Journal of Colloid and Interface Science 621 (2022) 131-138



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Salt-induced stability and modified interfacial energetics in self-faceting emulsion droplets



Pilkhaz M. Nanikashvili^{a,b}, Alexander V. Butenko^{a,b}, Moshe Deutsch^{a,b}, Daeyeon Lee^c, Eli Sloutskin^{a,b,*}

^a Department of Physics, Bar-Ilan University, Ramat-Gan 5290002, Israel

^b Bar-Ilan Institute of Nanotechnology and Advanced Materials, Bar-Ilan University, Ramat-Gan 5290002, Israel

^c Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA

G R A P H I C A L A B S T R A C T



ARTICLE INFO

Article history: Received 2 March 2022 Revised 30 March 2022 Accepted 31 March 2022 Available online 4 April 2022

Keywords: Self-faceting Interfacial freezing Polyhedral droplets Salt solution Emulsion stability

ABSTRACT

Hypothesis: The counterintuitive temperature-controlled self-faceting of water-suspended, surfactantstabilized, liquid oil droplets provides new opportunities in engineering of smart liquids, the properties of which are controllable by external stimuli. However, many emulsions exhibiting self-faceting phenomena have limited stability due to surfactant precipitation. The emulsions' stability may be enhanced, and their inter-droplet electrostatic repulsion tuned, through controlled charge screening driven by varyingconcentration added salts. Moreover, in many technologically-relevant situations, salts may already exist in the emulsion's aqueous phase. Yet, salts' impact on self-faceting effects has never been explored. We hypothesize that the self-faceting transitions' temperatures, and stability against surfactant precipitation, of ionic-surfactants-stabilized emulsions are significantly modified by salt introduction.

Experiments: We explore the temperature-dependent impact of NaCl and CsCl salt concentration on the emulsions' phase diagrams, employing optical microscopy of emulsion droplet shapes and interfacial tension measurements, both sensitive to interfacial phase transitions.

Findings: A salt concentration dependent increase in the self-faceting transition temperatures is found, and its mechanism elucidated. Our findings allow for a significant enhancement of the emulsions' stability, and provide the physical understanding necessary for future progress in research and applications of self-faceting phenomena in salt-containing emulsions.

© 2022 Elsevier Inc. All rights reserved.

Abbreviation: IF, Interfacial freezing.

* Corresponding author.

E-mail address: eli.sloutskin@biu.ac.il (E. Sloutskin).

1. Introduction

Oil-water interfaces, decorated by adsorbed ionic surfactants. are ubiquitous in science and technology, and play an important role in living matter [1–3]. The adsorption of water-dissolved ionic surfactants to such interfaces strongly depends on the presence and the precise concentration of salt in the aqueous medium [4-7]. While the role of salt concentration in surfactant adsorption has been extensively studied for disordered oil-water interfaces [8–10], no such studies exist for *interfacially-frozen* systems, where the two liquid bulk phases are separated, below an onset temperature T_s , by a crystalline monolayer of a self-assembled mixture of alkane and surfactant molecules [11–14]. Interfacial freezing (IF) occurs for a wide range of common oil:water systems [15], over a temperature range of coexistence between the crystalline monolayer and the liquid bulk phases of up to [16] 20 °C, both emphasizing the large technological importance of IF. Recent experimental evidence [17,15,18] proves that the IF crystals drive, and fully control, droplet shape transformations in oil-in-water [11,19-22] and water-in-oil [16] emulsions. These temperature-tunable transformations, where liquid droplets adopt faceted shapes (Fig. 1a-c) while remaining fully liquid [19,23], enable new strategies in synthesis of faceted colloidal particles [24,25], and allow these droplets to be decorated by precisely self-positioned particles [26-28] or ligands, enabling self-assembly into higher-hierarchy structures with precise inter-droplet positions and bond orientations. Future progress in many of these promising directions may require tuning the electrostatic field of the droplet by dissolving salts in the aqueous medium, as shown in a recent particle-on-droplet self-positioning study [28]. Moreover, future applications of droplets' self-shaping phenomena for high-efficiency industrial emulsification [29], may dictate the use of salt solutions. Finally, the lifetimes of many of the ionic-surfactant-stabilized self-faceting emulsions studied to date are limited by surfactant precipitation.



Fig. 1. Similar faceted shapes and shape transitions are observed for both the salt-free (a-c) and the salt-containing (d-g) emulsions. For all of these systems, the spherical droplets transform into icosahedra (a,d) on cooling below T_d . Then, on further cooling, the icosahedra distort into few- μ m-thick platelet-like tailed shapes, having parallelogram (b,e), triangular (c,f), hexagonal (g), and other polyhedral topview shapes. Salt concentrations are: 250 and 100 mM NaCl in (d) and (e), respectively, and 200 mM CsCl in (f) and (g). The inset to (d) shows an icosahedron in a 500 mM NaCl sample. The wetting by the oil droplets of the top wall of the glass capillary becomes significant at $c_s > 500$ mM, as demonstrated by the slightly-distorted shape of this icosahedron.

Adding salt to these systems may significantly increase their stability. All these directions in research and technology require the influence of salt on IF and self-shaping of emulsion droplets to be fully elucidated. Yet, no systematic studies in this direction have been published to date.

The study presented here employs systematic temperaturedependent interfacial tension measurements and optical microscopy of oil-in-water emulsions to elucidate the influence of monovalent (NaCl and CsCl) salts on the IF transitions and the IF-induced self-shaping of droplets. The oil used is n-hexadecane (CH₃(CH₂)₁₄CH₃; denoted as C₁₆). The oil droplets were stabilized by the cationic surfactant octadecyltrimethylammonium bromide (CH₃(CH₂)₁₇N(CH₃)₃Br; denoted as C₁₈TAB). This alkane:surfactant combination is, arguably, the most intensively studied system exhibiting IF [19,23,20,30,17,31]. We demonstrate that IF, and self-shaping phenomena, persist from zero to a very high salt concentration ($c_s \approx 1.5$ M) with the self-faceting onset temperature T_d monotonically increasing with c_s . The ionic non-ideal adsorption theory (iNAS) [32,33], is found to account well for the observed salt-dependent variations of the transition temperatures and the interfacial tension, γ . We also demonstrate that adding salts to the aqueous phase dramatically improves the stability of these emulsions. Our work provides a basis for future implementation of self-faceting and IF in salt-containing systems.

