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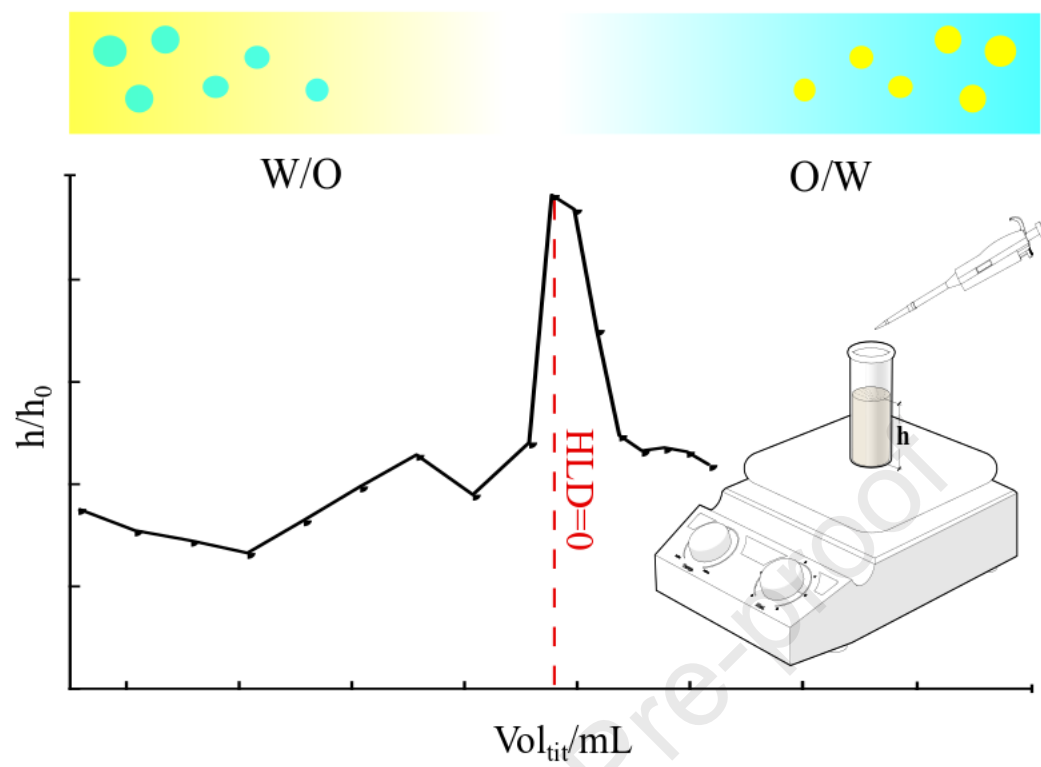
An HLD framework for cationic ammonium surfactants

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Abstract

The Hydrophilic-Lipophilic Difference (HLD) model can be described by additive contributions accounting for the effect of the oil and surfactant nature, temperature, ionic strength, and so on. The first step to build an HLD framework for a surfactant class is to have Winsor III phase equilibria in a restricted range of formulation variables. In this respect, anionic and nonionic surfactants are well suited for an HLD study. On the contrary, it is difficult achieve for pure cationic surfactant Winsor III phase equilibria without the addition of alcohols and this has precluded the extension of the HLD to cationic surfactants.

In the present contribution, we first propose a system based on a blend of single-tailed and double-tailed cationic surfactant to study the oil contribution, and then we afforded the determination of the surfactant contribution trough an experimental approach (the "HLD-titration") that is especially tailored for systems displaying a wide range of existence of Winsor III phase equilibria.

HLD-titration results confirmed the ionic strength contribution to HLD as a logarithmic function of salinity for cationic-based microemulsions similarly to anionic ones. However, the oil carbon number contribution is almost four-fold larger ($k=0.7\pm0.1$) with respect to anionic surfactants. A clearing point was observed in correspondence of the Winsor III phase equilibria under stirring. This approach allows us the determination of the so-called characteristic curvature (Cc), i.e. the term describing the surfactant nature contribution to the film curvature, of the cationic surfactant. Finally, the method was adopted to determine Cc values of 7 quaternary ammonium surfactants differing in the polar heads nature and further three amine oxide surfactant at pH=1 where they are protonated.

Introduction

The surfactant formulations are of paramount importance in a wide number of practical applications that involve microemulsions, emulsions, liquid crystalline phases, and micelles. Over the years, several theoretical models have been proposed to explain the features of surfactant systems. Among these, the theoretical approaches based on the concept of optimal packing parameter ($p°$) of surfactant molecule or on the spontaneous curvature ($H°$) of the interfacial film have been successfully exploited to rationalize the system microstructure as probed by experimental techniques (SAXS, SANS, diffusion NMR, etc.)[1–7].

However, the lack of quantitative relationships linking the chemical nature of the components (formulation variables) and the key parameters ($p°$ or $H°$) of the model limits the use of those models to predict "a priori" the microstructure of a generic system made of surfactants, brine and oils.

The Hydrophilic-Lipophilic Difference (HLD) model, first introduced in the 70s and lately improved to obtain the HLD-NAC model [8–10], represents a different approach. It consists in a semiempirical relation between several experimental parameter furnishing a numerical output that reflect the morphology of the microemulsion, the HLD:

$$(1) \qquad \frac{\mu_w^{*surf} - \mu_o^{*surf}}{RT} = HLD$$

On the left side of Eq. 1 the meaning of HLD is expressed in thermodynamic terms: it describes the difference in the chemical potential, in a suitable reference state, for the surfactant in water (μ_w^{*surf}) and oil (μ_o^{*surf}) phase normalized with respect to the thermal energy. The HLD considers the aqueous and oil phases in equilibrium with a bicontinuous microemulsion in the so-called Winsor III phase equilibrium as reference states. As such, the achievement of the reference state can be evaluated by visual inspection by finding the formulation variables leading to a three phases equilibrium.

Consequently, HLD does not depend on the concentration of the components (composition variables) but only on their number and chemical nature (formulation variables). Aqueous and oil phases are taken as pseudo components as long as their composition does not change. For example, μ_o^{*surf} will depends on the surfactant and oil nature but not on their concentration. Being a property of the chemical nature of surfactant, oil and aqueous phases is a feature the HLD shares with other descriptors of surfactant systems such as the spontaneous mean curvature ($H°$) or the optimal packing parameter ($p°$). Indeed, the HLD has been recently correlated to the spontaneous mean curvature of the interfacial film normalized by its thickness l via $HLD = p° - 1 \sim - H°l$ [11], where the last equality should be taken with caution because it holds only when H°<< l^{-1} [12].

Therefore, all the models rationalizing the system evolution upon changing the spontaneous curvature equally holds for changes in HLD. The surfactant chemical potential accounts for the effect of the oil and surfactant nature, temperature, ionic strength, and so on, in an additive manner, consequently the same holds for the dimensionless parameter HLD. This is the main advantage of the HLD approach leading to simple semiempirical relations, as eq.1 to be discussed in the next section that allows the numerical evaluation of the HLD value once the nature of surfactant and oil together with temperature and salinity of aqueous phase are known. For HLD~0 bicontinuous ultralow interfacial tension ($10^{-2} - 10^{-3} \, mN/m$) microemulsion are expected [8,13,14]; for HLD<0 direct oil swollen micelles are favoured while fore HLD>0 reverse micelle are expected to form.

The additive property of the HLD can be employed to quantify the contribution of a surfactant or oil that are not yet in a database. The procedure consists in finding the conditions (T and/or salinity) leading to a Winsor III phase equilibrium for a microemulsion made by the unknown surfactant (or oil) and a known oil (or surfactant). Operating in such a way, large data sets for systems made of anionic and nonionic surfactant have been constructed and are continuously updated and refined [15–18]. It worth to highlight that the HLD model does not consider explicitly the counterions nature and cannot predict ion-specific effects such as the Hofmeister series. On the other hand, using the HLD as a guide to rational formulation one often resorts to concentrate solutions of NaCl that furnishes the counterion, independently from the chemical formula of the pristine solid surfactant.

