB droplets in glycerol-water solution.

Figure 6: Rate of solubilization (-dR/dt) of the active 5CB droplets in different surroundings. Inset shows the corresponding linear decrease in size (R) with time.

Next, to explain the observed jittery motion, we focus on the continuous dissolution of the droplet leading to a linear decrease in size (-dR/dt > 0), in the course of their self-propelled motion. Continuous shrinkage of the active droplet has been attributed to micellar solubilization; a phenomenon essential for the locomotion. Figure 6 compares the rate of solubilization of the droplets in 6wt% TTAB aqueous solution with different solutes. It is clear, that in comparison to no solute and with PAAM as a solute, the presence of glycerol results in a higher -dR/dt. In fact, upon addition of 80wt% glycerol, rate of solubilization is approximately 3 times to that in its absence. Since, propulsion is directly related to the solubilization mechanism, a higher -dR/dt in 80wt% glycerol medium is consistent with the higher than expected \( v_{\text{inst}} \) values despite a significant increase in the viscosity.
Before proceeding further, we briefly discuss the proposed mechanism for solubilization induced self-propulsion, figure 7. For simplicity, we can understand the mechanism as a sequence of following events. (i) Since the surfactant concentration is significantly >> CMC, the droplet easily encounters a free micelle from an arbitrary direction. The micelle dumps free surfactants locally at the interface which reduces the local interfacial tension. By borrowing some additional surfactant molecules already adsorbed on the interface, a tiny oil droplet, in form of a filled micelle, is detached from the parent droplet. This process of micellar solubilization disturbs the otherwise symmetric surfactant coverage and generates a surface gradient i.e. $\nabla s_c$. (ii) This inhomogeneous surfactant coverage generates Marangoni slip along the interface. The slip drives the interface carrying surfactant from the high-density region to surfactant-lean region (solubilization zone). The interfacial flow is accompanied by the surrounding fluid flow in the same direction and to conserve the overall linear momentum the droplet self-propels in the opposite direction. (iii) Once the droplet starts moving, it encounters more free micelles at the leading edge compared to the trailing edge. The additional surfactant molecules procured by the collisions with free micelles are immediately transferred towards the trailing edge. Therefore, now, the solubilization mainly takes place from the posterior region of the droplet. (iv) The higher solubilization in the trailing region further lowers the surfactant concentration. At the same time, the leading edge gets fresh supply of surfactants by encountering free micelles via advection. Therefore, a gradient ($V_s$) is maintained which keeps the active motion sustained.

Based on the above discussion, we can understand that the mode of self-propulsion of an active droplet depends two critical time scales, namely, the mean time-scale of surfactant in-flux at the site of adsorption ($\tau_{\text{in-flux}}$) and their mean time-scale of migration away ($\tau_{\text{out-flux}}$) from the adsorbed region. Using these time scales we hypothesize a possible mechanism behind the unusual jittery motion in glycerol as described in the schematic shown in figure 8. If $\tau_{\text{in-flux}} < \tau_{\text{out-flux}}$, the migration of surfactant away from the leading edge where fresh surfactants are being adsorbed is slow. Hence, a surface tension gradient will always be maintained forcing the droplet to perform sustained active motion in

Figure 7: Schematic illustration of the micellar solubilization induced self-propulsion of an oil droplet in aqueous surfactant solution.

Figure 8: Schematic representation of the proposed mechanism behind the jittery motion observed in glycerol-water solution, in comparison to the usual unperturbed motion in absence of glycerol.
the same direction. On the other hand, if \( \tau_{\text{in-flux}} > \tau_{\text{out-flux}} \), the surfactant molecules adsorbed at the leading edge migrate quickly, before the adsorption of another incoming micelle. As a result, the droplet will momentarily lose the surface tension gradient and will come to a halt, until the motion is reinitiated in an independent direction resulting in a random jittery motion. Using an analytical approach Schmitt and Stark\(^{33}\) recently proposed a random trajectory under similar conditions. A similar line of argument has been proposed by other numerical predictions as well.\(^{41}\)

![Figure 9: Time series snapshots of a 5CB active droplet (61 µm) in 6wt% TTAB aqueous solution with 80wt% glycerol, with a tracer particle (2 µm PS) near the interface (see supporting video S11).](image-url)

To confirm this hypothesis, we decided to identify the relevant time scales i.e. \( \tau_{\text{in-flux}} \) and \( \tau_{\text{out-flux}} \), in our experiments. Here, we assume that adsorption of surfactant molecules due to the disintegration of free micelles in the vicinity of the droplet is instantaneous. Therefore, the overall rate of surfactant in-flux is limited by advection of the micelles to the apex of the droplet, hence \( \tau_{\text{in-flux}} \sim \frac{R}{V_{\text{out}}} \). These incident surfactant molecules will migrate away from the apex towards the back of the droplet, due to the solubilization (release of swollen micelles) generated Marangoni slip and diffusiophoretic slip at the interface. To measure this migration time-scale we injected small 2 µm (<<R) polystyrene particles as tracers to the optical cell with 5CB active droplet. Particles in the vicinity of the actively moving droplet were easily influenced by the resultant fluid profile in the bulk. It was observed that particles very close to the interface experienced a sling-shot along the curvature opposite to the direction of motion of the droplet, see figure 9. Using the trajectory of these particles we estimated the slip velocity \( V_{\text{slip}} \) at the interface using which the \( \tau_{\text{out-flux}} \sim \frac{R}{V_{\text{slip}}} \) was calculated. In table 1, we compare the relevant time scales for a few of our experiments which supports our hypothesis.

| Glycerol wt% | Size of the droplet (µm) | \( \tau_{\text{in-flux}} \) (s) | \( \tau_{\text{out-flux}} \) (s) |
|--------------|---------------------------|-------------------------------|-------------------------------|
| 80           | 61                        | 1.41±0.42                     | 0.80±0.05                     |
|              | 70                        | 1.95±0.80                     | 0.65±0.06                     |
| 0            | 64                        | 1.35±0.13                     | 1.62±0.03                     |
|              | 90                        | 1.95±0.05                     | 2.49±0.07                     |

Table 1: Comparison of \( \tau_{\text{in-flux}} \) and \( \tau_{\text{out-flux}} \) for 5CB droplets in 6wt% TTAB aqueous solution with and without glycerol.

To understand the faster migration of surfactant molecules at the 5CB droplet interface, we focus on the physico-chemical effect resulting from the addition of glycerol. Although the exact concentration profile at the droplet’s interface is unknown, for simplicity we assume that the at the leading-edge surface concentration will be close to \( \Gamma_{\text{CMC}} \) and at the trailing-edge \( \Gamma \ll \Gamma_{\text{CMC}} \), where \( \Gamma_{\text{CMC}} \) is the surface excess concentration at the interface in equilibrium to the bulk surfactant concentration of CMC. In that case, we can estimate the Marangoni slip as \( V_{\text{slip}} = \frac{dy}{dc} \frac{\Gamma}{\eta_0} \). Here, \( \gamma_0 \) is the interfacial tension in absence of surfactant (\( \Gamma \ll \Gamma_{\text{CMC}} \)) and \( \gamma_{\text{CMC}} \) is the interfacial tension at the interface with surface excess concentration of CMC. From the measured the variation in the interfacial tension (\( \gamma \)) of 5CB in aqueous solution with varying TTAB concentration (\( c_{\text{TTAB}} \)) with different solutes (see figure 15), we see that for small values of \( c_a \) a linear decrease in \( \gamma \) followed by a plateau at higher \( c_a \) was observed for all the systems. The concentration where the transition from a rapid decrease to a plateau region occurs is the CMC of TTAB in the respective continuous media. Based on these measurements, we calculate that \( v_{\text{in-water}} > V_{\text{M-Glycerol}} \) which is in contradiction to the experimental observations. We hypothesize, two possible reasons behind this:

a. The accumulation of swollen micelles close to the droplet interface leads to a reduced concentration of free micelles which has been previously reported to be responsible for negative-auto chemotaxis.\(^{21}\) Active oil droplet have been shown to avoid the trails filled with swollen micelles, and instead move towards untraced paths. Recent numerical studies\(^{20}\) have reported that the accumulation of free swollen micelles inhibit the transport of fresh surfactants to the interface. Therefore, we expect this phenomenon to contribute towards inhomogeneous surfactant adsorption at the interface. Since, in the presence of glycerol, the parent droplet releases more swollen micelles compared to that in just the aqueous surfactant solution, the former will experience higher \( V_{\text{c}} \) between the leading and the trailing edge.

b. The faster rate of solubilization of 5CB droplet in glycerol leads to a faster release of swollen micelles. These satellite droplets accumulate near the trailing edge and generate a non-uniform concentration gradient across the droplet. We believe that the gradient of these released solutes (non-attractive) also create a chemiosmotic slip which further enhances the transport of the surfactant molecules at the interface i.e. augment \( V_{\text{slip}} \). In fact it has been reported that a hydrodynamic slip can enhance the interfacial transport by 10-100 times.\(^{42}\)

Finally, we set out to discuss the possible reasons for observed higher rate of solubilization in the presence of glycerol. The process of micellar solubilization is governed by the molecular interactions of different species and
thermodynamic processes involved. Therefore, it is well established that the process is extremely sensitive to numerous physical and chemical factors including temperature, pressure, pH and presence of additives. Typically, additives which affect the CMC and the aggregation number in a micelle, noticeably, are expected to produce parallel effects on solubilization as well. In ionic surfactant solutions, it has been observed that the addition of polar additives such as phenols and other alcohols can enhance the micellar solubility. It has been proposed that such additives insert themselves between the adjacent surfactant molecules in a micelle and they act as co-surfactants.\(^{31}\)

As discussed in the earlier sections and observed in our experiments, the addition of glycerol was accompanied by modification of surfactant activity. Therefore, the discussion above is suitable to our experimental observations and it is likely that the addition of glycerol significantly enhances the rate of micellar solubilization by altering the thermodynamic processes involved. This is clearly evident from the change in CMC of TTAB with addition of glycerol in water. The CMC in 80wt\% glycerol-water solution, CMC\(_{\text{GW}}\)~0.4wt\%, which is significantly more than the CMC in pure water (CMC\(_{\text{water}}\)~0.1\%). A higher CMC in the presence of glycerol hints towards higher solubility of TTAB, consistent with previous study by Moya et al.\(^{41}\) The study also reported that a higher solubility of TTAB in glycerol resulted in an increased aggregation number \((N_{\text{agg}})\) of TTAB, i.e., number of TTAB surfactant molecules present in a single micelle. In water, \(N_{\text{agg}}\) is \(\sim 30\), which increases to \(\sim 70\) for the case of \(\sim 80\)wt\% glycerol-water solution. Additionally, we observed that the interfacial tension of 5CB in aqueous solution of TTAB is always lower in the presence of glycerol compared to pure water. In fact, glycerol has been used as a co-solvent to enhance oil solubilization in spontaneous emulsification.\(^{44}\) Thus, we conclude that the observed chaotic motion of active 5CB droplets in the presence of glycerol is primarily a consequence of glycerol enhanced micellar solubilization.

CONCLUSIONS

In this article we have investigated the effect of addition of glycerol as an additive on the active transport of 5CB liquid crystal (oil) droplets in aqueous surfactant (6wt\% TTAB) solution. In the absence of glycerol, our experiments demonstrated expected characteristics of the active motion of the droplets. Upon decreasing the droplet size, a decrease in self-propelled velocity, and a transition in mode of active motion from random to curling and then straight motion were observed. Addition of glycerol, however, resulted in a peculiar chaotic motion and fluctuations in trajectory were observed for all different droplet sizes investigated. The chaotic motion was also observed when the experiments were repeated at higher temperatures where 5CB droplets were in an isotropic phase. Additional experiments were performed using PAAM as an additive to achieve a similar increase in viscosity of the aqueous phase, as achieved upon the addition of glycerol. Interestingly, in the presence of PAAM the trajectories did not display any random fluctuations and the motion was similar to the case of pure water with surfactant only. Through these measurements, we established that the observed jittery motion in the presence of glycerol was neither due to the nematic phase of the droplet nor due to the enhanced viscosity. Another key observation was that, in the presence of 80 wt\% glycerol, the rate of solubilization of the active droplets was around three times higher in comparison to that observed in just water or in the presence of PAAM.

Overall, our observations suggest that the glycerol specific physico-chemical effects play an important role in the nature of the active motion. By altering the activity of the surfactant molecules, evident from the increase in CMC and reduction in saturation interfacial tension for 5CB-surfactant solution interface, addition of glycerol, enhances micellar solubilization. The enhanced micellar solubilization results in faster migration of the surfactant molecules at the interface in comparison to their influx time scale. Under these circumstances, the surfactant concentration gradient quickly re-homogenizes, bringing the droplet to a halt, until the motion is re-initiated from an independent direction. This hypothesis was further supported by our measurements of the speed of tracer particles in the vicinity of the active droplets.

AUTHOR INFORMATION

Corresponding Author
* Email: mangalr@iitk.ac.in

ORCID
Rahul Mangal: 0000-0003-1824-417X

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources
This work is supported by the Science and Engineering Research Board (SB/S2/RJN-105/2017), Department of Science and Technology, India.

Notes
Authors declare no competing financial interest.

ACKNOWLEDGMENT

We also thank Prof. Naveen Tiwari and Prof. Harshwardhan Katkar for useful discussions.

REFERENCES

(1) Lauga, E.; Goldstein, R. E. Dance of the Microswimmers. *Phys. Today* 2012, 65 (9), 30–35.
(2) Lauga, E.; Powers, T. R. The Hydrodynamics of Swimming Microorganisms. *Reports Prog. Phys.* 2009, 72 (9).
(3) Ishikawa, T.; Simmonds, M. P.; Pedley, T. J. *Hydrodynamic Interaction of Two Swimming Model Micro-Organisms*; 2006; Vol. 568.

(4) Hatwalne, Y.; Ramaswamy, S.; Rao, M.; Simha, R. A. Rheology of Active-Particle Suspensions. *Phys. Rev. Lett.* 2004, 92 (1), 1–4.

(5) Riedel, I. H.; Kruse, K.; Howard, J. Biophysics: A Self-Organized Vortex Array of Hydrodynamically Entrained Sperm Cells. *Science* (80-. ). 2005, 309 (5732), 300–303.

(6) Ishikawa, T.; Pedley, T. J. Coherent Structures in Monolayers of Swimming Particles. *Phys. Rev. Lett.* 2008, 100 (8), 1–4.

(7) Ginelli, F.; Peruani, F.; Bär, M.; Chaté, H. Large-Scale Collective Properties of Self-Propelled Rods. *Phys. Rev. Lett.* 2010, 104 (18), 1–4.

(8) Ramaswamy, S. The Mechanics and Statistics of Active Matter. *Annu. Rev. Condens. Matter Phys.* 2010, 1 (1), 323–345.

(9) Vicsek, T.; Zafeiris, A. Collective Motion. *Phys. Rep.* 2012, 517 (3–4), 71–140.

(10) Maass, C. C.; Krüger, C.; Herminghaus, S.; Bahr, C. Swimming Droplets. *Annu. Rev. Condens. Matter Phys.* 2016, 7 (1), 171–193.

(11) Zöttl, A.; Stark, H. Emergent Behavior in Active Colloids. *J. Phys. Condens. Matter* 2016, 28 (25).

(12) Bechinger, C.; Di Leonardo, R.; Löwen, H.; Reichhardt, C.; Volpe, G.; Volpe, G. Active Particles in Complex and Crowded Environments. *Rev. Mod. Phys.* 2016, 88 (4), 45006.

(13) Gao, W.; Wang, J. Synthetic Micro/nanomotors in Drug Delivery. *Nanoscale* 2014, 6 (18), 10486–10494.

(14) Gao, W.; Wang, J. The Environmental Impact of Micro/nanomachines: A Review. *ACS Nano* 2014, 8 (4), 3170–3180.

(15) Bialké, J.; Speck, T.; Löwen, H. Active Colloidal Suspensions: Clustering and Phase Behavior. *J. Non. Cryst. Solids* 2015, 407, 367–375.

(16) Lin, Z.; Si, T.; Wu, Z.; Gao, C.; Lin, X.; He, Q. Light-Activated Active Colloid Ribbons. *Angew. Chemie - Int. Ed.* 2017, 56 (43), 13517–13520.

(17) Wu, Z.; Lin, X.; Zou, X.; Sun, J.; He, Q. Biodegradable Protein-Based Rods for Drug Transportation and Light-Triggered Release. *ACS Appl. Mater. Interfaces* 2015, 7 (1), 250–255.

(18) Howse, J. R.; Jones, R. A. L.; Ryan, A. J.; Gough, T.; Vafabakhsh, R.; Golestanian, R. Self-Motile Colloidal Particles: From Directed Propulsion to Random Walk. *Phys. Rev. Lett.* 2007, 99 (4), 8–11.

(19) Anderson, J. L.; Pritev, D. C. Diffusioaphoresis: Migration of Colloidal Particles in Gradients of Solute Concentration. *Sep. Purif. Rev.* 1984, 13 (1), 67–103.

(20) Herminghaus, S.; Maass, C. C.; Krüger, C.; Thutupalli, S.; Goehring, L.; Bahr, C. Interfacial Mechanisms in Active Emulsions. *Soft Matter* 2014, 10 (36), 7008–7022.

(21) Jin, C.; Kru-ger, C.; Maass, C. C. Chemotaxis and Autochemotaxis of Self-Propelling Droplet Swimmers. *Proc. Natl. Acad. Sci. U. S. A.* 2017, 114 (20), 5089–5094.

(22) Ban, T.; Nakata, H. Metal-Ion-Dependent Motion of Self-Propelled Droplets Due to the Marangoni Effect. *J. Phys. Chem. B* 2015, 119 (23), 7100–7105.

(23) Banno, T.; Kuroha, R.; Toyota, T. PH-Sensitive Self-Propelled Motion of Oil Droplets in the Presence of Cationic Surfactants Containing Hydrolyzable Ester Linkages. *Langmuir* 2012, 28 (2), 1190–1195.

(24) Lagzi, I.; Soh, S.; Wesson, P. J.; Browne, K. P.; Gryzbowski, B. A Maze Solving by Chemotactic Droplets. *J. Am. Chem. Soc.* 2010, 132 (4), 1198–1199.

(25) Banno, T.; Asami, A.; Ueno, N.; Kitahata, H.; Koyano, Y.; Asakura, K.; Toyota, T. Deformable Self-Propelled Micro-Object Comprising Underwater Oil Droplets. *Sci. Rep.* 2016, 6 (August).

(26) Toyota, T.; Maru, N.; Hanczyc, M. M.; Ikegami, T.; Sugawara, T. Self-Propelled Oil Droplets consuming “Fuel” surfactant. *J. Am. Chem. Soc.* 2009, 131 (14), 5012–5013.

(27) Hanczyc, M. M.; Toyota, T.; Ikegami, T.; Packard, N.; Sugawara, T. Fatty Acid Chemistry at the Oil-Water Interface: Self-Propelled Oil Droplets. *J. Am. Chem. Soc.* 2007, 129 (30), 9386–9391.

(28) Thutupalli, S.; Seemann, R.; Herminghaus, S. Swimming Behavior of Simple Model Squirmers. *New J. Phys.* 2011, 13, 0–10.

(29) Morozov, M. Adsorption Inhibition by Swollen Micelles May Cause Multistability in Active Droplets. *2020, 1–10.

(30) He, Y.; Yazghur, P.; Salonen, A.; Langevin, D. Adsorption-Desorption Kinetics of Surfactants at Liquid Surfaces. *Adv. Colloid Interface Sci.* 2015, 222, 377–384.

(31) Myers, D. *Surfaces, Interfaces, and Colloids*, Second; Wiley-VCH, 1999; Vol. 4.

(32) Schmitt, M.; Stark, H. Marangoni Flow at Droplet Interfaces: Three-Dimensional Solution and Applications. *Phys. Fluids* 2016, 28 (1).

(33) Schmitt, M.; Stark, H. Active Brownian Motion of Emulsion Droplets Coarsening at the Interface and Rotational Diffusion. *Eur. Phys. J. E* 2016, 39 (8).

(34) Peedireddy, K.; Kumar, P.; Thutupalli, S.; Herminghaus, S.; Bahr, C. Solubilization of Thermotropic Liquid Crystal Compounds in Aqueous Surfactant Solutions. *Langmuir* 2012, 28 (34), 12426–12431.

(35) Banno, T.; Miura, S.; Kuroha, R.; Toyota, T. Mode Changes Associated with Oil Droplet Movement in Solutions of Gemini Cationic Surfactants. *Langmuir* 2013, 29 (25), 7689–7696.

(36) Iztí, Z.; Van Der Linden, M. N.; Michelín, S.; Dauchot, O. Self-Propulsion of Pure Water Droplets by Spontaneous Marangoni-Stress-Driven Motion. *Phys. Rev. Lett.* 2014, 113 (24), 1–5.

(37) Suga, M.; Suda, S.; Ichikawa, M.; Kimura, Y. Self-Propelled Motion Switching in Nematic Liquid Crystal Droplets in Aqueous Surfactant Solutions. *Phys. Rev. E* 2018, 97 (6), 1–8.

(38) Krüger, C.; Klös, G.; Bahr, C.; Maass, C. C. Curling Liquid Crystal Microswimmers: A Cascade of Spontaneous Symmetry Breaking. *Phys. Rev. Lett.* 2016, 117 (4), 1–5.

(39) Smalyukh, I. I.; Chernyshuk, S.; Lev, B. I.; Nych, A. B.; Ogynsta, U.; Nazarenko, V. G.; Lavrentovich, O. D. Ordered Droplet Structures at the Liquid Crystal Surface and Elastic-Capillary Colloidal Interactions. *Phys. Rev. Lett.* 2004, 93 (11), 1–4.

(40) Gennes, P. G. de; Prost, J. *The Physics of Liquid Crystals;*
Morożow, M.; Michelin, S. Nonlinear Dynamics of a Chemically-Active Drop: From Steady to Chaotic Self-Propulsion. *J. Chem. Phys.* **2019**, *150* (4).

Ajdari, A.; Bocquet, L. Giant Amplification of Interfacially Driven Transport by Hydrodynamic Slip: Diffusio-Osmosis and beyond. *Phys. Rev. Lett.* **2006**, *96* (18), 1–4.

Moyá, M. L.; Rodríguez, A.; del Mar Graciani, M.; Fernández, G. Role of the Solvophobic Effect on Micellization. *J. Colloid Interface Sci.* **2007**, *316* (2), 787–795.

Saberi, A. H.; Fang, Y.; McClements, D. J. Effect of Glycerol on Formation, Stability, and Properties of Vitamin-E Enriched Nanoemulsions Produced Using Spontaneous Emulsification. *J. Colloid Interface Sci.* **2013**, *411*, 105–113.