2. Experimental methods

2.1. Materials

Millipore Ultrapure 18.2 M Ω -cm water was used throughout. The C₁₈TAB surfactant (Sigma–Aldrich, 98% pure) was recrystallized twice from a methanol-acetone solution, then twice from a hexane–acetone solution. NaCl and CsCl (Sigma–Aldrich, > 99.999%) were baked at > 400 °C, to remove organic impurities. The aqueous C₁₈TAB solution, at concentrations $0 \le c_s < 1.5$ M of dissolved NaCl or CsCl, was stirred for > 40 minutes at 50°C, to ensure complete dissolution of the salt and the surfactant. C₁₆ (TCI, > 98% pure) was percolated 2–3 times through a freshly activated basic alumina powder column to remove acidic polar impurities.

2.2. Emulsion preparation

Emulsions were prepared by introducing 1–2 mass% C_{16} into a salt-containing aqueous 1 mM C_{18} TAB solution heated to $\gtrsim 40^{\circ}$ C, then stirring on the MH-4D, Fried ElectricTM hot plate by a 10 × 3 mm magnetic stirrer at 1200 rpm, for 1 – 2 min. Longer stirring splits the droplets further, increasing the interfacial area per unit volume of the sample, and thus depleting the bulk surfactant concentration by surfactant adsorption onto this larger interfacial area. In turn, this depletion may reduce the surfactant's bulk concentration below the CMC (critical micelle concentration), downshifting T_d , and thus complicating comparisons between studies of emulsions and of planar-interface $\gamma(T)$ measurements. To avoid surfactant depletion, stock emulsions were also kept at $T \gtrsim 40^{\circ}$ C, well above any possible droplet facetting and splitting transitions [17,19,23].

2.3. Optical microscopy

Emulsions were loaded by capillary suction into Vitrocom[®] $0.1 \times 2 \times 50$ mm rectangular borosilicate glass capillaries, sealed with instant Epoxy, and glued wide-face-down onto a rectangular brass slide, having a long narrow slit for illumination and microscopy imaging. The slide was then attached to a temperature-

controlled baseplate, residing on the translation stage of an inverted bright-field Nikon Ti-E optical microscope. $T \gtrsim 40^{\circ}$ C, well above the droplets' T_s , was maintained throughout the process. The baseplate's temperature was controlled to $< 0.01 \,^{\circ}$ C by a Lake Shore model 330 PID controller employing a $100k\Omega$ precision thermistor and Peltier elements. The typical temperature scan rate was 0.4 K/min, ensuring temperature equilibration, as demonstrated by the scan yielding T_s and T_d values coinciding with those measured at lower (0.25 K/min) and slightly higher (0.5 K/min) scan rates. The bright-field microscopy employed a dry Plan Apo 20x (NA = 0.75) and a dry Plan Fluor 100x (NA = 0.9) objective and a Nikon DS-Fi1 CCD camera for video acquisition.

2.4. Static light scattering

A goniometer-based PhotocorTM static and dynamic light scattering setup was employed. The sample was contained in a 20 mL vial immersed in a refractive-index-matching toluene bath, the temperature of which was controlled to 0.1 °C by a water circulator. The scattered intensity of a 633 nm He-Ne laser beam was measured at an angle of $\theta = 40^\circ$, corresponding to a wavevector of $q \approx 9 \ \mu m^{-1}$. Surfactant precipitation is indicated by a significant increase in the scattered intensity.

2.5. Interfacial tension measurements

The Wilhelmy plate method [13,19,20,34,35], with a 41-mm circumference glass plate, was employed for these *flat-interface* C_{16} : C_{18} TAB-solution measurements. The sample, contained in a glass beaker, was held inside a two-stage oven, with an inner temperature-controlled (±0.01°C) cell residing inside a passive outer aluminum cell. For each sample, all glassware contacting the sample were cleaned with fresh hot Piranha, then thoroughly rinsed with Millipore water. No such precautions were needed in our studies of emulsions, where the total oil–water interfacial area is much larger, reducing the sensitivity to possible impurities. As in



Fig. 2. (a) The temperature dependence of the interfacial tension, obtained for the interface between C_{16} alkane and a C_{18} TAB (0.3 mM) surfactant solution, for three different NaCl concentrations: $c_s = 0, 0.3$, and 1 M (see labels). The T_s values, where the IF takes place, are marked by up-pointing arrows. Note the identical slopes obtained for all the three plots at $T < T_s$, indicating that the entropy loss, and thus the structure of the interfacial crystal, are independent of c_s . The c_s -independent slopes, combined with the dramatic decrease in $\gamma_s \equiv \gamma(T_s)$ with the NaCl concentration, lead to a significant *increase* in T_{SE} (down-pointing arrows) for the high- c_s samples. (b) The measured decreasing $\gamma_s(c_s)$ values (symbols) are fitted by the iNAS theoretical model, with the adsorption coefficient either taken to be c_s -independent (blue dashes) or assumed to vary linearly with c_s (solid red curve).

our previous, salt-free, $\gamma(T)$ measurements [11,14,16,19,20], the C₁₈TAB concentration was set to c = 0.3 mM, slightly higher than the CMC. Increasing c further, does not change the interfacial energetics, but significantly reduces the solutions's stability by causing surfactant precipitation on the experimentally-relevant time scales. Note that no such destabilization occurs in our *emulsions*, where the nominal C₁₈TAB concentration is c = 1 mM \gg CMC (see Section 2.2), since the emulsion's total interfacial area per unit volume is considerably larger than that of the flat interface used in the $\gamma(T)$ measurements. Thus, the adsorption of C₁₈TAB to the droplets' interfaces depletes its bulk concentration [14], bringing it close to the CMC, and no noticeable precipitation occurs during our experiments.