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Anionic and nonionic surfactants have been intensively studied because of their use in economically important processes such as enhanced oil recovery (EOR), detergency, cosmetic and pharmaceutical formulations but also because they are well suited for an HLD study. Indeed, it is easy to find a pure anionic or nonionic surfactant that is able to give rise to Winsor III phase equilibria in a restricted range of formulation variables [19–22].Such a condition is the first step to build an HLD framework for a surfactant class.

On the other hand, cationic surfactants are of primary importance on some selected products such as sanitization formulation, hair conditioners, softeners, gene delivery systems, and so on. As such they have been widely investigated experimentally [5,23,24]. In particular the ternary mixtures of water and hydrocarbons with didodecyldimethylammonium bromide (DDAB) have yielded fascinating data on microstructure in microemulsion mesophases [25]. These water/alkane/DDAB microemulsions have been modelled by the so-called "DOC cylinder" approximation, a simple model reminiscent of connected water channels [26,27].

Unfortunately, it is not straightforward to apply to cationic surfactants the procedures developed for other surfactants to obtain the relevant HLD-parameters and this has considerably hindered the extension of HLD to cationic systems. To the best of our knowledge, the only HLD-investigation of cationic surfactant is found in a dated (1997) paper by Anton et al. that, however, loaded the systems with alcohol to obtain bicontinuous microemulsion [28].

In the present contribution, we first propose a system based on a blend of single-tailed and double-tailed cationic surfactant to study the oil contribution, and then we afforded the determination of the surfactant contribution trough an experimental approach (the "HLD-titration") that is especially tailored for systems displaying a wide range of existence of Winsor III phase equilibria.

2.Materials & Methods

2.1 Materials. The following chemicals have been purchased from Sigma Aldrich: hexane (>99%), heptane (>99%), octane (>99%), nonane (>99%), decane (>99%), sodium chloride (>99%) and HPLC grade water. Cationic surfactants are pure grade chemicals (>98-99%) purchased from Sigma Aldrich and have been used without further purification: didodecyldimethylammonium bromide (DDAB) is a double chain quaternary ammonium surfactant (quat); hexadecyltrimethylammonium bromide (cetyl-TAB or CTAB), tetradecyltrimethylammonium bromide (myristyl-TAB or MTAB), dodecyltrimethylammonium bromide (lauryl-TAB or LTAB), benzyldimethylhexadecylammonium chloride (BDHC), cetylpyridinium chloride (CPC) and 1-hexadecyl-3-methylimidazolium chloride (CMIC) are single chain quats. Stock solution of cationic surfactants have been prepared dissolving 2 g of surfactant in 100 g of water (2% w/w). Amine oxides 2% (w/w) solution at pH=1 have been prepared by acidification with HCl and dilution of stock solutions purchased from different dealers: LDAO (N,N-Dimethyldodecylamine N-oxide solution) is a 30% water solution purchased from Sigma; EMPIGEN® OB/EG is an industrial grade (32% water solution) C12-14 dimethyl N-oxides mixture from Huntsman Holland; AMMONYX CSO is an industrial grade (30% water solution) C12-18 dimethyl N-oxides mixture distributed by STEPAN EUROPE.

2.2 Salinity scans. Different volume ratio (from 1:4 to 1:2) of DDAB and CTAB stock solutions are mixed and tested for several electrolyte concentration from 1% to 25% (w/v). The organic phase is added keeping the water/oil volume ratio (WOR) at 1. Samples are vigorously shaken and allowed

to stay at 25°C until complete stabilization. The optimal salinity (S*) is determined as the salinity at which a three phase Winsor III equilibrium with equal oil and water excess phase volumes are found.

2.3 Perturbation experiments. Equal volumes of DDAB 2% solution and linear alkane have been mixed in a test tube with NaCl (10% w/v). Perturbations are performed adding progressive amount of single chain surfactant (2%) solution to the stabilized starting system: each step 20 µL are added then the sample is stabilized at 25°C. The stabilization is monitored using photos until the coalescence phenomenon ends revealing the microemulsion in equilibrium with perfectly transparent excess phase. Microemulsion conductivities are measured using the SevenCompact® S230 conductivity meter equipped with InLab®752-4mm microprobe from METTLER TOLEDO, conductivity has been normalized with respect to the corresponding brine conductivity.

2.4 Titration experiments. In a 12 mL vial, 2 mL of DDAB 2% aqueous solution and 2 mL of the organic phase have been mixed with 199.4 mg of NaCl (10% w/v). Progressive addition of 20 µL single chain surfactant solution (2%) is made using a micropipette under constant stirring. We performed the additions until a maximum added volume of 1 mL is reached to avoid the so called catastrophic emulsion inversion [29,30] (if the water phase exceed 75% the emulsion preferred morphology will be O/W having water as continuous-exceeding phase, in this regime Bancroft's rule irrelevant). The experiment is monitored with a conductometer and a fixed angle camera connected to a PC running an image analysis software (ImageJ 1.53a [31]).

2.5 Turbidity experiments. Turbidity measurements are performed using a homemade instrument pictured in the inset of Figure 5. The instrument consists in a red laser probe (650 nm) module (KY-008) and in a photoresistor module which function as detector (KY-018). Both modules are controlled by an ARDUINO UNO microcontroller: the probe is switched on and off through a digital port (D13) while the photocell signal is read through an analogical port (A0). Measurements are displayed on ARDUINO software's serial port and then processed using MATLAB (ver. R2019b).

3. Phenomenology of HLD

The general HLD equation is

$$(2) \qquad HLD = +Cc - k \cdot EACN - \alpha \Delta T + f(S)$$

The rhs of Eq. 2 is a semi-empirical relation in which the contributions of the nature of surfactant, oil and aqueous phases and of the temperature sum up [32].

Cc is a characteristic term for the surfactant that describes its contribution to the film curvature. More hydrophobic surfactant has large positive Cc and favours positive HLD ($p°>1$). Such a parameter is often called the characteristic curvature although the name is misleading (film curvature depends also on the oil and brine composition) but in the original works it was called surfactant characteristic parameter and denoted by the Greek letter σ.[8,13,14]

The EACN (equivalent alkane carbon number) is used for describing the contribution of the oil phase and, for linear alkanes, corresponds to the number of carbon atoms [33]. In the case of oil different from *n*-alkanes, EACN must be determined experimentally [19,34–36]. The constant *k* scales the EACN for a fair sum with the salinity function f(S); *k* is assumed to be roughly constant for a class of surfactants and must be determined experimentally (*k*~ 0.15-0.17 for anionic surfactants) [9,21,37,38].

The effect of changes in temperature with respect to the reference temperature (25°C) is handled by the term $\alpha\Delta T$ where α is slightly positive for ionic surfactant (0.01) and negative for ethoxylated (-0.06) [39]; ΔT is the difference between the actual and the reference (298 K) temperatures.

The term f(S) handles the influence of ionic strength on the film curvature. For convenience it is expressed as a function of the salinity, S, of the aqueous phase expressed as equivalent grams of NaCl per 100 mL and it equals ln(S) for ionic surfactants (as expected for the counterion contribution to their chemical potential) while it is linear (b·S) for nonionic (b~0.13 dL/g) surfactants [21,40]. The latter can be attributed to osmotic dehydration of the polyethyleneoxide surfactant brush [41].

Thus, the HLD equation for ionic surfactant is:

$$(3) \qquad HLD = \ln(S) - k\, EACN - \alpha\Delta T + Cc$$

While the analogous equation for nonionic can be written as:

$$(4) \qquad HLD = b \cdot S - k\, EACN - \alpha\Delta T + Cc$$

Ionic surfactants contribute to the overall salinity of the system, and this must be considered in the calculation of HLD so that ln(S) does not diverge in the case of no added salt. According to the "dressed micelle" model [42] only a fraction of ionic surfactants present on the micellar surface are fully ionized so that the surfactant contribution to the salinity is usually approximate as the 30% of its molar equivalent in NaCl [43].