A $\gamma(T)$ scan starts by loading the C₁₈TAB solution into the beaker, and lowering the Wilhelmy plate into it to full immersion. C₁₆ is then added on top of the solution and the plate lifted to have its bottom edge touching the oil-water interface. The pull applied by the interface on the Wilhelmy plate is measured by an electronic Precisa^M semi-micro balance. A LabView program scans the temperature, records and divides the measured pull force by the plate's circumference to obtain γ . The scan employs $0.1 - 0.14^{\circ}$ C steps, waiting 30s after each step. 20 measurements are averaged at each temperature, so that smooth $\gamma(T)$ curves are obtained (see, e.g., Fig. 2a). The standard error of γ is negligibly small on this scale.

3. Results and discussion

3.1. Shape transitions in emulsion droplets

3.1.1. Salt-free emulsions

We discuss first salt free emulsions, to establish baselines for the salt-laced ones. Salt-free C₁₆ emulsion droplets, suspended in aqueous C₁₈TAB solutions at concentrations exceeding the CMC (~ 0.2 mM), exhibit an IF transition at [19,20,23] $T_s \approx 26$ °C, forming a mixed C₁₆:C₁₈TAB crystalline monolayer covering their surfaces, thus reducing their interfacial entropy. The entropy reduction renders the slope of γ positive at $T < T_s$, $d\gamma/dT \approx$ 0.8 mN m⁻¹K⁻¹, causing γ to reach zero on cooling to [19,20,23] $T_{SE} \approx 20$ °C (Fig. 2a, blue circles). The hydrocarbon molecular tails comprising the IF crystal are fully extended (i.e. in a full-trans conformation) and interface-normal oriented, forming a laterallyhexagonal lattice fully covering the droplet's surface [13,36]. However, Euler's polyhedral formula [37,38] requires an hexagonal lattice fully covering a closed surface to include exactly 12 fivecoordinated lattice sites, known as disclinations, with the rest of the lattice sites being six-coordinated [15,23,39]. The extensional stress induced in the IF crystal by the disclinations is minimized by maximizing their separation on the droplet's surface, so that the disclinations self-position at the vertices of the sphericaldroplet-inscribed icosahedron [15]. The stress may be further reduced by the disclinations' buckling out of the droplet's spherical surface [31]. Since such a buckling increases the surface area of the droplet, this shape transition is energetically unfavourable at $T = T_s$, where $\gamma > 5.5$ mN/m (in a salt-free system). However, the reduction of γ on cooling below T_s , due to the positive $d\gamma/dT$, tips the energy balance, so that a sphere-to-icosahedron transition takes place at [20] $T = T_d \approx T_{SE} + 0.1$ °C, with the icosahedron's 12 vertices formed by the buckled-out disclinations [40] (see Fig. 1a).

Finally, on rapid cooling to $T < T_{SE}$, the slope of $\gamma(T)$ renders γ transiently negative [17], leading to icosahedrons' distortion into platelet- and rod-like tailed objects [31] (Fig. 1b-c), which have a larger surface area *A* for a given volume, thus reducing the total surface energy γA (< 0). This increase in the total interfacial area

of the emulsion, with the consequent adsorption of C_{18} TAB from the bulk to the newly-created interface, depletes the bulk C_{18} TAB concentration and allows the system to reach an equilibrium [19,20,23], where $\gamma \rightarrow 0$. The present study aims at exploring the evolution of the effects presented above upon significantly increasing the ionic strength of the aqueous phase by the introduction of monovalent salts. The results are presented in the following subsections.

3.1.2. Salty emulsions

To study the impact of salts on the droplets' IF and shape transitions, we followed the evolution with temperature of C_{16} droplets suspended in NaCl-containing C_{18} TAB solution, using bright-field microscopy. Upon cooling, the droplets were found to undergo a sphere-to-icosahedron transition at T_d (Fig. 1d), then to higher aspect ratio objects, such as polygonal platelets (Fig. 1e), and rods (Supplementary video 1). Thin tails were also found to emanate from the platelet's sharpest vertices (Fig. 1e). The platelets commonly undergo spontaneous self-division transitions, splitting into multiple 'daughter' droplets, each of which then undergoes a similar sequence of shape transformations and often self-divides further [17].

The observed shapes and shape transitions were similar to those reported above for the salt-free C₁₆:C₁₈TAB emulsions (Fig. 1a-c), suggesting that the structure of the interfaciallyfrozen monolayers governing these transitions is not significantly altered by the presence of NaCl. Moreover, in salt emulsions, where CsCl was used instead of NaCl, the observed shapes and transitions were also very similar (Fig. 1f-g; Supplementary video 2). Importantly, for $c_s > 0.5$ M of either salt, the large droplets (> 10 μ m in diameter) were observed to wet significantly the top wall of the sample-containing borosilicate glass capillary (Vitrocom[™]). Elucidation of the precise mechanism driving this wetting transition is beyond the scope of the present study, and may possibly be related to the recently-discovered hydrophilic-hydrophobic transitions of glass surfaces [14]. Importantly, while the large droplets are significantly distorted by this wetting (see inset to Fig. 1d), the smallest optically-resolvable droplets remain undistorted up to at least $c_s = 1.5$ M. This finding indicates that the intrinsic physics of droplets' self-shaping, unperturbed by the wetting, is c_s -independent.

Although the geometric shapes observed for the salt-free and the salt-containing emulsions are similar, the transition temperatures exhibit a significant increase as a function of c_s (Fig. 3a). Since for optically-resolvable droplets the difference between T_d and T_{SE} is [19] < 0.3 °C, too small to be shown on the present scale, in view of the statistical error bars associated with both T_d and T_{SE} , we only show T_d in Fig. 3a. While the observed increase in T_d is less dramatic than that of the previously-studied long-chain alcoholdoped emulsions [16,14], the use of these salts may be instrumental for stabilizing these systems in situations where long-term samples' stability is an issue (see next paragraph). Note that the self-faceting transition in salt-free, near-CMC, C₁₆:C₁₈TAB systems occurs at $T_d \approx 20$ °C, far below the Krafft temperature [41] of C_{18} TAB ($T_k \approx 37$ °C). Thus, the self-faceted salt-free emulsions are only stable for about an hour, after which surfactant precipitation out of the aqueous phase sets in. The introduction of the presentlystudied salts into the system plays, therefore, a dual role: it increases T_d , while at the same time *decreasing* [41] T_k . Thus, the lifetime of the high- c_s self-faceted emulsions is much longer than that of their salt-free counterparts, rendering the salt-containing emulsions amenable to long-time experiments and applications.