Numerical parameters for Eq.s 3-4 have been found through the so-called salinity scans. In these experiments, the aqueous phase salinity is changed and the salinity at which a Winsor III system occurs is labelled as S*. When S = S* the HLD = 0, this condition is called optimum (or balanced) formulation for historical reasons linked to EOR. The condition of balanced formulation is easily detected by the three phases coexistence (oil/microemulsion/water) and is associated to minimum interfacial tension and maximum solubilization of oil and water. Salinity scans are performed, at the same temperature, for several oil i.e. at different EACN. In case of anionic surfactant microemulsion (at T = 25°C) Eq. 3 at optimum formulation condition can be written as:

$$(5) \qquad lnS^* = k\, EACN - Cc$$

Therefore, by plotting ln(S*) versus EACN one finds a linear trend whose slope is the k of eq. 1 and the intercept equals -Cc. Nowadays, plenty of values of Cc are available for many surfactants [14,21,32,44–47].

Surfactant blend can be handled as well by the HLD framework: the so-called mixing rule can describe efficiently a surfactant mixture (if the two surfactants do not interact synergically) with a proper Cc value computed as a mole average of Ccs of the surfactants in the mixture [21,40,48–52]:

$$(6) \qquad Cc_{Mix} = \sum_i Cc_i \chi_i$$

χ_i and Cc_i are the molar fraction and the Cc-values of surfactant i in the blend, respectively. An analogous relationship holds for the EACN of a mixture of oils but in this case the EACNs are weight-averaged [43,53,54].

The key parameters of the HLD are defined (and measured) for microemulsion systems, however, macroemulsion properties made with the same components can be predicted by the HLD model as well [55–57]. HLD>0 implies that stable W/O emulsion are formed while systems with HLD<0 give rise to direct O/W emulsion.

For balanced formulation HLD~0, bicontinuous microemulsion coexists with excess oil and water in the Winsor III phase equilibrium. In such a balanced state, any attempt to emulsify the three phases in each other fails because the resulting emulsions are very unstable and break within several seconds after emulsification.
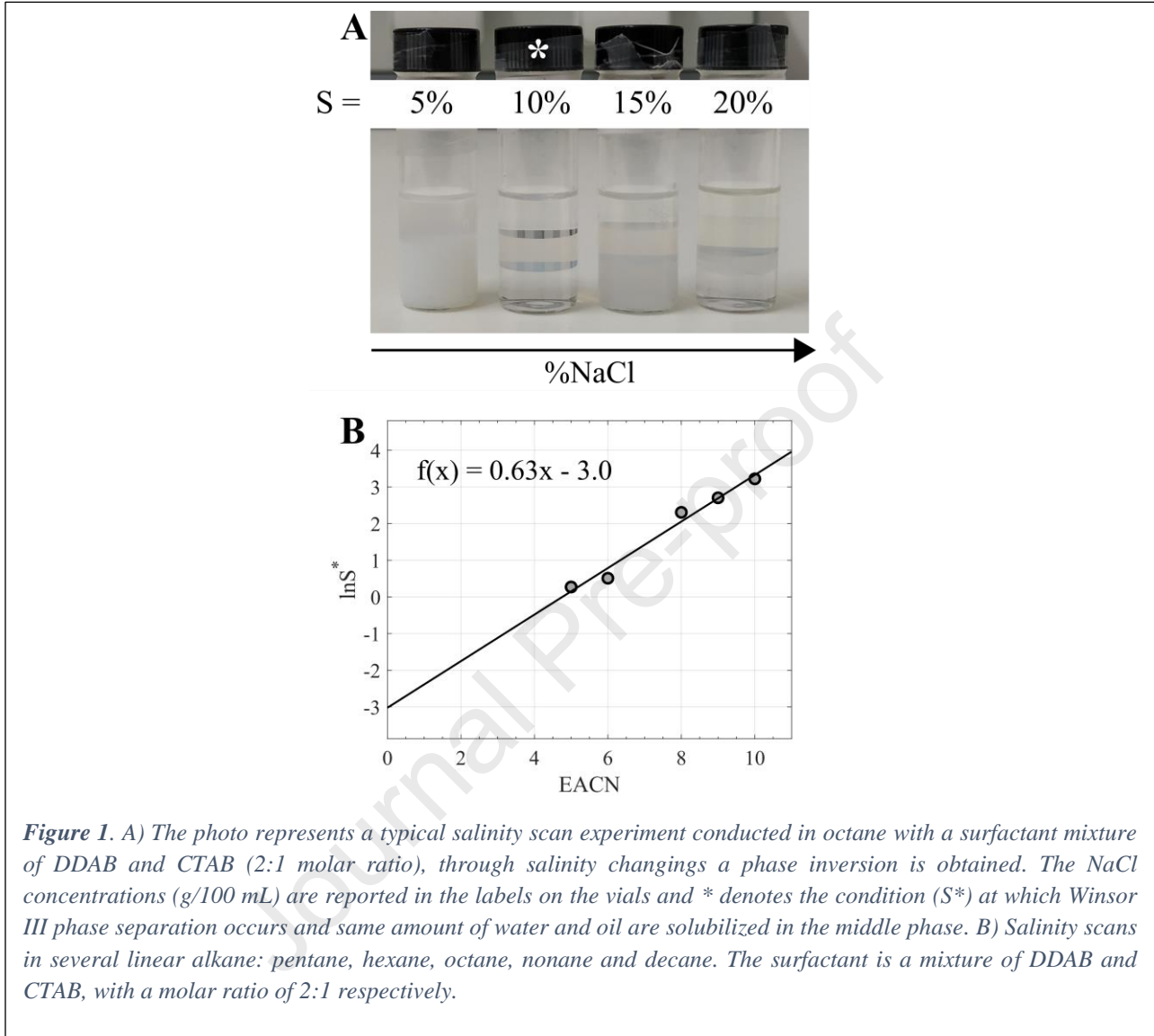
Extensive studies about macroemulsion stability have been conducted in mid-90s. Kabalnov showed how macroemulsion lifetime can be related to activation energy expressed according to Helfrich's model: this energy barrier depends on the spontaneous curvature (H_0), the bending modulus (κ) and the saddle-splay modulus ($\bar{\kappa}$) [58,59]. In the Winsor III regime, the stabilization kinetic is mostly driven by the spontaneous curvature: for small absolute value of H_0 the macroemulsion is unstable, the film quickly breaks up. H_0 has been related to HLD in case of non-ionic surfactants, so near balanced formulation we can expect a strong dependency of macroemulsion stability upon HLD [11,60,61].

4. Results and Discussion

The first obstacle in applying HLD to cationic surfactants is the lack of a commercially available surfactant that easily forms a Winsor III equilibrium. Among the cationic surfactants, the asymmetric quaternary ammonium salts (quats) are widely used. The two-tail quats (such as DDAB) form reverse microemulsions that loaded with water give rise to a Winsor II equilibrium, while single tail quats form oil-in-water (o/w) microemulsion prone to Winsor I equilibrium. Increasing ionic strength in single tail quats-based microemulsions leads to surfactant precipitation, i.e. it is challenging to increase their lipophilic character.

We have circumvented this difficulty by exploiting the property that a blend of surfactants is characterized by its own Cc-value keeping constant the mole ratio between the two surfactants.

The interfacial film tendency to form bicontinuous microemulsion has been tuned by mixing suitable amounts of two-tailed and single-tailed cationic surfactant. The optimal salinity content, S*, to achieve the balanced state in the mixtures of DDAB and CTAB (2:1 molar ratio) is achieved through

Figure 1. *A) The photo represents a typical salinity scan experiment conducted in octane with a surfactant mixture of DDAB and CTAB (2:1 molar ratio), through salinity changings a phase inversion is obtained. The NaCl concentrations (g/100 mL) are reported in the labels on the vials and * denotes the condition (S*) at which Winsor III phase separation occurs and same amount of water and oil are solubilized in the middle phase. B) Salinity scans in several linear alkane: pentane, hexane, octane, nonane and decane. The surfactant is a mixture of DDAB and CTAB, with a molar ratio of 2:1 respectively.*

a scan for each n-alkanes adopted. A representative experiment is shown in Figure 1A, while Figure 1B reports the logarithm of S* that scales linearly with the EACN. These experiments corroborate the idea of extending the use of Equation 3 to cationic surfactants and allows an estimate of the *k*-value (slope) and of the Cc (-intercept) of the blend.