To investigate the stability of the salt-containing emulsions, we measured the time-dependence of the static light scattering, I(t), from the corresponding aqueous solutions. A salt-free, 1 mM aqueous solution of C_{18} TAB, premixed at a high temperature and cooled



Fig. 3. (a) The temperatures of the sphere-to-icosahedron transitions, T_d , exhibit a significant, roughly-linear, increase with the aqueous phase salt concentration, c_s . Remarkably, a stronger increase is observed for the CsCl-containing samples, compared to the NaCl-containing ones (see labels). The error bars reflect the statistical uncertainty in T_d among similarly-prepared samples. (b) The same data as in (a), plotted as a function of the aqueous-phase Debye length, L_D (note the logarithmic L_p scale).

down rapidly to 20 °C, exhibits after only one hour a dramatic increase in I(t), indicative of surfactant precipitation (Fig. 4, solid brown triangles). Since no self-faceting phenomena occur in saltfree C_{16} : C_{18} TAB emulsions at T > 20 °C, our observations set a \sim 1 hr stability limit on self-faceting in these systems. Unsurprisingly, the time-lag prior to the onset of surfactant precipitation is even shorter (\sim 30 min) for salt-free solutions kept at T = 16 °C (Fig. 4, solid blue circles). While some increase in stability may be achieved by reducing the C₁₈TAB molarity, this reduction may lower T_d , so that the lifetime of self-faceted emulsions would not be extended. Instead, we increased the stability of these emulsions significantly by introducing salt at a low concentration into the aqueous medium. Specifically, a 1 mM C₁₈TAB aqueous solution, doped by 0.02 M of NaCl, is stable at 20 °C for at least 2.5 days. A significant increase in stability is observed at T = 16 °C as well (Fig. 4, open symbols), emphasizing the high importance of understanding the effects of salts on the self-faceting phenomena.

We hypothesize that the monotonic increase of T_d with salt concentration, observed in Fig. 3a, is due to the screening of the electrostatic repulsions between the charged, surface-adsorbed, $C_{18}TA^+$ cations. To test this hypothesis, we plot our T_d values vs. L_D , the aqueous-bulk's Debye charge-screening length [42,43]. Assuming that the (monovalent) salt ions are fully dissociated in



Fig. 4. Light scattering intensity, I(t), exhibits a substantial increase for salt-free 1 mM C₁₈TAB aqueous solutions (solid symbols), indicative of surfactant precipitation occurring after only a short lag time at the indicated incubating temperatures (see labels). A time-independent I(t) is observed for similar solutions, doped with 0.02 mM NaCl (open symbols), demonstrating that the stability has been dramatically improved by the doping. Note the break in the x-axis scale.

our concentration range ($c_s < 1.5$ M), the Debye length is given by [44]: $L_D = [(\epsilon_r \epsilon_0 k_B T)/(2N_A e^2 c_s)]^{1/2}$, where $\epsilon_r, \epsilon_0, N_A, k_B$, and *e* are, respectively, the dielectric constant, vacuum permitivity, Avogadro's number, Boltzmann constant, and the elementary charge. The self-faceting temperatures in Fig. 3b exhibit at low L_D a sharp decrease followed by a plateau for $L_D > 1$ nm (Fig. 3b). With the ~ 0.48 nm lattice constant of the monolayer [45,46] and a 0.5-0.6 surfactant fraction within the monolayer [13], the average surfactants' headgroup separation is ~ 0.6 nm. Since the fraction of the ionized headgroups may be smaller than 1, the average separation between the $C_{18}TA^+$ cations is expected to be of the order of 1 nm, coinciding with the break in the $T_d(L_D)$ plot (Fig. 3b). When $L_{\rm D}$ is much larger than the separation between the cations, the repulsion between the cationic headgroups is not very sensitive to L_D . Thus, the strong decrease of $T_d(L_D)$ for $L_D < 1$ nm and its flattening out for $L_D > 1$ nm are consistent with our hypothesis that the added salt efficiently screens the electrostatic repulsions between the C₁₈TA⁺ cations and leads to the observed increase in $T_d(c_s)$.

3.2. Surface thermodynamics

3.2.1. Surface tension measurements

To reveal the thermodynamic mechanism of the salt-induced increase in T_d , we measure the temperature dependence of the interfacial tension $\gamma(T)$. Such measurements probe directly the interfacial entropy, which changes abruptly at the IF transitions [20,34]. Since *in situ* $\gamma(T)$ measurements of individual emulsion droplets are highly challenging, we measured $\gamma(T)$ of a planar liquid–liquid interface between bulk C_{16} and a bulk salt-containing C_{18} TAB aqueous solution, employing the Wilhelmy plate method discussed above. Previous measurements, carried out for salt-free systems, demonstrate that the *in situ* $\gamma(T)$ of emulsion droplets fully agrees with the values obtained for the planar interface [19,20].

A few representative scans of $\gamma(T)$ for different concentrations are shown in Fig. 2a, exhibiting the typical features indicative of the IF: a near-zero slope at high temperature region, typical of disordered interfaces, a much higher positive slope at low temperatures, typical of the frozen interfaces, and a sharp transition between these two regimes identifying T_s , the onset of IF in Fig. 2a (marked by \uparrow). Similar behavior of $\gamma(T)$ has been observed for other (liquid–liquid and liquid–vapor) interfaces, undergoing an IF transition [11,12,16,19,20,34–36,45,47,48].