To evaluate the Cc value of the single surfactants another dimension must be introduced in the scan experiments [62].

According to the mixing rule we can write Eq. 6 as

$$(7) \quad Cc_{Mix} = Cc_{DDAB} \, \chi_{DDAB} + Cc_{CTAB} \, (1 - \chi_{DDAB})$$

Where χ_{DDAB} il the DDAB mole fraction in the blend.

Combining the HLD equation for ionic surfactant with the mixing rule as written as in Eq. 7, and exploiting the fact that our blend is made by surfactants with ammonium head group which should share the same *k*-value [20], the equation of a plane comes out (Eq. 8).

$$(8) \quad lnS^* = k \cdot EACN - Cc_{DDAB} \, \chi_{DDAB} - Cc_{CTAB}(1 - \chi_{DDAB})$$

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Salinity scans were performed at different χ_{DDAB}, using five n-alkanes as oil and the corresponding lnS* as a function of EACN and of χ_{DDAB} are shown in Figure 2. By the interpolation of the experimental data to the plane's equation in eq. 5, the value of k=0.7±0.1 and the Cc values for CTAB (-6.5±1.1) and DDAB (8.3±1.4) have been obtained.
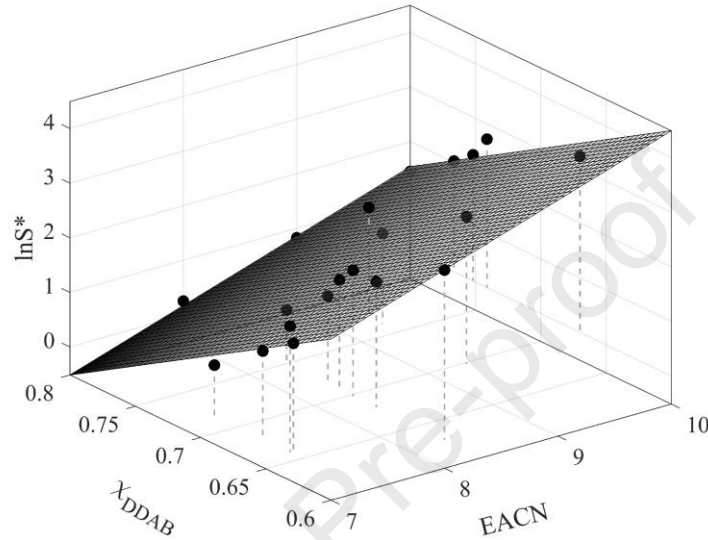

Figure 2. *Three-dimensional scan performed by varying alkane carbon number as well as the relative composition of the DDAB/CTAB surfactant mixture. The interpolation results:* $Cc_{DDAB} = 8.3 \pm 1.4$, $Cc_{CTAB} = -6.5 \pm 1.1$ *and* $k_{Cat} = 0.69 \pm 0.11$.

4.1 Perturbation method.   The three-dimensional (3D) scan is time demanding. However, the 3D scan leads to the Cc determination of DDAB's allowing the implement of a perturbation method to evaluate the Cc-values of other single tails cationic surfactants.

The initial reference system is a DDAB/oil/brine system that is in a Winsor II equilibrium with a positive HLD value given by:

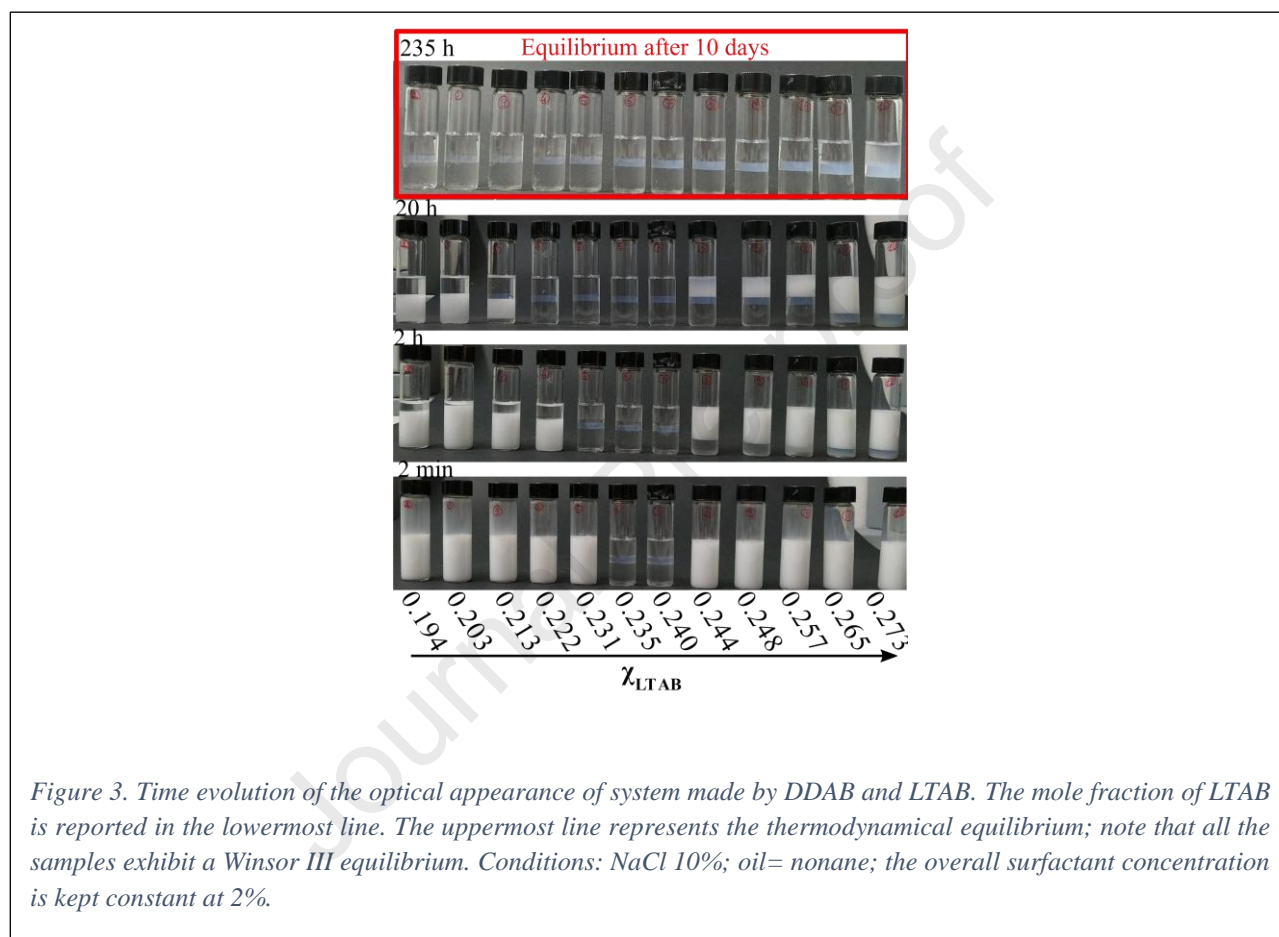$$(9) \quad HLD_i = lnS - k\,EACN + Cc_{DDAB}$$

Then the composition is perturbed: a surfactant scan is performed by keeping constant the oil and salinity and adding the surfactant under scrutiny (mole fraction in the blend χ_2) having care to keep constant total surfactant concentration. Different samples varying in the χ_2 are prepared. At a given mole fraction, χ_2*, the balanced condition is met (HLD=0) and combining eq.s 5, 6 and 9 one easily evaluate the unknown Cc_2 of the unclassified cationic surfactant as:

$$(10) \quad Cc_2 = Cc_{DDAB} - HLD_i/\chi_2^*$$

The precision of such an estimate depends on the error on the balanced blend composition and this rises another difficulty encountered with cationic surfactants. In Figure 3 (upmost line) is shown the picture of surfactant scan made with LTAB in the range 0.19<χ_{LTAB}<0.27 at the equilibrium (10 days from the preparation). Unmistakably all the samples feature a three phase Winsor III equilibrium. This poses a big issue with the identification of the balanced formulation. The identification of the optimum formulation as the average among all the samples showing a three-phase behaviour works

well when the compositional range is limited [8,63,64] (as often found for anionic and nonionic surfactants) but in this case results in high errors (25%).

Indeed, for all the three-phases samples, the middle phase is a truly bicontinuous microemulsion as demonstrated by its conductivity normalized to the conductivity of the aqueous phase ($154.4 \pm 0.2 \ mS/cm$) shown in Figure 4. In the whole set of samples, the normalized conductivity remains in the range 0.1 to 0.45. These values are typical of bicontinuous microemulsions being much higher than the expectation for reverse micelles (0) and much lower than the expectation for direct micelles (0.8-1) [65].

Figure 3. Time evolution of the optical appearance of system made by DDAB and LTAB. The mole fraction of LTAB is reported in the lowermost line. The uppermost line represents the thermodynamical equilibrium; note that all the samples exhibit a Winsor III equilibrium. Conditions: NaCl 10%; oil= nonane; the overall surfactant concentration is kept constant at 2%.

A restricted range of surfactant blend composition, where the phase separation is accomplished within few minutes, can be detected by visual monitoring (see Figure 3). Minimum stability is a well-known property of Winsor III phase equilibrium, Shinoda was the first one who reported this observation studying the emulsion lifetime near the PIT [66] and in 1996 Kabalnov & Wennestrom successful rationalized such an evidence in terms of the energy barrier for the nucleation of an hole across the surfactant films connecting two touching emulsion droplets [58,59]. The rate of coalescence depends exponentially on the nucleation barrier that in turn has a minimum for a null curvature. Accordingly, the criterion of minimum stability of a surfactant/oil/brine emulsion to accurately locate the balanced formulation or temperature was proposed [59] and lately it has been translated into the HLD framework as a time saving approach to the Cc determination of nonionic surfactants[44].

We have extended such an approach to blends of cationic surfactants. Representative results for the pair DDAB & LTAB are shown in Figure 3 where twelve systems based on equal volumes of nonane and NaCl 10% g/vol and differing in the DDAB/LTAB ratio have been examined.

The different emulsions are mixed with vortex before starting the measure of macroemulsion lifetime. Stabilization times are measured in an arbitrary way as described by Kabalnov and Weers: τ is the time (measured in seconds) necessary for half of the cream layer to coalesce [59]. Results of stabilization time experiments are reported in the graph in Figure 4.

A minimum in macroemulsion lifetime occurs when $\chi_{LTAB}=0.24$ that we identify as the balanced composition for this system. The corresponding Cc for LTAB is evaluated according to eq. 10 and is listed in Table 1.

4.2 HLD titration. Determination of balanced formulation of microemulsions through stabilization experiments is an unambiguous and time-consuming method. Here, we are proposing a dynamical time-saving experimental approach in which the surfactant is added to the initial sample under stirring, i.e., changes in sample composition takes place on the same sample similarly to the acid-base titration where amount of titrant volume are added continuously. While the addition under stirring of a concentrated solution of the unclassified surfactant does not pose problem, the lack of an instantaneous determination of the Winsor III regime is a serious hindrance to such an approach.
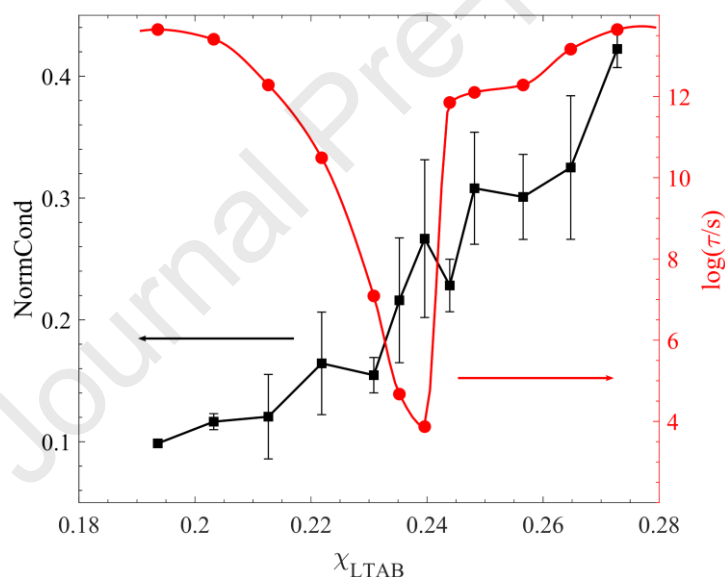

Figure 4. System made by DDAB and LTAB (same samples of Figure 3). Conductivity (left ordinate, black line) of the middle phase stabilized microemulsion and logarithm of macroemulsion lifetime in seconds (right ordinate, red circles) versus LTAB mole fraction. See text for details.

For this reason, we explored different parameters that could be used to probe the formation of a balanced state. Conductivity, under vigorous stirring, has been already proposed as a method to probe the nature of the continuous phase of emulsions exploiting the fact that, under stirring, a Winsor I equilibrium forms highly conductive O/W emulsion, while a Winsor II equilibrium forms non-conductive W/O emulsion [29,55,57]. We have therefore compared the evolution of conductivity along a "HLD titration".

Starting from a DDAB/brine/nonane Winsor II equilibrium, the system has been perturbed through the addition of an aqueous solution of LTAB. The system was under vigorous stirring and after each addition the conductivity was measured. This resulted in milky emulsions due to the Mie light scattering. A representative result is shown in Figure 5 (right ordinate). For small addition of titrant,
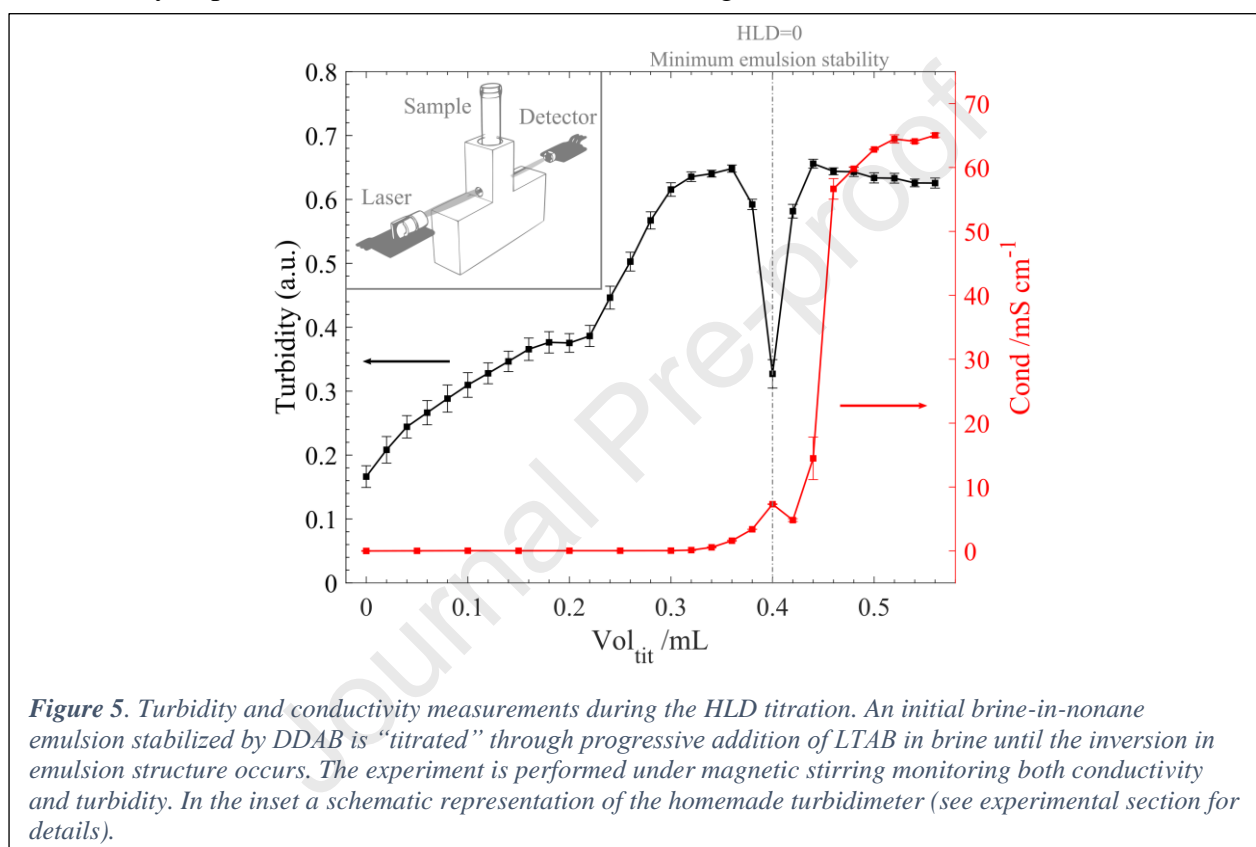
the HLD remains positive leading to a water-in-oil emulsion that is, essentially, nonconductive. When the ratio LTAB/DDAB approaches the condition HLD=0 there is a measurable increase in the conductivity (from 0 to ~ 10 mS/cm). In the experiment of Figure 5 this corresponds to 0.4 mL of titrant added. However, the increase in conductivity continues, up to 65 mS/cm, for further LTAB loading. The comparison of the conductivity evolution along titration with the composition at which the emulsion stability is minimum (Figure 4) indicates the conductivity measurement cannot be proposed as an accurate indicator to determine the balance condition along a HLD-titration.