 $\gamma(T)$ is the interfacial free energy excess (per unit area) over the bulk's, so that its temperature-derivative $d\gamma/dT$ yields the entropy difference between surface and bulk [34,35]. Since no bulk phase transition occurs at $T = T_s$, the loss of surface entropy upon IF is $\Delta S = (d\gamma/dT)_{T < T_s} - (d\gamma/dT)_{T > T_s}$. Although originally derived for two-component systems, this relation holds also for multicomponent ones, such as ours, where either the oil-solubility of both water and surfactant is very low, or for any oil:water system where the surfactant:water solution is ideal [20]. Our samples fulfill both conditions for the full c_s range studied. The measured ΔS shows only a weak c_s dependence, as demonstrated in Fig. 5a. Specifically, while the salt-free sample yields $\Delta S \approx 0.8$ mJ m⁻² K⁻¹, the value at $c_s = 1.25$ M is higher by only $\sim 40\%$. For a comparison, the IF bilayer, forming at the free surface of an octadecanol melt yields [49] $\Delta S \approx 1.8$ mJ m⁻² K⁻¹, almost twice our ΔS . A four-layer IF crystal formed at the octadecanol:hexacosanol mixture's surface yields [49] $\Delta S \approx 4.4$ mJ m⁻² K, roughly fourfold our ΔS . The much smaller c_s -variation of our ΔS in Fig. 5a implies only relatively minor changes in our IF layer upon varying c_s, and



Fig. 5. (a) The loss of interfacial entropy upon the IF, ΔS , exhibits only a weak dependence on salt concentration, c_s . Note that for $c_s = 1.5$ M, the positive-slope temperature range of $\gamma(T)$ is very narrow, yielding significantly larger error bars for the corresponding ΔS . (b) The IF temperature, T_s (green hexagons), shows a weak minimum at $c_s \approx 0.3$ M, but ultimately returns to its salt-free value, at higher c_s . This behavior contrasts the strong monotonic increase of T_{SE} . As a result of these two trends, the temperature range where the frozen interface exhibits a positive non-zero γ is strongly reduced, from 6 °C for $c_s = 0$ M, to 1.1 °C for $c_s = 1.5$ M. The lines are guides to the eye.

excludes the formation of additional layers. This conclusion is further supported by the measured T_s , which exhibit a very weak NaCl c_s dependence(Fig. 5b, green hexagons). While a slight T_s reduction occurs at $c_s \approx 0.3$ M, the salt-free T_s value is recovered at higher c_s . Notably, the near-independence of T_s on c_s does not necessarily mean that the system's free energy is c_s -independent, since T_s is controlled by the free energy difference between the interfaciallymolten and the interfacially-frozen system, so that a simultaneous shift of both free energies would keep T_s constant. In particular, if the separation between the ionized surfactant headgroups does not significantly change upon the interfacial freezing, since the alkanes' interdigitation between the surfactant molecules takes place both above and below T_s (and thus the chain-chain spacing determines also the surfactants' charged headgroup spacing), no $T_{\rm s}$ -shift would result from the salt-induced enhancement of the electrostatic screening. These arguments can also rationalize the recent observation that in a similar (but salt-free) system T_s is insensitive to the specific type of the surfactant's counterion[50]. Remarkably, this situation contrasts with the thermodynamic balance leading to the Krafft temperature precipitation of the surfactant, upon which a drastic change in the separation between surfactant molecules takes place, resulting in a strong dependence of the Krafft temperature on the type of the counterion [50]. Finally, note that while T_s is nearly c_s -independent, a strong monotonic growth intriguingly occurs in T_{SE} (Fig. 5b, red squares) and T_d (Fig. 3a), both of which are central to the physical properties of these emulsions.

The constant $(d\gamma/dT)_{T < T_s}$, causes γ to vanish at $T_{SE} = T_s - \gamma(T_s)/(d\gamma/dT)_{T < T_s}$ (Fig. 2a). Since both T_s and $(d\gamma/dT)_{T < T_s}$ do not significantly vary with c_s , the main c_s -dependence of T_{SE} is due to $\gamma(T_s)$ (denoted here as γ_s), which strongly decreases, monotonically, with increasing c_s (Fig. 2b). Remarkably, since T_s is almost c_s -independent and is precisely at the boundary between the interfacially-frozen and the interfacially-molten states, $\gamma_s(c_s)$ is almost identical with an *iso-therm*, $\gamma(T \rightarrow T_s^+, c_s)$, of an interfacially-molten system. Such iso-therms are extensively discussed in the literature [5,6,32,33,51,4,8,7]. The decrease of γ with c_s in such isotherms, is mainly attributed to the increased salt-provided electrostatic screening of the surfactant's charged heagroups, which, in turn, increases the surfactants' interfacial adsorption and consequently *decreases* γ .

3.2.2. Theory: the $\gamma_s(c_s)$ isotherm

While many previous studies of these isotherms employed pseudo-nonionic models, where the effect of charge on adsorption and tension is ignored, we describe our data by a more advanced model, known as iNAS (ionic non-ideal adsorption) theory, which explicitly takes the electrostatic interactions into account [32,33,51,52]. The interfacial adsorption Γ is described here by the so-called, Combined isotherm, explicitly accounting for the effects of both the interfacial potential ϕ and the pair-interaction energy of adsorbed surfactant molecules, A_F :

$$\Gamma = \Gamma_m \left[\frac{K_a c^0}{\exp\left(\frac{zF\phi}{RT} + A_F \frac{\Gamma}{\Gamma_m}\right) + K_a c^0} \right].$$
(1)

Here Γ_m , c^0 , K_a , z = +1, F and R are, respectively, the maximal surface density of a close-packed C_{18} TAB monolayer, estimated [53,36] as $\approx 5.2 \times 10^{-6}$ moles/m², the bulk concentration of free, unmicellized, C_{18} TAB, it's interfacial adsorption coefficient, the surface-adsorbed C_{18} TA⁺ charge (in e units), the Faraday and the gas constants. To solve Eq. 1 for Γ and ϕ , we use the Gouy-Chapman theory, relating ϕ to the interfacial charge density, $(1 - \beta)\Gamma$, where $(1 - \beta)$ is the ionized fraction of the interfacial

monolayer, with $\beta = 1$ corresponding to a completely uncharged monolayer. Finally, Γ , thus obtained, is plugged into the Gibbs adsorption isotherm, yielding the interfacial tension, γ (see Supplementary Information).

We fit the theoretical $\gamma(c_s)$ isotherm to the experimental data by tuning the values of A_F , β and K_a . Assuming a c_s -independent K_a , we obtain $K_a = 4 \times 10^3$ m³/mole, $A_F = 54k_BT$ and $\beta = 0$, with the theoretical $\gamma(c_s)$ matching the experimental isotherm reasonably well, considering the statistical error bars (Fig. 2b, blue dashes). An even better fit to the experimental data is obtained upon allowing K_a to vary linearly with $c_s : K_a = K_{a,0} + \alpha c_s$. Here $K_{a,0}$ and α are tunable parameters, fitted to 4.15×10^3 m³/mole and 0.21 m⁶/mole², respectively. With this choice, we obtain $A_F = 79k_BT$, $\beta = 0$ and an excellent agreement with the experimental isotherm (Fig. 2b, red line). Note, that our present assumption of a c_s -dependent K_a is consistent with previous studies of other similar surfactant systems [51].

The successful reproduction of $\gamma_s(c_s)$ by the iNAS theoretical model demonstrates that the main effect of the added salt is the γ reduction, occurring independently of IF. This reduction, and the fixed (IF-caused) $d\gamma/dT_{T<T_s}$, yield a monotonic T_{SE} and T_d increase, accounting for our observations for the NaCl emulsions. Note, however, that the $T_d(c_s)$ slope obtained for the CsCl emulsions is larger than that obtained for the NaCl ones (Fig. 3). This sensitivity to the cation's type cannot be explained by the iNAS model. According to the classical adsorption models, the cations are expelled almost completely from the $C_{18}TA^+$ -rich, near-interface, region. Thus, their effect on T_d is highly surprising, and calls for future studies[54].

4. Conclusions

We have demonstrated that liquid hexadecane (C_{16}) emulsion droplets, suspended in salt-containing octadecyltrimethylammonium bromide (C₁₈TAB) aqueous solutions, exhibit sphere-toicosahedron and other self-shaping transitions. Self-shaping phenomena were proposed to make possible numerous technological applications, such as highly efficient industrial self-emulsification [29] and the precise positioning of surface ligands on liquid [26,28] and solid[24,25,27] colloids, allowing higher-hierarchy self-assembly of these colloids [15]. However, for these prospects to be realized, the influence of salts on the self-shaping mechanisms had to be determined since many industrial emulsions include salt as an ingredient, so that an emulsification technology which strongly depends on salt concentration is unlikely to become widely-applicable. Similarly, the attachment of surface ligands commonly requires the presence of salt to reduce electrostatic barriers for desirable surface adsorption of specific species [28]. However, no systematic studies of salt effects on selfshaping phenomena were hitherto reported in the literature. In this study we report that the observed self-faceted shapes do not significantly depend on the salt (NaCl, CsCl) concentration c_s. However, the shape transition temperatures increase significantly with increasing c_s . This increase, combined with the salt-induced reduction of C18TAB's Krafft temperature, significantly increases the stability of the self-faceting emulsions against C₁₈TAB precipitation. This increased stability, and consequent orders-of-magnitude longer shelf lifetime, is important for the emulsions' future scientific and technological applications [24,15]. We have employed the iNAS theoretical model to quantitatively describe the NaClinduced increase in the shape transition temperatures of the droplets. However, classical theoretical models predict independence of salt effects from the cation type, contrary to our observation of a stronger transition temperatures' dependence on salt concentration for CsCl-containing emulsions as compared to NaCl-containing ones. Furthermore, our present studies do not address the possible dependence of both the self-faceting temperatures and the emulsion stability on the type of the *anion*. Anion-specific effects have been demonstrated to control surfactant stability[50], ion binding to cationic micelles[55], and other properties of these micelles. Future studies, systematically exploring $\gamma(T, c_s)$ for a wide range of different salts, may elucidate the origin of ion-specific effects in our, and similar, emulsion systems, with potentially important implications for emulsion technology.

CRediT authorship contribution statement

Pilkhaz M. Nanikashvili: Investigation. **Alexander V. Butenko:** Investigation, Validation, Formal analysis. **Moshe Deutsch:** Supervision, Writing – review & editing. **Daeyeon Lee:** Supervision, Writing – review & editing. **Eli Sloutskin:** Methodology, Supervision, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported by Grant No. 2110611 from the United States National Science Foundation (NSF) and the United States-Israel Binational Science Foundation (BSF). We acknowledge the Kahn foundation for funding of some of the equipment. We thank J. Ricardo for discussions and technical assistance.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2022.03.146.

References

- S. Hosseinpour, V. Götz, W. Peukert, Effect of surfactants on the molecular structure of the buried oil/water interface, Angew. Chem. Int. Ed. 60 (47) (2021) 25143–25150.
- [2] R. Dubey, C.E. Stivala, H.Q. Nguyen, Y.-H. Goo, A. Paul, J.E. Carette, B.M. Trost, R. Rohatgi, Lipid droplets can promote drug accumulation and activation, Nat. Chem. Biol. 16 (2020) 206–213.
- [3] Y.-H. Han, E.J. Onufer, L.-H. Huang, R.W. Sprung, W.S. Davidson, R.S. Czepielewski, M. Wohltmann, M.G. Sorci-Thomas, B.W. Warner, G.J. Randolph, Enterically derived high-density lipoprotein restrains liver injury through the portal vein, Science 373 (6553) (2021) eabe6729.
- [4] E. Ruckenstein, R. Krishnan, Effect of electrolytes and mixtures of surfactants on the oil-water interfacial tension and their role in formation of microemulsions, J. Colloid Interface Sci. 76 (1980) 201–211.
- [5] V.B. Fainerman, E.V. Aksenenko, N. Mucic, A. Javadi, R. Miller, Thermodynamics of adsorption of ionic surfactants at water/alkane interfaces, Soft Matter 10 (2014) 6873–6887.
- [6] N. Mucic, N.M. Kovalchuk, E.V. Aksenenko, V.B. Fainerman, R. Miller, Adsorption layer properties of alkyltrimethylammonium bromides at interfaces between water and different alkanes, J. Colloid Interface Sci. 410 (2013) 181–187.
- [7] R.E. Vera, F. Salazar-Rodríguez, R. Marquez, A.M. Forgiarini, How the influence of different salts on interfacial properties of surfactant-oil-water systems at optimum formulation matches the Hofmeister series ranking, J. Surfactants Deterg. 23 (3) (2020) 603–615.
- [8] E. Ruckenstein, R. Krishnan, Can negative surface excesses of surfactant be a cause of minima in oil-water interfacial tension?, J Colloid Interface Sci. 98 (1984) 55–60.
- [9] R. Aveyard, T.A. Lawless, Interfacial tension minima in oil-water-surfactant systems. Systems containing pure non-ionic surfactants, alkanes and inorganic salts, J. Chem. Soc., Faraday Trans. 1 82 (1986) 2951–2963.
- [10] R. Aveyard, B.P. Binks, J. Mead, Interfacial tension minima in oil+water +surfactant systems. Effect of salt, temperature, and alkane in systems

containing ionic surfactants, J. Chem. Soc., Faraday Trans. 1 (81) (1985) 2169-2177.

- [11] E. Sloutskin, C.D. Bain, B.M. Ocko, M. Deutsch, Surface freezing of chain molecules at the liquid-liquid and liquid-air interfaces, Faraday Discuss. 129 (2005) 339–352. see, also the General Discussion, p. 353–366.
- [12] Q. Lei, C.D. Bain, Surfactant-induced surface freezing at the alkane-water interface, Phys. Rev. Lett. 92 (2004) 176103.
- [13] L. Tamam, D. Pontoni, Z. Sapir, S. Yefet, E. Sloutskin, B.M. Ocko, H. Reichert, M. Deutsch, Modification of deeply buried hydrophobic interfaces by ionic surfactants, Proc. Natl. Acad. Sci. U.S.A. 108 (2011) 5522–5525.
- [14] L. Shool, A.V. Butenko, S.R. Liber, Y. Rabin, E. Sloutskin, Anomalous temperature-controlled concave-convex switching of curved oil-water menisci, J. Phys. Chem. Lett. 12 (29) (2021) 6834–6839.
- [15] O. Marin, M. Tkachev, E. Sloutskin, M. Deutsch, Polyhedral liquid droplets: Recent advances in elucidation and application, Curr. Opin. Colloid Interface Sci. 49 (2020) 107–117.
- [16] S.R. Liber, O. Marin, A.V. Butenko, R. Ron, L. Shool, A. Salomon, M. Deutsch, E. Sloutskin, Polyhedral water droplets: Shape transitions and mechanism, J. Am. Chem. Soc. 142 (19) (2020) 8672–8678.
- [17] S. Guttman, E. Kesselman, A. Jacob, O. Marin, D. Danino, M. Deutsch, E. Sloutskin, Nanostructures, faceting, and splitting in nanoliter to yoctoliter liquid droplets, Nano Lett. 19 (2019) 3161–3168.
- [18] I. García-Aguilar, A. Atkins, P. Fonda, E. Sloutskin, L. Giomi, García-Aguilar et al. Reply, Phys. Rev. Lett. 126 (2021) 259802.
- [19] S. Guttman, Z. Sapir, M. Schultz, A.V. Butenko, B.M. Ocko, M. Deutsch, E. Sloutskin, How faceted liquid droplets grow tails, Proc. Natl. Acad. Sci. U.S.A. 113 (3) (2016) 493–496.
- [20] S. Guttman, Z. Sapir, B.M. Ocko, M. Deutsch, E. Sloutskin, Temperature-tuned faceting and shape-changes in liquid alkane droplets, Langmuir 33 (5) (2017) 1305–1314.
- [21] D. Cholakova, N. Denkov, S. Tcholakova, I. Lesov, S.K. Smoukov, Control of drop shape transformations in cooled emulsions, Adv. Colloid Interface Sci. 235 (2016) 90–107.
- [22] N. Deńkov, S. Tcholakova, I. Lesov, D. Cholakova, S.K. Smoukov, Self-shaping of oil droplets via the formation of intermediate rotator phases upon cooling, Nature 528 (7582) (2015) 392–395.
- [23] S. Guttman, B.M. Ocko, M. Deutsch, E. Sloutskin, From faceted vesicles to liquid icoshedra: Where topology and crystallography meet, Curr. Opin. Colloid Interface Sci. 22 (2016) 35–40.
- [24] O. Marin, M. Alesker, S. Guttman, G. Gershinsky, E. Edri, H. Shpaisman, R.E. Guerra, D. Zitoun, M. Deutsch, E. Sloutskin, Self-faceting of emulsion droplets as a route to solid icosahedra and other polyhedra, J. Colloid Interface Sci. 538 (2019) 541–545.
- [25] I. Lesov, Z. Valkova, E. Vassileva, G.S. Georgiev, K. Ruseva, M. Simeonov, S. Tcholakova, N.D. Denkov, S.S. K, Bottom-up synthesis of polymeric micro- and nanoparticles with regular anisotropic shapes, Macromolecules 51 (2018) 7456–7462.
- [26] S.R. Liber, A.V. Butenko, M. Caspi, S. Guttman, M. Schultz, A.B. Schofield, M. Deutsch, E. Sloutskin, Precise self-positioning of colloidal particles on liquid emulsion droplets, Langmuir 35 (2019) 13053–13061.
- [27] O. Marin, M. Deutsch, D. Zitoun, E. Sloutskin, Nanoparticle positioning on liquid and polymerized faceted droplets, J. Phys. Chem. C 123 (46) (2019) 28192–28200.
- [28] D. Cholakova, Z. Valkova, S. Tcholakova, N. Denkov, B.P. Binks, Spontaneous particle desorption and 'Gorgon' drop formation from particle-armored oil drops upon cooling, Soft Matter 16 (2020) 2480–2496.
- [29] S. Tcholakova, Z. Valkova, D. Cholakova, Z. Vinarov, I. Lesov, N. Denkov, S.K. Smoukov, Efficient self-emulsification via cooling-heating cycles, Nat. Commun. 8 (2017) 15012.
- [30] N. Denkov, D. Cholakova, S. Tcholakova, S.K. Smoukov, On the mechanism of drop self-shaping in cooled emulsions, Langmuir 32 (2016) 7985–7991.
- [31] I. García-Aguilar, P. Fonda, E. Sloutskin, L. Giomi, Faceting and flattening of emulsion droplets: A mechanical model, Phys. Rev. Lett. 126 (2021) 038001.
- [32] A.J. Prosser, E.I. Franses, New thermodynamic/electrostatic models of adsorption and tension equilibria of aqueous ionic surfactant mixtures: application to sodium dodecyl sulfate/sodium dodecyl sulfonate systems, J. Colloid Interf. Sci. 263 (2) (2003) 606–615.
- [33] A.J. Prosser, Thermodynamics of equilibrium adsorption and surface tension of single and binary ionic surfactant systems, Ph. D. thesis, Purdue University, USA, 2002.
- [34] X.Z. Wu, B.M. Ocko, E.B. Sirota, S.K. Sinha, M. Deutsch, G.H. Cao, M.W. Kim, Surface tension measurements of surface freezing in liquid normal alkanes, Science 261 (1993) 1018–1021.
- [35] B.M. Ocko, X.Z. Wu, E.B. Sirota, S.K. Sinha, O. Gang, M. Deutsch, Surface freezing in chain molecules: Normal alkanes, Phys. Rev. E 55 (1997) 3164–3182.
- [36] E. Sloutskin, Z. Sapir, C.D. Bain, Q. Lei, K.M. Wilkinson, L. Tamam, M. Deutsch, B. M. Ocko, Wetting, mixing, and phase transitions in Langmuir-Gibbs films, Phys. Rev. Lett. 99 (13) (2007) 136102.
- [37] L. Euler, Elementa doctrinae solidorum, Comment. Acad. Sci. Imp. Petropol. 4 (1758) 109–140.
- [38] E. Pairam, J. Vallamkondu, V. Koning, B.C. van Zuiden, P.W. Ellis, M.A. Bates, V. Vitelli, A. Fernandez-Nieves, Stable nematic droplets with handles, Proc. Natl. Acad. Sci. U.S.A. 110 (23) (2013) 9295–9300.
- [39] A. Jangizehi, F. Schmid, P. Besenius, K. Kremer, S. Seiffert, Defects and defect engineering in soft matter, Soft Matter 16 (2020) 10809.

- [40] The precise value of $(T_d T_{SE})$ depends on the radius of the droplet [19,31].
- [41] K.K. Sharker, M.N. Islam, S. Das, Counterion effect on Krafft temperature and related properties of octadecyltrimethylammonium bromide, J. Surfact. Deterg. 20 (2017) 923–932.
- [42] P. Debye, E. Hueckel, Zur theorie der elektrolyte. i. gefrierpunktserniedrigung und verwandte erscheinungen, Phys. Zeitsch. 24 (1923) 185–206.
- [43] J.N. Israelachvili, Intermolecular and surface forces, 2nd ed., Academic Press London, San Diego, 1991.
- [44] G. Para, E. Jarek, P. Warszyński, Z. Adamczyk, Effect of electrolytes on surface tension of ionic surfactant solutions, Colloids Surf. A: Physicochem. Eng. Asp. 222 (1) (2003) 213–222.
- [45] E. Sloutskin, Z. Sapir, L. Tamam, B.M. Ocko, C.D. Bain, M. Deutsch, Freezing transition of Langmuir-Gibbs alkane films on water, Thin Solid Films 515 (14) (2007) 5664–5668.
- [46] S. Yefet, E. Sloutskin, L. Tamam, Z. Sapir, M. Deutsch, B.M. Ocko, Surfactantinduced phases in water-supported alkane monolayers: II. Structure, Langmuir 30 (27) (2014) 8010–8019.
- [47] H. Sakamoto, A. Masunaga, T. Takiue, H. Tanida, T. Uruga, K. Nitta, A. Prause, M. Gradzielski, H. Matsubara, Surface freezing of cetyltrimethylammonium chloride-hexadecanol mixed adsorbed film at dodecane-water interface, Langmuir 36 (48) (2020) 14811–14818.
- [48] Y. Tokiwa, H. Sakamoto, T. Takiue, M. Aratono, H. Matsubara, C.D. Bain, Effect of surface freezing on stability of oil-in-water emulsions, Langmuir 34 (21) (2018) 6205–6209.

- [49] E. Sloutskin, H. Kraack, O. Gang, B.M. Ocko, E.B. Sirota, M. Deutsch, A thin-thick transition in the surface-frozen layer of a binary alcohol mixture, J. Chem. Phys. 118 (2003) 10729–10734.
- [50] Y. Tokiwa, H. Sakamoto, T. Takiue, M. Aratono, H. Matsubara, Effect of alkane chain length and counterion on the freezing transition of cationic surfactant adsorbed film at alkane mixture - water interfaces, J. Phys. Chem. B 119 (20) (2015) 6235–6241.
- [51] A.J. Prosser, E.I. Franses, Adsorption and surface tension of ionic surfactants at the air-water interface: review and evaluation of equilibrium models, Colloids Surf. A: Physicochem. Eng. Asp. 178 (1) (2001) 1–40.
- [52] P.A. Kralchevsky, K.D. Danov, G. Broze, A. Mehreteab, Thermodynamics of ionic surfactant adsorption with account for the counterion binding: effect of salts of various valency, Langmuir 15 (1999) 2351–2365.
- [53] B. Janczuk, A. Zdziennicka, K. Jurkiewicz, W. Wojcik, The surface free energy and free energy of adsorption of cetyltrimethylammonium bromide, Tenside, Surfactants, Deterg. 35 (1998) 213–217.
- [54] I. Borukhov, D. Andelman, H. Orland, Steric effects in electrolytes: A modified Poisson-Boltzmann equation, Phys. Rev. Lett. 79 (3) (1997) 435–438.
- [55] L. Sepúlveda, J. Cortés, Ionization degrees and critical micelle concentrations of hexadecyltrlmethylammonium and tetradecyltrlmethylammonlum micelles with different counterions, J. Phys. Chem. 89 (1985) 5322–5324.