Notably, the sample under stirring appeared clearer in correspondence of the LTAB/DDAB ratio associated to the minimum in emulsion stability, i.e. the balanced state. Roger et al. observed a clearing boundary caused by the solubilization of the oil into surfactant-rich objects, as a function of temperature. Here, the clearing point take place exactly at the balanced LTAB/DDAB ratio and thus have been investigated as potentially useful as indicator of the HLD=0 state [67].

The turbidity of the stirred sample along the HLD-titration has been probed in parallel with the conductivity measurements discussed above and the results are also shown in Figure 5 (left ordinate). Experimentally the initial DDAB-brine-nonane W/O emulsion has a lower turbidity (0.2) than the O/W emulsions found in presence of large amount of LTAB (~0.6). Upon loading the initial DDAB-brine-nonane system with LTAB, the turbidity increases steadily towards the value observed for O/W emulsion but, at the balanced condition, a deep minimum in turbidity is observed, i.e., the clearing point. The stirred emulsion is more whiteish than milky at this clearing point, it looks like water and alkane stirred without the surfactant. This is likely linked to the high emulsion instability previously observed at the balanced formulation where large amounts of water and oil coexists. Upon further loading with LTAB a relatively stable, milky, O/W emulsions forms leading to a dramatic increase in the turbidity. It is worth to recall that the oil-to-water ratio here is 1 and we expect to always have some excess phase so that the transformation of droplets into micelles leading to the clearing boundary found in T-scan around the PIT with nonionic surfactants [67] can hardly account for this minimum in turbidity.
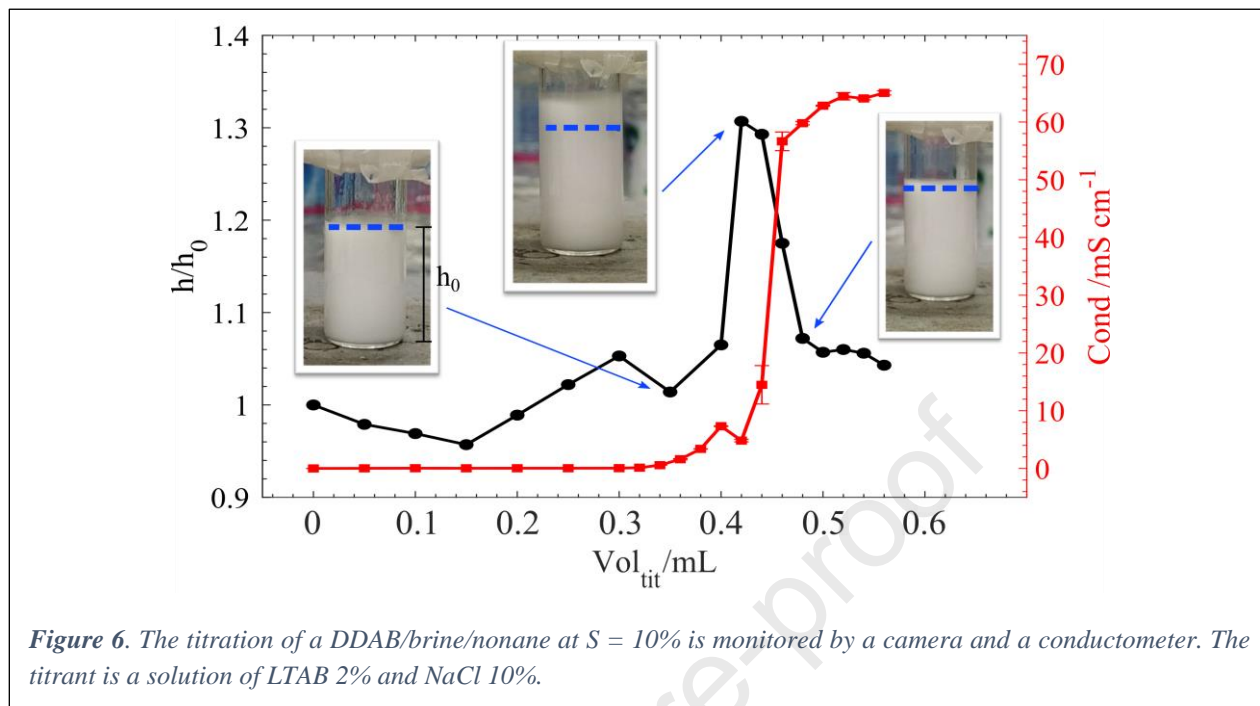
However, performing these experiments we have observed that in correspondence of the balanced state, the level reached by the fluid under stirring has a consistent jump.

Such a sudden increase in the fluid level of the stirred sample can also be adopted as readout of the balanced condition similarly to the turbidity measurements. First at all the initial level of the DDAB-brine-nonane system under stirring is marked as a reference. Then, leaving unchanged the stirring rate, the system is loaded with aqueous solution of the unclassified cationic surfactant. When the salinity of the brine is properly chosen the volume of titrant required to pass from a Winsor II to a Winsor I equilibrium is negligible with respect to the starting volume. Therefore, the stepwise loading with the titrant does not change the height of the stirred fluid until one reaches the balanced condition at which a sudden jump in the level is observed. The relative increase in the height of the stirred fluid (h) normalized by the initial level (h_0) is clearly visible by naked eye ($h/h_0 \sim 30\%$) and remain stable in time. Very important, further addition of titrant leading to leave the balanced state results in a drop
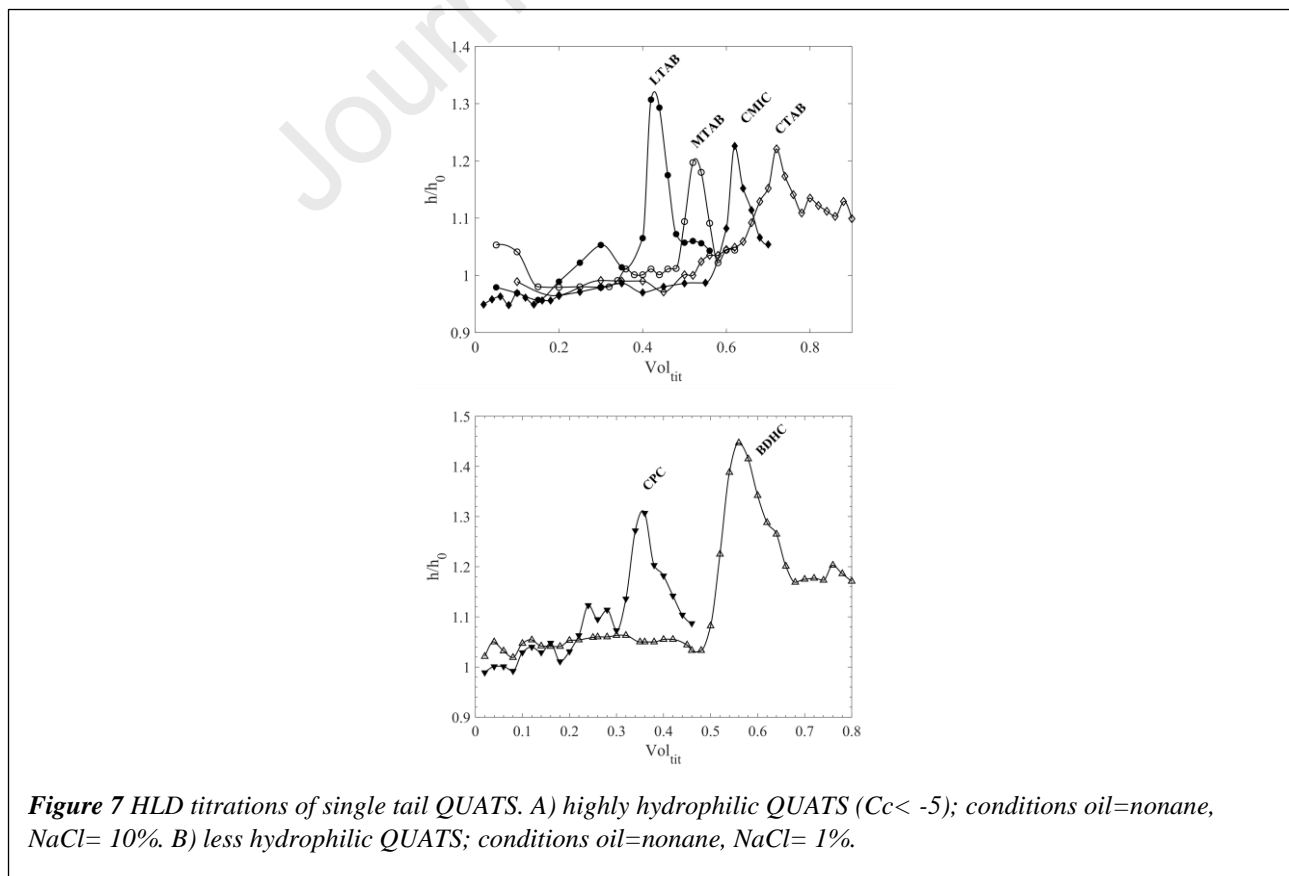

Figure 5. Turbidity and conductivity measurements during the HLD titration. An initial brine-in-nonane emulsion stabilized by DDAB is "titrated" through progressive addition of LTAB in brine until the inversion in emulsion structure occurs. The experiment is performed under magnetic stirring monitoring both conductivity and turbidity. In the inset a schematic representation of the homemade turbidimeter (see experimental section for details).

in the stirred fluid level that returns to the previous value. In Figure 6 this version of the HLD-titration is showed by plotting the h/h_0 ratio versus the added titrant volume. A movie describing the process is provided in the Supporting Information section. Stability time measurements proof that the maximum in the stirred fluid level always corresponds to the null spontaneous curvature case.

The height of the stirring vortex in a fluid is inversely proportional to its viscosity[68]. For this reason, the dramatic increase the level reached under stirring, when the balanced condition is fulfilled, should be associated to the minimum in the viscosity of emulsified systems in the Winsor III equilibrium previously reported by others [55,61,69–73]. This minimum has been associated to the ultralow

interfacial tension that allows elongating the oil, water and microemulsion domains along the stream lines with a very low energy cost [55–57,74,75].

Figure 6. The titration of a DDAB/brine/nonane at S = 10% is monitored by a camera and a conductometer. The titrant is a solution of LTAB 2% and NaCl 10%.

4.3 Cc values of Quaternary ammonium surfactants

The balanced condition for several quats has been routinely determined by means of HLD-titration using the jump in the stirred fluid level as an indicator and using the same salinity in the titrant and in the titrand. Examples of titrations are shown in Figure 7. Experimentally, a suitable NaCl

Figure 7 HLD titrations of single tail QUATS. A) highly hydrophilic QUATS (Cc< -5); conditions oil=nonane, NaCl= 10%. B) less hydrophilic QUATS; conditions oil=nonane, NaCl= 1%.

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concentration must be chosen. In the case of very hydrophilic surfactants a relatively high salinity is required to reach the balanced situation but for less hydrophilic surfactants this can results in the surfactant salting out and a smaller salinity is advisable. The Cc values have been then evaluated according to eq.s 9 and 10 using the previously determined values of k and Cc_{DDAB} to estimate the HLD value in the initial state (HLDi) and the experimental χ_2^* value is taken from the added volume during the titration that correspond to balanced composition. A subsequent estimate based on the stability of emulsions around the HLD=0 confirm such estimates.

 The Cc values are listed in Table 1.

A comparison with the literature for anionic surfactants evidences that the value $k = 0.7$, in eq. 3, obtained for quaternary ammonium surfactants is more than four-fold larger than the value reported for anionic surfactants ($k \sim 0.16$) [9]. An analogous discrepancy is observed for the absolute value of the Cc values [9]. For example, the Cc of LTAB reported in Table 1 is -10 while for SDS, an anionic surfactant with the same alkane tail, Cc=-2.3. Similarly, the Cc for two typical double tail surfactants, usually forming reverse microemulsions are 8.3 for the cationic DDAB and 2.55 for the anionic AOT. Such differences in the k and Cc values obtained for anionic and cationic surfactants reflect the difference in their sensitivity to salinity. For both the classes of surfactant the dependence of the HLD on the salinity is logarithmic (see Figs. 1B and 2) according to eq. 3, but, experimentally, the relative influence of the salinity on the HLD is weaker for quats.

This means that to keep a balanced Winsor III equilibrium upon changing the oil (EACN), or the surfactant, one should change the salinity to a larger extent in the case of cationic compared to anionic surfactant. Since for HLD equations the multiplicative term of the ln(S) in eq. 3 is fixed to one, a weaker salinity influence is formalized by larger contributions of the Cc and $k \cdot EACN$ terms.

To compare the amphiphilicity of surfactants of different charge, accounting for the different weight of the ln(S) term, it has been proposed to normalize the measured Cc by the corresponding k-value [13,76]. This is equivalent to write the HLD equation having unit coefficient in front of the only variable which has exactly the same effect in both cases, and this is not the salinity but the oil EACN [77].

 The corresponding values of Cc/k are listed in Table 1. In terms of Cc/k a substantial agreement between cationic and anionic surfactants is found. Indeed, we observe for LTAB (Cc/k= -14) almost the same value reported for the analogous anionic SDS (Cc/k= -15) and also the Cc/k values of lipophilic AOT (+16) and DDAB (+12) are mutually close.

A dated way to categorize surfactants according to their relative 'philicity' for water or oil phases is the hydrophile/lipophile balance, or HLB [78,79]. Such an approach cannot take into accounts the impact of salinity, oil nature and temperature on the affinity of surfactant for water and oil but is yet widely used.

Figure 8 presents a comparison between the Cc values obtained by experimental HLD-titration and the HLB values calculated by Davies computational approach [80]. A linear correlation shows how Ccs values can describe hydrophilic-lipophilic tendency of cationic surfactant as well as HLB computational values, as found in previous work by Acosta and coworkers for non-ionic surfactants [21].

Focusing on the quats sharing the hexadecyl (often called cetyl) tail, Table 1 evidences as pyridinium or benzyl-dimethyl ammonium heads lead to sensibly more hydrophobic surfactants (Ccs are -3.5 and 0.1, respectively) compared with CTAB and CMIC. Therefore, one expects pyridinium and

benzalkonium based surfactant have a large affinity for biological membranes and this could be related to their reported higher antimicrobial efficiency [81].
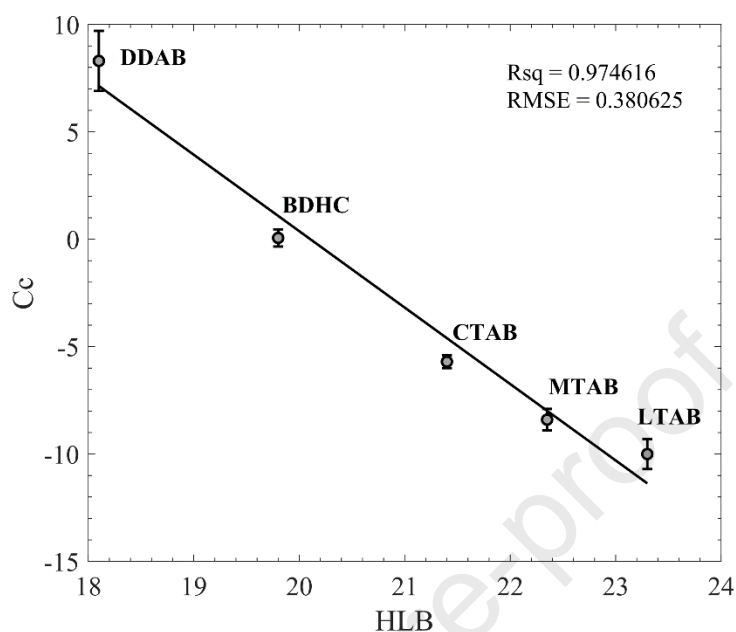

Figure 8 Linear regression obtained by plotting data in Table 1: f(x) = ax + b, a = -0.27 ± 0.08 and b = 20.1 ± 0.6 are the coefficient with 95% confidence bounds.

TABLE 1 Cc values of cationic surfactants, also shown is χ^* the mol fraction of the surfactant in the blend with DDAB that corresponds to the balanced state

	χ^*	Cc	Cc/k	HLB	P°
LTAB	0.240 ± 0.009	-10.0 ± 0.7	-14.0±0.2	23.3	0.335
MTAB	0.263 ± 0.008	-8.4 ± 0.5	-12.0±0.15	22.35	0.325
CTAB	0.314 ± 0.006	-5.7 ± 0.3	-8.14±0.15	21.4	0.329
CMIC	0.288 ± 0.007	-7.0 ± 0.1	-10.0±0.1	–	
BDHC	0.259 ± 0.013	0.1 ± 0.4	+0.14±0.3	19.8	
CPC	0.181 ± 0.007	-3.5 ± 0.5	-5±0.2	–	
DDAB	–	$+8.3 \pm 1.4$	+12±0.2	18.1	
LDAO (PH=1)	0.1951 ± 0.013	-1.0 ± 0.6	-1.4±0.6	–	
EMPIGEN (PH=1)	0.2388 ± 0.012	$+0.7 \pm 0.6$	+1.0±0.8	–	
AMMONYX (PH=1)	0.2701 ± 0.010	$+1.6 \pm 0.2$	+2.3±0.2	–	
Anionic surfactant from reference [21]					
SDS		-2.3 with k=0.16	-15		0.42
AOT		2.55 with k=0.16	+16		0.53

For cationic surfactant Cc data are collected from titration experiments, except for DDAB data that comes from 3d scan; in all cases the constant entering eq. 3 is $k=0.7\pm0.1$. HLB comes from reference [80]; the optimal packing parameter is from reference [82] and refers to surfactant in water without oil.

4.4 Cc values of amine oxide surfactants in acidic conditions

Amine oxide-based surfactants are a particular class of non-ionic surfactants used in many household commercial products. In these formulations, amine oxides are mixed with other non-ionic and anionic surfactants enhancing cleaning performance and foam stability [83]. Moreover, the low toxicity and biodegradability of this class of surfactant make them more appealing to the detergents market [84]. Amine oxides are also known as amphoteric surfactant: at low pH they show a positive net charge and behave as cationic, going to higher pH they change to zwitterionic and behave as non-ionic surfactants [85,86]. This equilibrium has a constant of pKa=-4.90 for LDAO which is a weak base, thus at pH=1 amine oxides can be described through the HLD framework here developed for cationic surfactants. The pH of the initial DDAB emulsion is adjusted using HCl 1M as well as the titrant solution. As titrant solution three different amine oxides are studied: LDAO pure surfactant purchased from Sigma; EMPIGEN, a mixture of C12-14 amine oxides; AMMONYX, a mixture of C12-C18 amine oxides. Both EMPIGEN and AMMONYX are polydisperse stock solutions because their aliphatic portion comes from feedstocks. Titration are performed to compute a Cc value for these surfactants at pH=1, results are shown in Table 1. As expected, going from LDAO to AMMONYX the lipophilic part of the molecule and the Cc value increase. These results are potentially valuable for acidic household formulations.

Conclusion

For the first time cationic surfactants have been introduced into HLD framework avoiding the complication of the use of cosurfactants. To this purpose we have selected a blend of single (CTAB) and double (DDAB) tail cationic surfactants to achieve the Winsor III phase equilibrium through salinity scans at different DDAB/CTAB ratio. Using different *n*-alkanes as oil the investigation has allowed the evaluation of the surfactant characteristic parameter of the DDAB (Cc=8.3) and CTAB (Cc=-5.7) and the multiplicative constant (*k=0.7*) for the contribution of EACN in the case of cationic surfactants.

For the classification of the other single chain cationic surfactants a novel "HLD-titration" procedure was proposed. The procedure is very simple, does not require special instrumentation and circumvent the long equilibrium times required for conventional compositional scans. This opens the way to the extension of HLD-based rational formulation to systems composed by cationic surfactants.

The obtained Cc values scale linearly with the HLB as observed for nonionic surfactants [21].

The characteristic parameters (Cc) of cationic surfactants determined in the present work are about 4 times larger than the ones reported for anionic surfactants with similar tails and the same holds for the constant *k* [9]. This is because, in the case of cationic surfactant, the salinity influences weakly the stability of the balanced Winsor III equilibrium and this is reflected in larger contributions of the +Cc and -*k*·EACN opposite terms in the HLD equation.

To compare different classes of surfactants, it has been proposed to use the ratio Cc/*k* as meaningful descriptor of the surfactant amphiphilicity [77]. Indeed, we have observed a good agreement between cationic and anionic surfactant sharing the same tail in terms of Cc/*k*.

The mismatch between the *k*-values observed for surfactants bearing different head-groups is one of the limits of the simple HLD approach for which only the balanced state (HLD= 0 equivalent to p°=1) has a clear physicochemical definition. Under such a condition, eqs. 3 or 4 can be divided by any coefficient and still be equal to zero at the balanced formulation. This not a problem as long the HLD is used as guideline for formulation with a single class of surfactants. Indeed, it easy to see how at moderate salinity (say 4.5% g/mL) eq. 3 foretells in the case of DDAB an HLD>0 (i.e. reverse microemulsion) for all the alkanes shorter than dodecane and HLD~0 (balanced state) for tetradecane in qualitative agreement with the literature [25,26,87–92].

On the other hand, according to eq. 3, to have reverse microemulsion with water, CTAB and alkanes would take (because of the negative Cc value) impractical salt concentration at which the surfactant precipitates (e.g. > 20% NaCl for hexane as oil). Indeed, to attain reverse micelles with CTAB requires the addition of cosurfactants to the alkanes [23] or the use as oil of aromatic (EACN ~0) [22] or chlorinated (EACN<0) solvents [93].

A more quantitative comparison with literature data is difficult because most of the published experiments have been performed in the absence of salt and at large surfactant concentration so that the definition of salinity (S) entering eq. 3 is ambiguous. In the future, the comparison between the prediction of the HLD parameters obtained in the present work and the microstructure of ad-hoc systems (Winsor equilibria with background electrolyte and low surfactant concentration) will be important and profitable for two reasons.

The first is that the characterization of the droplets existing far from the balanced state gives a well-defined state where it is possible test the relationship between HLD and film curvature through the improved model called HLD-NAC [8–10]. This should reduce considerably any ambiguity in the numerical vale of the HLD parameters.

The second reason is that such an investigation will give insight on the connection between the effective packing parameter (a molecular quantity) and the HLD parameters.

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Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: