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Exploring the Charging Mechanisms in Non-aqueous Multiphase Surfactant Solutions, Emulsions and Colloidal Systems via Conductivity Behaviors Predicted with Eyring's Rate Process Theory

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Abstract

The common charging agents and charging mechanisms in non-aqueous multiphase systems available in literature are analyzed, and the conductivity equations derived on the basis of the charging mechanisms with the Eyring's rate process theory are compared with experimental observations. The popular charging mechanisms in non-aqueous systems, such as the ion preferential absorption, ion pair dissociation, and micelle disproportionation/fluctuation models are found to be incapable of explaining all experimental evidences. Particularly, the ion pair dissociation and micelle disproportionation/fluctuation models apparently suffer a major drawback: How charges are separated and most importantly how charging entities are stabilized in non-aqueous systems, are not adequately addressed; In low dielectric constant non-aqueous media separated ions tend to bind together rather than stay separately. A new charging mechanism incorporating an electric field internally available or externally applied into the charging process is proposed to explain charge separations and stabilizations. The conductivity equations derived on the basis of this new mechanism predict that conductivity should linearly increase with both the electric field and the concentrations of inverse micelles at very low concentration regions, which is consistent with experimental evidences.

Keywords: Charging mechanisms; Non-aqueous; Emulsions; Colloidal systems; Inverse Micelles; Conductivity.

I. Introduction

Particles, droplets, and micelles usually carry charges in both aqueous and non-aqueous multiphase surfactant solutions, emulsions, and colloidal systems. The charge properties of those small entities play a critical role in controlling aggregation and agglomeration properties in both dry process like film coatings and wet process like electrophoretical motions. These properties are directly related to physical stability of whole systems and are important in handling and manufacturing powder related products in many industrial areas like inks, paints, foods, pharmaceutics etc.. Understanding charging mechanisms will definitely help us gain insights into why and how charges are generated and attained, and thus desirable charge properties can be smartly controlled.

Dry particulates usually carry charges that are mainly resulted from the triboelectric effect [1,2,3] , which could be explained with the following four mechanisms. 1) Powder particles may be polarized by a nearby weak electric field created by the local charging species; 2) Ions could transfer from one particle surface to another due to inter-particle collision; 3) Ions from adsorbed water residing on the surfaces of non-ionic insulators could be shared by adjacent particles; 4) Electrons could transfer among conductors, semiconductors, and insulators, such as from metallic instrument/container surfaces to particle surfaces.

Once small particles are dispersed into water, particles will continue to carry charges, however, the charging mechanisms are different from that at dry states. In aqueous systems, particle surface charges are generated due to [4,5,6]: 1) different preferences for ions in solid and liquid two phases; 2) direct ionization of surface groups; 3) specific ion adsorptions; 4) defects of specific crystal structures that break down the charge neutralization status.

If dry particles are dispersed into non-aqueous liquids like oil and organic solvents, particle charging mechanisms become more complicated, as the ionization and dissolution in non-aqueous systems typically are very low. The primary reason, as pointed out in literature [7], is that the Coulombic attractive force is almost 30 times stronger in organic media than that in aqueous systems, since the dielectric constant of organic media is about 2.5, and that of water is 80; Ions in non-aqueous systems tend to coalesce together rather than stay apart. For particles to be charged, surfactants or dispersants typically are required for inducing charges or stabilizing charged entities in non-aqueous media; Those surfactants or dispersants are called charging agents.

Unlike in aqueous systems, charging agents in non-aqueous systems would create inverse micelle structures with hydrophobic groups extending into oil phases and hydrophilic groups forming center cores; Inorganic ions or other hydrophilic species thus stay within those center core places. For this reason, a trace amount of residue water or other water soluble ionic impurities were believed to be critical to charge inverse micelles in non-aqueous systems [8,9]. Those inverse micelle structures are soft and easily deformable, but can travel under an external electric field and show measurable Zeta-potentials, behaving similarly as solid particles. For this regard, the inverse micelles will be considered as soft "particles" in this article. If solid particles are present in non-aqueous systems, inverse micelles can easily absorb on particle surfaces, travelling together under an external electrical field [10,11] and making particles charged in non-aqueous systems [12,13,14]. For emulsions of both oil-in-water [15,16]and water-in-oil [17]systems, droplets are assumed to be charged very similarly as particles in colloidal systems via micelles or inverse micelles. In this hypothetical physical picture, charged inverse micelles seem critical to the charging mechanisms for both water-in-oil emulsions and colloidal systems, however, how inverse micelles are charged remains a question.

There are many studies and discussions in literature addressing how inverse micelles are charged in non-aqueous systems [7,10,13,18,19,20,21,22,23], indeed. Typical experimental methods in revealing charging mechanisms are conductivity and transient current measurements against physical sizes, valencies, and concentrations of charging agents. One of experimental observations in conductivity studies across many non-aqueous systems is that conductivity linearly increases with the concentrations of charging agents at low concentration regions [21,22,23]. Another interesting phenomenon is that inverse micelles under an electric field behave differently than those intrinsically carrying charges in the absence of an electric field [18]. This may indicate that something with inverse micelles under the reaction of an electric field has changed, and the electric field may participate the charging process of inverse micelles.

For unveiling charging mechanisms across all types of non-aqueous systems including both emulsions and colloidal suspensions with the presence of ionic and non-ionic surfactants, conductivity properties are thus focused in this article for easy evaluation with the experimental evidences. Theoretical derivations of conductivity equations on the basis of charging mechanisms with the Eyring's rate process theory are carried out in a generic manner rather than limited to certain type of non-aqueous systems. Many experimental results indicate that conductivity behaviors of non-aqueous systems could be dramatically different [22]. For example, the conductivity of a non-aqueous system containing ionic surfactant shows a very good linear relationship with the concentrations of the surfactant [21]; while the conductivity of another non-aqueous system with non-ionic surfactant doesn't show linear relationship with the concentrations and it levels off at high concentrations of the surfactant [24]. A successful charging mechanism in theory should be able to explain rich conductivity phenomena observed so far.

The article is arranged as below. Widely used charging agents and dispersants in non-aqueous systems is briefly reviewed, and the charging mechanisms available in literature are analyzed afterwards; The corresponded conductivity equations derived on the basis of those mechanisms are examined against the experimental observations, followed by a new charging mechanism proposed to explain currently observed experimental facts. The focuses are placed on theoretical derivations of conductivity equations with the Eyring's rate process theory, which is, however, not the purpose; The goal is by no mean to develop an universal conductivity equation for non-aqueous systems nor the conductivity mechanisms in general; Instead the conductivity is merely employed as a tool to distinguish which charging mechanisms works.

II. Charging agents and dispersants

The charging agents or dispersants used in non-aqueous systems are surfactants for making particles charged or well dispersed, forming stable emulsions and colloidal suspensions. The charging agents usually form inverse micelle structures, trapping all polar imputrities or residues from non-aqueous oil phase into the center cores. Commonly used charging agents include calcium diisopropylsalicylate [25], tetraisoamylammonium picrate [25], polyisobutylene succinimide, OLOA 1200 [26,27,28], di-(2-ethylhexyl) sodium sulfosuccinate (AOT) [29,30,31], octyl pheol ethoxylate (Triton X-100) [32], phosphatidylcholine (lecithin) [33], sorbitan oleate (Span 80) [34] etc.. The molecular structures of these charging agents are shown in Figure 1.

As one may notice, all charging agents may contain both a positive and negative groups, except Triton X-100 and Span 80. Those two surfactants are more commonly used as dispersants, but also can function as charging agents [24,34], even though they are well considered as non-ionic surfactants. The spatial separation of positive and negative groups in those surfactants creates amphipolar structures that are believed to make particles charged. For examples, the negative groups may be hydrophilic and thus can comfortably stay inside the centers of inverse micelles; while the positive groups may be hydrophobic and can only stay outside of the inverse micelle structures. The separated charges may further polarize the neighboring surfactant molecules, driving the charged entities even further away from each other. If solid particles or liquid droplets are available in the systems, charged inverse micelles may preferentially absorb on the surfaces of those entities, making them charged. For non-ionic surfactants, there are no amphipolar centers and thus there should be no such a kind of charge separations happening in the system. However, they still function as charging agents as indicated in literature [24,34], indicating that charge separations happen in non-ionic surfactant systems, indeed. Apparently, not only pre-existing charges from charging agents but also later induced or generated charges should be responsible for charging mechanisms in non-aqueous systems. This observation should be a key point for validating the charging mechanisms.

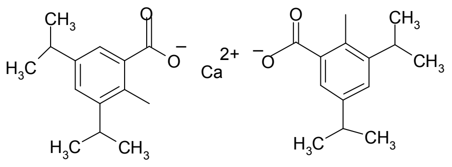
III. Charging mechanisms in non-aqueous systems.

In this section, theories or models presented in literature to account for charging mechanisms in non-aqueous systems will be briefly reviewed, with the emphasis on the theoretical ideas rather than theoretical details. Readers are encouraged to go to several recent review articles for more detailed information [10,22,23,35].

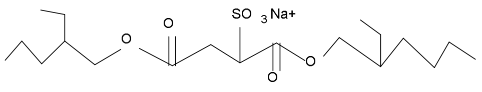
As mentioned previously, a common phenomenon observed for non-aqueous systems is that the conductivity linearly increases with the concentrations of the charging agent [21,36,37]. A very good linear relationship was observed for the conductivity of AOT/dodecane solution vs. AOT concentration ranging from 0.8 to 200 *mM* [21]. Similar linear relationship between the conductivity and the charging agent concentrations was observed in OLOA 1200/dodecane [36], AOT/benzene [38], and lecithin/hydrocarbon (Isopar H) system [37]. However, at sufficiently high concentrations, conductivity was found to deviate from this linear relationship [39] . This common phenomenon frequently is employed to verify if the proposed charging mechanisms work.

In 1920s, the “ion pairs” or “ion association” concept [40,41] was proposed to explain the conductivity properties of weak electrolyte systems like non-aqueous emulsions and colloidal suspensions. The main idea is that in non-aqueous systems ions tend to associate together and form pair structures due to much stronger electrostatic attractive forces in comparison with aqueous systems, almost 30 times stronger than that in aqueous systems due to much smaller dielectric constant of organic solvents than that of water, as mentioned earlier. The equilibrium between ion dissociation and association determines the conductivity, resulting in a linear relationship between the conductivity and the concentrations of the charging agent. However, at sufficient high concentrations, the conductivity will deviate from linear relationship [39], and "ion triplets" concept was even proposed. Since ion pairs or more complex structures are formed in non-aqueous systems, ion dissociations are thus widely regarded as a means for generating free ions carrying charges, which may be expressed as $AB \leftrightarrow A^{+} + B^{-}$. However, as indicated in literature [22], ion pairs may dissociate at certain conditions, but the question is where the original ion pairs come from; More importantly, there is no reason for dissociated ions to stay separated in non-aqueous media.

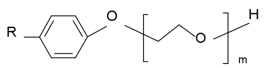
For overcoming the shortcomings of the ion pair dissociation model, the disproportionation model was proposed in literature [22,42,43], which may be expressed as $2A \leftrightarrow A^{+} + A^{-}$. In such a case, no ion pairs are initially needed, and surfactant molecules could attain charges via inverse micelle structures due to charge center separations or charge transfer as discussed earlier.



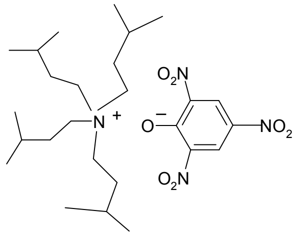
Calcium diisopropylsalilyte



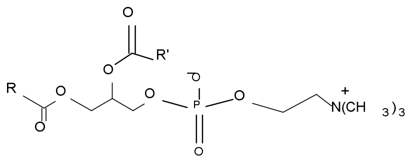
di-(2-ethylhexyl)sodium sulfosucinate, AOT



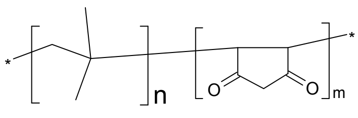
R=Octyl, m=9.5 (average)
Octylphenol ethoxylate, Triton X-100



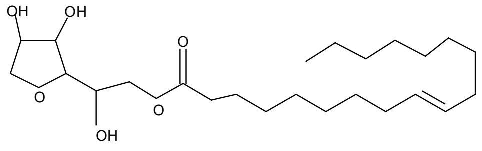
tetraisoamylammonium picrate



Phosphatidylcholine, Lecithin



Polyisobutylene succinimide, OLOA 1200



Span 80

Figure 1 Charging agents or dispersants commonly used in non-aqueous systems.

Nonetheless, in my discretion, the disproportionation model suffers a similar drawback as the dissociation model: the separated two oppositely charged centers tend to pair instead of separate in non-aqueous systems for the same reason, almost 30 times stronger electrostatic attractive forces in comparison with that in aqueous systems. For microemulsions, a so called fluctuation model [44] is proposed to account for the conductivity data, with the argument that droplets may exchange the electrical charges during droplets collisions, as the aqueous droplets contain dissolved ions inside. Essentially, the fluctuation model is similar to the disproportionation model; the only difference is that the former is for water droplets and the latter is for inverse micelles. Again, the same question may come up: After charge separations, how free ions stably remain separated in non-aqueous media? Such a question poses a big challenge to all charging mechanisms proposed in literature.

IV. Theory

1. Conductivity equations derived with Eyring's rate process theory

In next few sections, conductivity equations are first derived on a generic base and then extended to non-aqueous systems; The obtained conductivity equations are further modified on the basis of charging mechanisms available in literature for evaluating if the charging mechanisms work. A new model or mechanism is proposed and the corresponded conductivity equation is examined against the charging phenomena in non-aqueous systems, too.

The conductivity of a pure organic liquid typically is about 10^{-13} S/m. Once a charging agent is added in, the conductivity of whole system can easily reach 10^{-7} S/m, an increase of several orders of magnitudes. Such a dramatic increase may suggest that the substantial amount of ions is created in systems, though again how the charges are generated and where the charges come from remains a question.

The conductivity of materials in general and liquids containing ions in specific is well understood [45,46,47,48,49]. Usually the thermal energy is not strong enough to dissociate the molecules. Suppose that the ionic conductivity may follow the Eyring's rate process theory [48]. Due to the collision from neighboring molecules, the molecules may be activated and only the activated molecules may dissociate and contribute to the conductivity; Therefore the relative number of the molecules staying at the ground state and the activation state determines the conductivity. Assume that the potential at the ground state is U_1, and that at the activation state is U_2, and the number of molecules per unit volume is n_o, then:

$$n_1 = A n_0 e^{-\frac{U_1}{k_B T}} V_1 \qquad (1)$$

$$n_2 = A n_0 e^{-\frac{U_2}{k_B T}} V_2 \qquad (2)$$

where V_1 and V_2 are the volumes occupied by each state of molecules, and A is a constant.
Assuming $V_1 \approx V_2$, the dissociation constant α may be expressed as:

$$\alpha = \frac{n_2}{n_0} = \frac{n_2}{n_1 + n_2} = \frac{e^{-\frac{U_2 - U_1}{k_B T}}}{1 + e^{-\frac{U_2 - U_1}{k_B T}}} \qquad (3)$$

$U_2 - U_1 = U_0$, which is the dissociation energy.

$$\alpha = \frac{e^{-\frac{U_0}{k_B T}}}{1 + e^{-\frac{U_0}{k_B T}}} = \frac{1}{1 + e^{\frac{U_0}{k_B T}}} \qquad (4)$$

For low dielectric constant liquids like non-aqueous media, U_0 is very large, $U_0 >> k_B T$, making $\alpha \approx 0$. Eq. (1) to (4) clearly show that the thermal motion is unable to make contribution to the conductivity. Without an external electric field, the molecule motions are random and there should be no or extremely low conductivity. Statistically, the number of molecules in one of three perpendicular axes in a space is $\frac{n_0}{3}$, and the number of molecules in the positive axis is $\frac{1}{2} \bullet \frac{n_0}{3}$. So in a unit time period the number of molecules overcoming the energy barrier, U_0, is:

$$n = \frac{n_0}{6} \nu e^{-\frac{U_0}{k_B T}} \qquad (5)$$

where ν is the molecule vibration frequency at certain positions, and equals to the hopping time of a molecule trying to overcome the energy barrier, U_0, per unit time. Once an electric field E is applied, the activation energy in the direction of the applied electric field will be lowered by ΔU and that in the opposite direction will be increased by the same amount. The excess amount of ions moving along the direction of the electric field thus is expressed as:

$$\Delta n = \frac{n_0}{6} \nu \left(e^{-\frac{U_0 - \Delta U}{k_B T}} - e^{-\frac{U_0 + \Delta U}{k_B T}} \right) \qquad (6)$$

where

$$\Delta U = \frac{qE\delta}{2} \qquad (7)$$

where q is the charge of ions, δ is the ion free walking distance in the scale of 10^{-9} m. Usually $\Delta U << k_B T$, which can be confirmed by a simple calculation as follows. Suppose $\Delta U = k_B T$, and at room temperature $300\ K$,

$$E = \frac{2k_B T}{q\delta} = \frac{2\times 1.38\times 10^{-23}\times 300}{1.6\times 10^{-19}\times 10^{-9}} = 5.18\times 10^{7} \quad V/m \qquad (8)$$

The applied electric field usually is far less than 5.18 $\times 10^7$ *V/m*, making the assumption, $\Delta U << k_B T$, always valid. Eq. (6) can be approximated by using the equation $e^x \approx 1 + x$ ($|x| < 1$):

$$\Delta n = \frac{n_0}{6} \nu e^{-\frac{U_0}{k_B T}} \frac{2\Delta U}{k_B T} = \frac{n_0 q E \delta \nu}{6 k_B T} e^{-\frac{U_0}{k_B T}} \qquad (9)$$

The velocity of the excess amount of ions moving along the electric field is the relative number of the excess amount of ions multiplying the moving distance per second

$$v_E = \frac{\Delta n}{n_0}\delta \qquad (10)$$

So the mobility of ions is:

$$\mu_E = \frac{v_E}{E} = \frac{q\delta^2 \nu}{6k_B T} e^{-\frac{U_0}{k_B T}} \qquad (11)$$

On the basis of Eq. (3), if one activated molecule may generate two ions, then the number of dissociated ions per unit volume may equal to $2\alpha n_0$. According to the generic conductivity equation **50**, the conductivity contributed from ion motions in non-aqueous systems thus can be expressed as:

$$\begin{aligned}\sigma &= n_i q \mu_E \\ &= 2\alpha n_0 q \mu_E = \frac{\alpha n_0 q^2 \delta^2 \nu}{3k_B T} e^{-\frac{U_0}{k_B T}} \qquad (12)\end{aligned}$$

where n_i represents the number of ions per unit volume. Eq. (12) indicates that the conductivity is dependent on the number of molecules that may dissociate into ions, the charge quantity of ions, the ion free walking distance, the vibration frequency of ions, temperature, and the energy barrier for ion to move away from neighboring ions. The important feature of Eq. (12) is that the conductivity may linearly increase with the number of molecules in non-aqueous systems, i.e., the concentrations of the charging agent, which has been evidenced in many non-aqueous systems. However, this equation doesn't predict that the conductivity may deviate from the linear relationship at high concentration regions. We may need to extend this equation to non-aqueous systems containing inverse micelles.

2. Conductivity equations extended to non-aqueous systems containing inverse micelles

Note that Eq. (12) is derived on a generic basis without being limited to any specific systems. When Eq. (12) is applied to non-aqueous systems containing large inverse micelle structures formed by the molecules of the charging agents listed in Fig. 1, one may need to make further assumptions, as the sizes of inverse micelles should be much larger than regular ions and most importantly, they may change with the concentrations of charge agents [34]. In addition, many experimental evidences suggest that the charge quantity of inverse micelles is strongly dependent on the concentrations of charging agents 51,52,53. Those mean that both the parameters q and δ cannot be assumed as an invariable in inverse micelle systems and their relationships with the concentrations of charging agents must be worked out.

Since the Bjerrum length in water at room temperature is about 0.7 *nm* and would be 28.3 *nm* in non-aqueous systems [19], one cannot continue to assume that such large inverse micelles can still travel the distance comparable to the diameter of inverse micelle structures. However, one may always assume inverse micelles can travel the distance between two micelle structures freely available to each inverse micelle. This distance is called the inter-particle spacing (IPS), and Hao provides an approach to calculate [6,54,55]:

$$IPS = (\sqrt[3]{\phi_m / \phi} - 1) d_m \qquad (13)$$

where ϕ_m is the maximum packing fraction that the inverse micelles can achieve, ϕ is the inverse micelle volume fraction, and d_m is the diameter of the inverse micelles. Since an inverse micelle may travel both left and right sides, the free walk distance δ may be expressed as:

$$\delta = 2\,IPS = 2(\sqrt[3]{\phi_m / \phi} - 1) d_m \qquad (14)$$

Note the parameter n_0 in Eq. (12) is the number of molecules of the charging agent per unit volume. If one inverse micelle structure contains n_m molecules, $n_0 = \frac{6 n_m \phi}{\pi d_m^3}$, based on the definition. Therefore, Eq. (12) may be rewritten as:

$$\sigma = \frac{8\alpha q^2 n_m \phi (\sqrt[3]{\phi_m / \phi} - 1)^2 \nu}{\pi k_B T d_m} e^{-\frac{U_0}{k_B T}} \qquad (15)$$

One may certainly anticipate that the diameter of inverse micelles changes with the volume fraction and a relationship must be worked out. According to Hao, the size of inverse micelle could be derived with Stokes-Einstein equation and Hao's interparticle spacing equation, and it may be expressed as [6]:

$$d_m = \left[\frac{k_B T \tau}{2\pi\eta (\sqrt[3]{\phi_m / \phi} - 1)^2} \right]^{1/3} \qquad (16)$$

where τ is the relaxation time related to the parameter ν, and η is the viscosity of medium. Substituting Eq. (16) into Eq. (15) leads to

$$\sigma = \frac{2^{10/3}\alpha q^2 n_m \eta^{1/3}\phi(\sqrt[3]{\phi_m/\phi}-1)^{8/3}\nu}{\pi^{2/3}(k_B T)^{4/3}\tau^{1/3}} e^{-\frac{U_0}{k_B T}} \qquad (17)$$

Typically, for ionic systems the parameter ν has such a relationship with the relaxation time τ[45,56,57]:

$$\tau = \frac{1}{2\nu} e^{\frac{U_0}{k_B T}} \qquad (18)$$

a simple Arrhenius relaxation process. Replacing τ in Eq. (17) with Eq. (18) leads to:

$$\sigma = \frac{2^{11/3}\alpha q^2 n_m \eta^{1/3}\phi(\sqrt[3]{\phi_m/\phi}-1)^{8/3}\nu^{4/3}}{\pi^{2/3}(k_B T)^{4/3}} e^{-\frac{4U_0}{3k_B T}} \qquad (19)$$

Now, we may need to determine the parameter q in Eq. (19), as it is not a constant in non-aqueous systems. One may continue to assume the electrical double layer theory is still valid in non-aqueous inverse micelle systems, the charge quantity on inverse micelles may be expressed as[4,6,58]:

$$q = 4\pi\varepsilon_m\varepsilon_0 r(1+\kappa r)\zeta \qquad (20)$$

where ε_m and ε_0 are the dielectric constant of the liquid medium and vacuum respectively, r is the radius of the inverse micelle, $r = d_m/2$, κ^{-1} is the Debye length, and ζ is the Zeta potential. In non-aqueous systems, the electrical double layer is usually very thick, $\kappa r < 0.1$, Hückel equation, $\zeta = 3\eta\mu_E/(2\varepsilon_m\varepsilon_0)$, can be used and Eq. (20) is re-written as :

$$q \approx 6\pi\eta\mu_E r = 3\pi\eta\mu_E d_m \qquad (21)$$

under an assumption $1 + \kappa r \approx 1$. Again, η is the viscosity of the medium, μ_E is the mobility of inverse micelle that can be measured experimentally using the Zeta potential instruments. Note that μ_E expressed in Eq. (11) cannot be used in Eq. (21), as Eq. (11) is obtained under an assumption that the charge quantity is constant and μ_E is a variable, while in Eq. (21) the charge quantity is a variable and μ_E is a measurable constant. They are just obtained under different theoretical frameworks for different purposes. Nonetheless, d_m expressed in Eq. (16) can be still used in Eq. (21), as Eq. (16) is purposely derived to estimate the sizes of inverse micelles. If the term $3\pi\eta\mu_E$ in Eq. (21) is considered as a constant, then the charge quantity is linearly proportional to the size of inverse micelle, which is consistent with both the experimental[58] and theoretical[59,60] results obtained, however, in colloidal suspensions. One may thus assume that, as suggested in the literature[58], Eq. (21) may be expressed as:

$$q = Ad_m \qquad (22)$$

where A is a material related constant. Substituting Eq. (22) into Eq. (19) and re-arranging leads to the expression of conductivity of inverse micelle systems:

$$
\begin{aligned}
\sigma &= \frac{2^{7/3}\alpha A^2 n_m \phi(\sqrt[3]{\phi_m/\phi}-1)^{4/3}\nu^{2/3}}{\pi^{4/3}\eta^{1/3}(k_BT)^{2/3}} e^{-\frac{2U_0}{3k_BT}} \\
&= \frac{2^{7/3}\alpha A^2 n_m \phi^{5/9}(\phi_m^{1/3}-\phi^{1/3})^{4/3}\nu^{2/3}}{\pi^{4/3}\eta^{1/3}(k_BT)^{2/3}} e^{-\frac{2U_0}{3k_BT}}
\end{aligned}
\qquad (23)
$$

Eq. (23) indicates that the conductivity of non-aqueous systems containing inverse micelles may be dependent on the concentration of the inverse micelle and even the viscosity of the medium, though it has a relatively complicated relationship with the volume fraction of inverse micelles. It would be interesting to evaluate how the conductivity is going to change with the volume fraction. Figure 2 shows the normalized conductivity $\frac{\sigma\pi^{4/3}(k_BT)^{2/3}}{2^{7/3}\alpha A^2 n_m \eta^{1/3}\nu^{2/3}} e^{\frac{2U_0}{3k_BT}}$ against ϕ for illustrative purpose. Since inverse micelle structures are soft and can be deformed easily, two dense packing structures are assumed to happen theoretically: $\phi_m = 0.72$ and $\phi_m = 0.84$, which corresponds to non-lattice tetrahedra and Icosahedra [61,62], respectively. At extremely low volume fractions, the term $(\phi_m^{1/3}-\phi^{1/3})^{4/3}$ in Eq. (23) may be approximated as a constant, $(\phi_m^{1/3}-\phi^{1/3})^{4/3} \approx \phi_m^{4/9}$, and the conductivity may change with $\phi^{5/9}$. Clearly, the conductivity doesn't have a linear relationship with the volume fraction of the inverse micelles at low concentration regions. Only in the relatively high concentration region, starting at the volume fraction about 2×10^{-3} and until reaching a the concentration about 5×10^{-2}, there seems to be a linear relationship between the conductivity and the volume fraction. A further volume fraction increase makes the conductivity dramatically increase by obeying a power law and then reach a peak, a very unusual phenomenon. As indicated earlier, the linear dependence of conductivity on the concentrations of the surfactants at low concentration regions has been reported in many articles. However, the drop off at high concentration regions is rarely reported, besides one system with Span 80 [22], showing the surface charge converted from the conductivity drops at relatively higher concentrations, which is qualitatively consistent with Eq. (23). Since the inverse micelles are formed by the surfactant molecules, the high surfactant concentrations could create more charged inverse micelles, resulting in linear increase of conductivity at the beginning; Once more charged micelles are created, those charged micelles will impose electric fields to neighboring inverse micelles, making them charged, too. This chain-reaction like charging process leads to an exponential increase of conductivity at relatively higher concentrations due to the large number of charged inversed micelles. As shown in Eq. (13) and (14), higher concentrations of charging agents will eventually lead to a smaller free walk distance, thus lower conductivity.

The parameter ν is assumed to be independent of volume fraction in deriving Eq. (23), which may not be true. The related parameter τ is actually dependent on the volume fraction, according to Wagner--Maxwell model for diluted suspensions for $\emptyset < 0.1$ [6,63]:

$$\tau = \frac{2\varepsilon_m+\varepsilon_p+\emptyset(\varepsilon_m-\varepsilon_p)}{2\sigma_m+\sigma_p+\emptyset(\sigma_m-\sigma_p)}\varepsilon_0 \qquad (24)$$

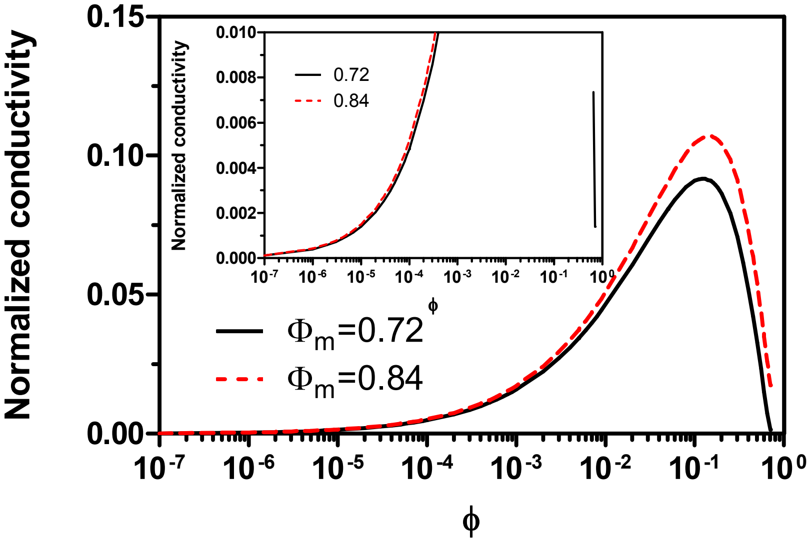


Figure 2, The normalized conductivity $\frac{\sigma\pi^{4/3}(k_BT)^{2/3}}{2^{7/3}\alpha A^2 n_m \eta^{1/3}\nu^{2/3}}e^{\frac{2U_0}{3k_BT}}$ *against* ϕ *based on Eq. (23) under the assumptions of* $\phi_m = 0.72$ *and* $\phi_m = 0.84$. *The inset is the same data but plotted in a very small normalized conductivity range for clearly demonstrating the linear relationship.*

where $\varepsilon_0, \varepsilon_m, \varepsilon_p$ are the dielectric constant of vacuum, the dispersing medium, and the dispersed phase, respectively, and σ_m, σ_p are the conductivity of the dispersing medium and the dispersed phase, respectively. From Eq. (18), the parameter v may be written as:

$$v = \frac{1}{2\tau}e^{\frac{U_0}{k_BT}} \qquad (25)$$

Substituting Eq. (25) into Eq. (23) and replacing τ with Eq. (24) leads to:

$$\sigma = \frac{2^{5/3}\alpha A^2 n_m \phi(\sqrt[3]{\phi_m/\phi}-1)^{4/3}}{\pi^{4/3}\eta^{1/3}(k_BT)^{4/3}\tau^{2/3}} = \frac{2^{5/3}\alpha A^2 n_m \phi(\sqrt[3]{\phi_m/\phi}-1)^{4/3}\left[2\sigma_m+\sigma_p+\phi(\sigma_m-\sigma_p)\right]^{2/3}}{\pi^{4/3}\eta^{1/3}(k_BT)^{2/3}\varepsilon_0^{2/3}\left[2\varepsilon_m+\varepsilon_p+\phi(\varepsilon_m-\varepsilon_p)\right]^{2/3}} \qquad (26)$$

Eq. (26) presents a complicated relationship for conductivity: The conductivity of non-aqueous multiphase systems is a function of many parameters, such as the conductivities and dielectric constants of both the dispersing medium and the dispersed phase, the viscosity of the medium, the volume fraction of the dispersed phase, and temperature. Intuitively, high conductivities of both the dispersing and dispersed phases should lead to high conductivities of the whole system, which is demonstrated in Eq. (26). Eq. (26) also tells us that the conductivity is independent of the applied electric field strength, which is inconsistent with experimental observation presented in literature 53,64,65 , where the conductivity was found to linearly increase with the applied electric field strength up to 10^6 V/m, a relatively low electric field strength in non-aqueous systems.

3. Evaluating the current charging mechanisms

As briefly stated earlier, there basically are three charging mechanisms proposed for explaining how inverse micelles attain charges in non-aqueous media [26,66,67,68,69,70]. Those mechanisms can be roughly classified as: a) Preferential ion adsorption mechanism. The ions from either impurities or a trace amount of water can be trapped by inverse micelles, making inverse micelles charged, In this mechanism, the charge is uncontrollable as the impurities are hard to control in practice; b) Ion pair model or dissociation of weak electrolyte. The inverse micelles behave like a weak electrolyte, dissociating into positively charged or negatively charged parts; c) Disproportionate mechanism due to colloision. The inverse micelles become charged by exchange of charges between two uncharged micelles due to collision. However, according to the rate process theory, the probability of charge exchange between micelles is extremely low without an additional driving force. Those three mechanisms are schematically depicted in Figure 3, and the corresponded conductivity equations are derived below for evaluation purpose.

According to the first ion preferential adsorption mechanism, the concentrations of charged inverse micelles are dependent on the concentrations of impurities and independent of the concentrations of charging agent; Apparently, this mechanism is contradictory to the experimental fact that the conductivity linearly increases with the concentrations of the charging agent. The concentration of impurities is a random parameter and the impurities may come from various sources like the container surfaces, the contamination from operators and instruments, and the environment conditions, etc.. It is hard to imagine that the conductivity may have any predictable patterns with the concentrations of impurities. This mechanism is therefore not discussed further.

According to the second ion pair dissociation mechanism, suppose that the concentration of the original inverse micelles is M_{AB}, and the dissociation equilibrium may be expressed as:

$$M_{AB} \Leftrightarrow M_A^+ + M_B^- \tag{27}$$

The equilibrium constant of such a process can be expressed:

$$K_{eq} = \frac{\left[M_A^+\right]\left[M_B^-\right]}{\left[M_{AB}\right]} \tag{28}$$

The charged micelle concentrations are:

$$n^+ = n^- = K_{eq}^{1/2}(n_0 / n_m)^{1/2} \tag{29}$$

Again, n_0 is the number of molecules of the charging agent per unit volume and n_m is the number of molecules in a single inverse micelle. Substituting Eq. (29) into Eq. (12) and considering both positive and negative inverse micelles may contribute to the conductivity leads to:

$$\sigma = \frac{K_{eq}^{1/2} n_0^{1/2} q^2 \delta^2 \nu}{3k_B T n_m^{1/2}} e^{-\frac{U_0}{k_B T}} \tag{30}$$

Eq. (30) can be rewritten as below after replacing δ with Eq. (14) and replacing n_0 with $n_0 = \frac{6n_m \phi}{\pi d_m^3}$:

$$\sigma = \frac{4q^2 d_m^{1/2} K_{eq}^{1/2} (6\phi)^{1/2} (\sqrt[3]{\phi_m / \phi} - 1)^2 \nu}{3\pi^{1/2} k_B T} e^{-\frac{U_0}{k_B T}} \tag{31}$$

Eq. (31) can be further rewritten below by following the previous methodology, i.e., replacing q with Eq. (22), d_m with Eq. (16), and ν with Eq. (25):

$$\begin{aligned}\sigma &= \frac{2^{2/3} A^2 K_{eq}^{1/2} \phi^{1/2} (\sqrt[3]{\phi_m / \phi} - 1)^{1/3} \tau^{-1/6}}{3^{1/2} \pi^{4/3} (k_B T)^{1/6} \eta^{5/6}} \\ &= \frac{2^{2/3} A^2 K_{eq}^{1/2} \phi^{7/18} (\phi_m^{1/3} - \phi^{1/3})^{1/3} \tau^{-1/6}}{3^{1/2} \pi^{4/3} (k_B T)^{1/6} \eta^{5/6}}\end{aligned} \tag{32}$$

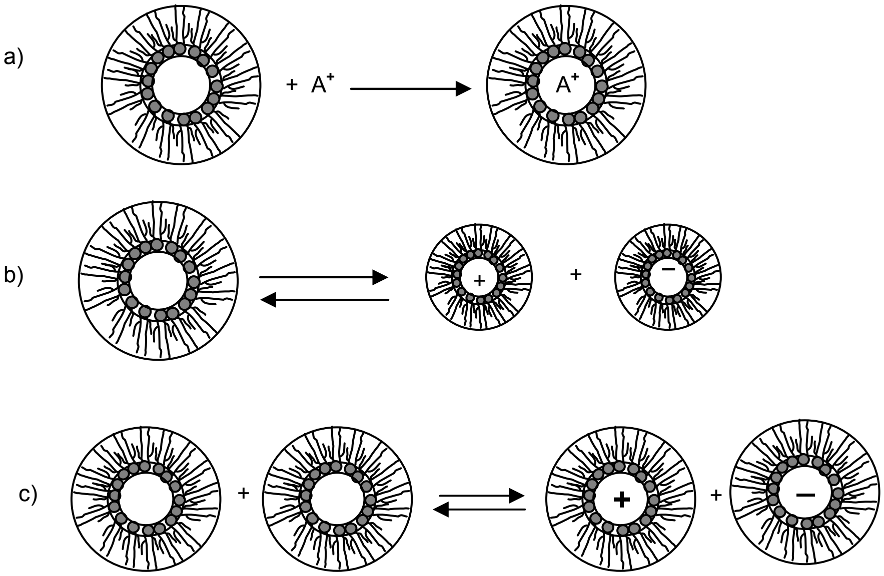


Figure 3 Schematic illustration of micelle charging mechanisms proposed in literature. a) Preferential ion adsorption: ion A^+ is trapped in the center of an inverse micelle structure; b) Ion pair dissociation or called weak-electrolyte-like ionization: a charge neutral inverse micelle containing oppositely charged sites dissociates into two oppositely charged inverse micelles; c) Disproportionation between micelles due to collisions: charge transfer happened after two inverse micelles collide each other.

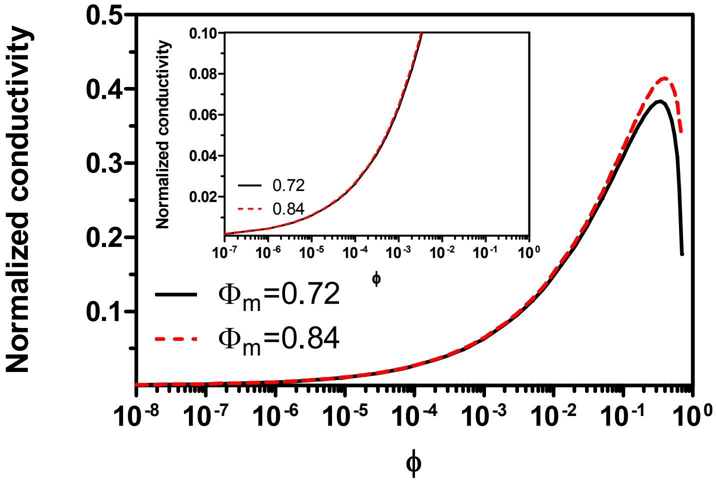


Figure 4, The normalized conductivity $\frac{3^{1/2}\pi^{4/3}\sigma(k_BT)^{1/6}\eta^{5/6}\tau^{1/6}}{2^{2/3}A^2K_{eq}^{1/2}}$ *against* ϕ *based on Eq.(32) under the assumptions of* $\phi_m = 0.72$ *and* $\phi_m = 0.84$. *The inset is the same data but plotted in a* *very small normalized conductivity range for clearly demonstrating the linear relationship. This conductivity relationship with the concentration of the inverse micelles is predicted on the basis of the ion pair dissociation charging mechanism*

For illustrative purpose, the normalized conductivity $\frac{3^{1/2}\pi^{4/3}\sigma(k_BT)^{1/6}\eta^{5/6}\tau^{1/6}}{2^{2/3}A^2K_{eq}^{1/2}}$ against ϕ based on Eq. (32) is shown in Figure 4. The predicted conductivity doesn't have a linear relationship with the concentrations of charging agent in any concentration region: it is proportional to $\phi^{7/18}$ even if the term $(\phi_m^{1/3}-\phi^{1/3})^{1/3}$ is considered as a constant in very low concentration regions or a narrow concentration range. This prediction is inconsistent with experimental evidences mentioned earlier. The ion pair dissociation mechanism seemingly answers the question how the charges are generated. However, such a mechanism physically predicts non-linear conductivity dependence on the concentrations of the charging agent. So it may not work for non-aqueous systems.

For the third mechanism, the disproportionation model in literature, the dissociation equilibrium may be expressed as:

$$M_A + M_B \Leftrightarrow M_A^+ + M_B^- \qquad (33)$$

The charge exchange may happen between the same type of inverse micelles as expressed earlier, $2A \leftrightarrow A^+ + A^-$. However, it essentially is same as expressed in Eq. (33) and thus Eq. (33) will be evaluated. The equilibrium constant can be expressed as:

$$K_{eq} = \frac{[M_A^+][M_B^-]}{[M_A][M_B]} \qquad (34)$$

Since there is no difference between the inverse micelles A and B statistically, their concentrations should be same and equal to:

$$[M_A] = [M_B] = \frac{n_0}{2} \qquad (35)$$

Thus the charged micelle concentration is:

$$n^+ = n^- = \frac{1}{2}K_{eq}^{1/2}n_0 \qquad (36)$$

Substituting Eq. (36) into Eq. (12) and considering that both positive and negative inverse micelles may contribute to the conductivity leads to:

$$\sigma = \frac{K_{eq}^{1/2} n_0 q^2 \delta^2 \nu}{6k_B T} e^{-\frac{U_0}{k_B T}} \qquad (37)$$

Replacing the parameters n_0 , q, δ, and v with the same methodology used before leads to:

$$\begin{aligned}\sigma &= \frac{2^{2/3} A^2 n_m K_{eq}^{1/2} \phi(\sqrt[3]{\phi_m/\phi} - 1)^{4/3}}{\pi^{4/3}(k_B T\tau)^{2/3}\eta^{1/3}} \\ &= \frac{2^{2/3} A^2 n_m K_{eq}^{1/2} \phi^{5/9}(\phi_m^{1/3} - \phi^{1/3})^{4/3}}{\pi^{4/3}(k_B T\tau)^{2/3}\eta^{1/3}}\end{aligned} \qquad (38)$$

Comparing Eq. (23) with Eq. (38), one may easily tell that Eq. (38) may give a similar normalized conductivity dependence on the volume fraction, i.e, the conductivity may change with the inverse micelle concentrations at very low concentrations, $\sigma \sim \phi^{5/9}$, show a "quasi" linear relationship at the concentration range $2\times10^{-3} \sim 5\times10^{-2}$, and finally reaches a peak at about 0.1. In both equations, the conductivity is inversely proportional to the cubic root of viscosity, which seems to be reasonable; High viscosity usually means low mobility and thus low conductivity intuitively. Although the third mechanism may successfully explain the conductivity behavior of the inverse micelles, the charge separation proposed in this mechanism is unlikely to happen, as the Coulombic attraction is so strong in low dielectric constant media, and the probability of charge exchanges is so low based on the rate process theory [**48**].

In summary, the preferential ion adsorption mechanism leads to the independence of the conductivity to the concentration of the charging agent, which conflicts with the experimental evidences; The ion pair dissociation mechanism looks like a reasonable charging mechanism, but the associated conductivity equation predicts that the conductivity may change with the concentrations of the charging agent as $\sigma \sim \phi^{7/18}$ most time; The disproportionation model predicts that the conductivity could increase with the concentrations of the charging agent at low concentration regions as $\sigma \sim \phi^{5/9}$. All those equations show that conductivity peaks at relatively high concentration regions, and further increase of the volume fraction leads to a decrease of the conductivity. Those mechanisms may qualitatively answer the question why non-ionic surfactants could be charged in non-aqueous systems. However, they fail to predict the linear relationship between the conductivity and the concentration of the charging agent, and most importantly, the electric field dependence of conductivity. A new charging mechanism is thus needed.

4. New charging mechanism

As one may know, the Coloumb's law may be expressed as below:

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_m\delta^2} \qquad (39)$$

where q_1, q_2 are two charge entities, δ is the distance between them. As mentioned earlier, the dielectric constant of non-aqueous media is about 2.5 and that of water is about 80, the Coloumbic attraction forces in non-aqueous media is almost 30 times stronger than that in aqueous systems. In addition, the electric fields created by charge entities should be almost 30 times stronger in non-aqueous media than that in aqueous media as expressed below:

$$\Psi = \frac{q_1}{4\pi\varepsilon_0\varepsilon_m\delta} \tag{40}$$

where Ψ is the surface electrical potential created by the charge entity *1* at the distance δ from the center of the charge entity. Such strong electric fields created by many inverse micelles may polarize the neighboring neutral uncharged micelles to disproportionate as shown earlier like $2A \overset{E}{\leftrightarrow} A^+ + A^-$. Under such a scenario, the charge separation may become plausible and non-ionic surfactants could be charged, too.

We therefore argue that the charges in inverse micelles may most likely be induced by electric fields, especially for non-ionic surfactant systems. The electric fields could be externally applied or generated internally from other charged entities in non-aqueous systems. The primary origin of an electric field could come from many ways: the electrostatic charges from both the containers and the non-aqueous systems themselves, the polar impurities/residues in the non-aqueous systems, the environmental electromagnetic fields, the applied electric field when the conductivity is measured, etc.. If a species contains weakly bound charge pairs, the external electric field may induce ion dissociations and create more charged species. Actually, the field-induced charge separation is a generic physical phenomenon widely observed in many other materials [71,72]. For non-aqueous systems, this phenomenon was first addressed by Onsager [65] who found that the equilibrium constant of such a process is directly proportional to the electric field strength and inversely proportional to the dielectric constant of the medium. In other word, in non-aqueous systems this effect is much more profound than that in aqueous systems [73]. Based on the conductivity data, Denat contended [38,74] that the inversed micelles may contain a small fraction of completely ionized (strong electrolytes) component, which may be induced by an external electric field. Lane [75] found that the charging process takes place by partitioning ionic species into the inverse micelles. A plausible physical picture for how inverse micelles become charged may be that weakly bound charge pairs on the charging agent or in the inverse micelles may dissociate under an electric field, and the dissociated ions are subsequently stabilized in the polar pool of another neighboring inverse micelle. This charging mechanism is schematically depicted in Figure 5, and can be simply expressed as:

$$M \overset{E}{\Leftrightarrow} M_A^+ + B^- \tag{41}$$

$$M + B^- \rightarrow (MB)^- \tag{42}$$

Eq. (41) shows that under an electric field an inverse micelle dissociates into a positively charged inverse micelle and a negative ion. This is an equilibrium process and the equilibrium constant is dependent on the applied electric field; The negative ion is immediately trapped into a polar pool of other neighboring micelles, making this inverse micelle negatively charged. The overall process can be expressed as:

$$M + M \overset{E}{\Leftrightarrow} M_A^+ + (MB)^- \qquad (43)$$

Comparing the processes expressed in Eq. (42) with Eq. (43), one may easily reach the conclusion that Eq. (43) may predict a similar conductivity behavior, as shown in Eq. (38) and Eq. (23). However, the equilibrium constant K_{eq} should be changed, as it is now a function of the applied electric field strength and the resulted conductivity should be different, too. According to Eyring's rate process theory [48,49], once an electric field is applied, there is a potential gradient that will facilitate the process indicated in Eq. (43), thus generating more separated charges entities. Suppose that at the initial state the free energy is increased by βw and thus the free energy at the final state will be lowered by $(1-\beta)w$, where β is a fractional operator and w is the work needed to separate two charge entities to a certain distance. The net rate k per unit time, representing the "absolute reaction rate" for generating ions, may be expressed as [48,49]:

$$k = K_{eq}\delta\left[exp\frac{\beta w}{k_B T} - exp\frac{-(1-\beta)w}{k_B T}\right] \qquad (44)$$

Again, K_{eq} is the equilibrium constant, δ is the distance between two separated charge entities.

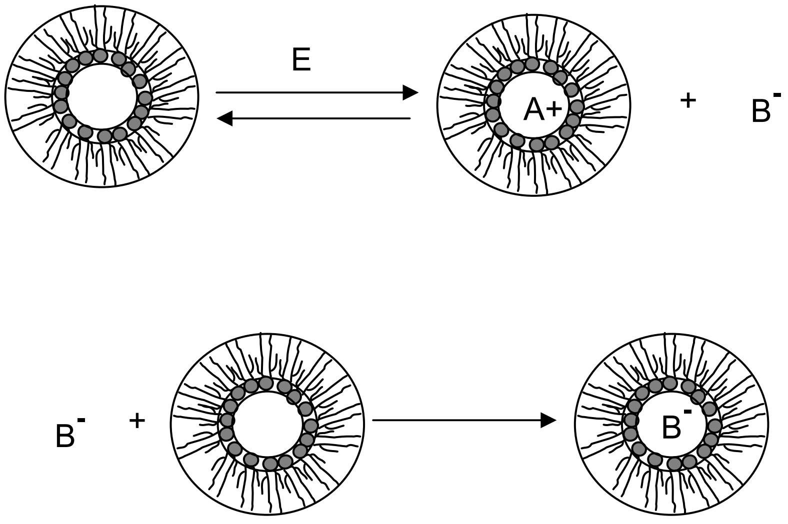


Figure 5 The electric-field-induced charging mechanism in inverse micelle systems. A charge neutral inverse micelle becomes charged with the aid of an electric field either from an external or internal sources. The released counterion B⁻ could be further trapped into the center of another charge neutral inverse micelle, making it charged, too.

As indicated earlier and shown in Eq. (8), αw is usually very small in comparison with $k_B T$. Using the approximation $e^x \approx 1 + x, x \ll 1$ leads:

$$k = K_{eq}\delta\frac{w}{k_BT} \tag{45}$$

Since $w = q\delta E$ by the definition, Eq. (45) thus can be rewritten as:

$$k = K_{eq}\frac{Eq\delta^2}{k_BT} \tag{46}$$

Eq. (46) shows the absolute rate for generating ions under an influence of an electric field. According to Eyring [48], the concentration of M_A^+, n_{MA}, based on Eq. (43) could be expressed as:

$$n_{MA} = kn_M^2 \tag{47}$$

where n_M is the number of inverse micelles per unit volume, $n_M = n_0/n_m$, by the definition. Therefore, Eq. (47) may be written as:

$$n_{MA} = K_{eq}\frac{n_0^2Eq\delta^2}{n_m^2k_BT} \tag{48}$$

Again, using the generic conductivity equation expressed in Eq. (12) leads to:

$$\sigma = \frac{K_{eq}En_0^2q^3\delta^4\nu}{6n_m^2(k_BT)^2}e^{-\frac{U_0}{k_BT}} \tag{49}$$

Replacing the parameters, n_0, q, δ, and ν, with the same methodology used before leads to:

$$\begin{aligned}\sigma &= \frac{2^{11/3}\times 3A^3EK_{eq}\phi^2(\sqrt[3]{\phi_m/\phi}-1)^{10/3}}{\pi^{7/3}(k_BT)^{5/3}\tau^{2/3}\eta^{1/3}} \\ &= \frac{2^{11/3}\times 3A^3EK_{eq}\phi^{8/9}(\phi_m^{1/3}-\phi^{1/3})^{10/3}}{\pi^{7/3}(k_BT)^{5/3}\tau^{2/3}\eta^{1/3}}\end{aligned} \tag{50}$$

Eq. (50) clearly shows that the conductivity should increase linearly with the applied electric field, which is consistent with experimental results. In most cases, the volume fraction of charging agent is much smaller than the maximum packing fraction, $\phi \ll \phi_m$, thus $(\phi_m^{1/3}-\phi^{1/3})^{10/3} \approx \phi_m^{10/9}$, a constant. Therefore, the conductivity may change with the volume fraction as $\sigma \sim \phi^{8/9}$, a almost linear relationship. For illustrating the relationship between the conductivity and the concentrations of inverse micelles, the normalized conductivity $\frac{\sigma\pi^{7/3}(k_BT)^{5/3}\tau^{2/3}\eta^{1/3}}{3\times 2^{11/3}A^3EK_{eq}}$ against ϕ predicted with Eq. (50) is plotted in Figure 6. It looks like that the conductivity goes through a maximum at the concentration of inverse micelle about 5×10^{-2}; In the extremely low concentration region from 10^{-9} to 10^{-5}, the conductivity approximately linearly increases with the concentrations; In the region from 10^{-5} to 2×10^{-3}, the conductivity follows a power law with the concentrations; Above 2×10^{-3} and below 5×10^{-2}, the conductivity again linearly increases with the concentrations, before it reaches the maximum point; In high concentration region above 5×10^{-2}, the conductivity dramatically decreases with the concentrations, which is hard to understand intuitively. The possible reason could be that high concentrations of inverse micelles may impede the movement of charged inverse micelles due to the crowdedness; The competition between different inverse micelles for donating or accepting charges may also slow down charge exchange rate and then the charge movements. All those factors may lead to a low conductivity resulted from the low mobility of charged inverse micelles.

In a word, Eq. (50) seems to perfectly catch four major experimental observations: 1) the conductivity linearly increases with the applied electric field; 2) the conductivity may linearly increase with the charge agent concentrations at two concentration regions; 3) the conductivity deviates from the linear relationship at relatively high concentration region; 4) the conductivity may dramatically drop at very high concentration regions. It also may explain why non-ionic surfactants may get charged; It may be reducible to the disproportionation model in term of charging equilibrium process expressed in Eq. (43). The electric field induced charging mechanism is therefore considered to correctly reflect how charges are generated in non-aqueous systems. In addition, this mechanism also answers how separated charges are stabilized: It is the electric field that keeps charges separated.

Since the relaxation time τ can be expressed in Eq. (24), a function of conductivity and dielectric constants of both phases, Eq. (50) may be further written as:

$$\sigma = \frac{3 \times 2^{11/3} A^3 E K_{eq} \phi^2 \left(\sqrt[3]{\phi_m / \phi} - 1\right)^{10/3} \left[2\sigma_m + \sigma_p + \phi\left(\sigma_m - \sigma_p\right)\right]^{2/3}}{\pi^{7/3} (k_B T)^{5/3} \eta^{1/3} \varepsilon_0^{2/3} \left[2\varepsilon_m + \varepsilon_p + \phi\left(\varepsilon_m - \varepsilon_p\right)\right]^{2/3}} \qquad (51)$$

Eq. (51) lists all parameters that may have an impact on conductivity. The conductivity measurement would potentially yield important information like the equilibrium constant K_{eq} and the material related parameter A. The major difference between the electric-field-induced charging mechanism and the collision or disproportionation mechanism, is that the former shows

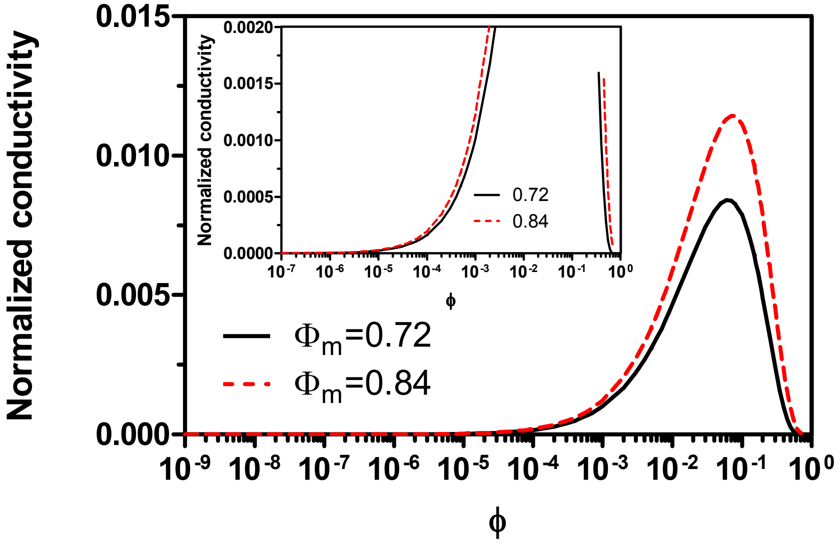


Figure 6, The normalized conductivity $\frac{\sigma\pi^{7/3}(k_BT)^{5/3}\tau^{2/3}\eta^{1/3}}{3\times 2^{11/3}A^3EK_{eq}}$ *against* ϕ *based on Eq.(50) under the assumptions of* $\phi_m = 0.72$ *and* $\phi_m = 0.84$. *The inset is the same data but plotted in a very small normalized conductivity range for clearly demonstrating the linear relationship. This conductivity relationship with the concentrations of the inverse micelles is predicted on the basis of electric-field-induced charging mechanism.*

the conductivity dependence on the electric field strength; while the disproportionation charging mechanism predicts that the conductivity is independent of the electric field. Randriamalala [64] found that the conductivity of AOT solutions indeed increases with applied electric field as predicted by Onsager's theory up to 5.6x10^6 *V/m* over a wide AOT concentration range. Park 53 showed that the conductivities of both AOT/dodecane and Span80/dodecane systems are linearly dependent on the applied electric field even as low as 5×10^4 V/m. The charging mechanisms in non-aqueous systems must take the electric field dependence into account, and the electric-field-induced charging mechanism is thus preferred than other mechanisms like preferential ion absorptions, the ion pair dissociations, and disproportionations.

Note that the relaxation time is assumed to be independent of the applied electric field strength, however, this assumption becomes invalid at high enough electric fields [76,77]. Both the dielectric constant and the conductivity have a complicated relationship with strong electric fields [45,76,77,78] due to the nonlinear dielectric effect. The relaxation time therefore becomes dependent on the applied strong electric fields, according to Eq. (24). This complication may further make the conductivity deviate from the linear relationship with the concentrations at very high electric field.

V. Experimental comparisons

For checking the validity of the new mechanism and the associated conductivity equations, Eq. (50) and (51), experimental comparisons are made in this section. Figure 7 shows the experimental conductivity data of Span 80/kerosene solution from literature [52] vs. the volume fraction of Span 80. The same data are fitted with Eq. (51) and the fitting curve is shown in the same plot. The fitting quality in term of R^2 is 0.952, a very good fitting in the light of that the exact conductivity of kerosene used in the experiment was not specified and is taken from another literature [79] for estimation. The deviation from the linear relationship at very low concentration regions could be resulted from the fact that Eq. (51) only works for the systems where the inverse micelles have already formed, i.e., above the critical micelle concentration. If the three low concentration data points were removed from the regression, the fitting quality in term of R^2 would become 0.983, a much better fitting. This may imply that Eq. (51) may not only work for very diluted surfactant systems below the critical micelle concentration. Note that Span 80 is a non-ionic surfactant but frequently used a charging agent. We have to say that Eq. (51) fits the experimental conductivity data of Span 80/kerosene solutions pretty well, indicating that charged inverse micelle may form, indeed, in spite of the non-ionic nature of this surfactant.

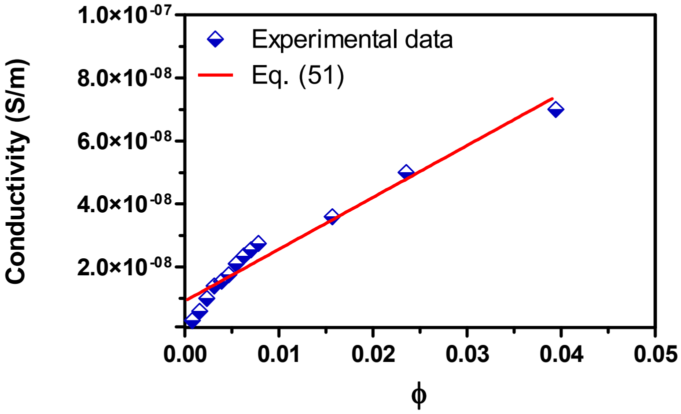


Figure 7 Conductivity of Span80/kerosene solution is plotted against the volume fraction of Span 80 and fitted with Eq. (51). The experimental data are taken from Figure 3 of the literature [52]. The conductivities of Span 80 and kerosene are taken as 3.55×10^{-7} S/m from the literature [52] and 4×10^{-13} S/m from the literature [79], and the dielectric constants of Span 80 and kerosene are taken as 4.7 from the literature [52] and assumed as 2.0, respectively. The fitting quality in term of R^2 is 0.952. Note that Span 80 is a non-ionic surfactant.

For further validating the new mechanism and the associated conductivity equation for ionic surfactant systems, the conductivity data of AOT/hexadecane solution is taken from the literature [80] and plotted against the volume fraction of AOT in Figure 8. Again, the fitting curve generated from Eq. (51) is also shown in Figure 8**.** Since there is no experimental data available for the conductivities and dielectric constants of both individual AOT and

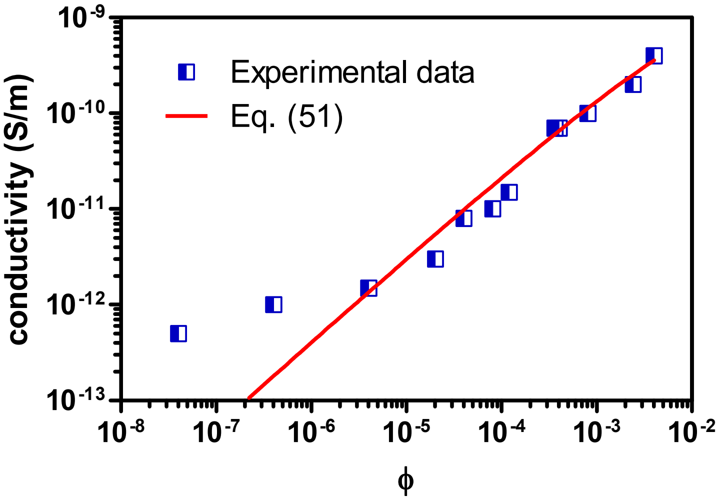


Figure 8 *Conductivity of AOT/hexadecane solution is plotted against the volume fraction of AOT and fitted with Eq. (51). The experimental data are taken from Figure 3 of the literature* **80** *and the critical micelle concentration is*10^{-6}. *The conductivities of AOT and hexadecane are assumed as* 6×10^{-8} *S/m and* 3×10^{-13} *S/m, and the dielectric constants of AOT and hexadecane are assumed as 5.0 and 2.0, respectively, due to the lack of data from the literature. The fitting quality in term of* R^2 *is 0.9695 for entire data set, though Eq. (51) may fit the data much better once the concentration is above the critical micelle concentration,* 10^{-5}. *Note that AOT is an ionic surfactant.*

hexadecane, the conductivities of AOT and hexadecane are assumed as 6×10^{-8} S/m and 3×10^{13} S/m, and the dielectric constants of AOT and kerosene are assumed as 5.0 and 2.0, respectively. The fitting quality in term of R^2 is 0.9695, again a pretty good fit with Eq. (51). It is noteworthy that the fitting quality is insensitive to what the dielectric constants and conductivities of both AOT and hexadecane are chosen, if they are in a right order of magnitude. Another interesting thing is that Eq. (51) may fit the conductivity data very well once the concentration of AOT exceeds the critical micelle concentration, 10^{-6} according to literature **80**, though the fitting quality in term of R^2, 0.9695, is for entire data set. If the two data points at very low concentrations below the critical micelle concentration are taken away, the fitting quality in term of R^2 will increase to 1, a perfect linear fit. This may be inherited from the fact that Eq. (51) is derived under the assumption that a large quantity of inverse micelles is formed and the charged inverse micelles solely contribute to the conductivity. Again, this may indicate that Eq. (51) is only applicable to the systems where the charging agent concentration is above the critical micelle concentration. Clearly, both Figures 7 and 8 indicate that Eq. (51) works for both non-ionic and ionic surfactant systems, once the charging agent concentration is above the critical micelle concentrations and a large amount of inverse micelle structures form. Those inverse micelle structures would contribute to the conductivity of the whole systems.

We would like to check how Eq. (51) is going to fit the electric field dependence of conductivity. Figure 9 shows the normalized experimental conductivity data of 1 wt% span 85/dodecane against the applied electric field strength from the literature 53. The same data are fitted with Eq. (51) and Onsager's equation expressed as $\sigma/\bar{\sigma} = 1 + \gamma E$, where $\sigma/\bar{\sigma}$ is the normalized conductivity, γ is a constant $\gamma = \frac{e^3}{16\pi\varepsilon_m k_B^2 T^2} = 2.82 \times 10^{-7}$ *m/V* for dodecane. Onsager's theory predicts a linear but relative high conductivity, and Eq. (51) again presents a perfect fit with R^2*=0.9953.*

From Figure 7~9, one may easily tell that Eq. (51) works for inverse micelle systems and is capable of predicting a correct conductivity dependence on both the charging agent concentrations and the applied electric field.

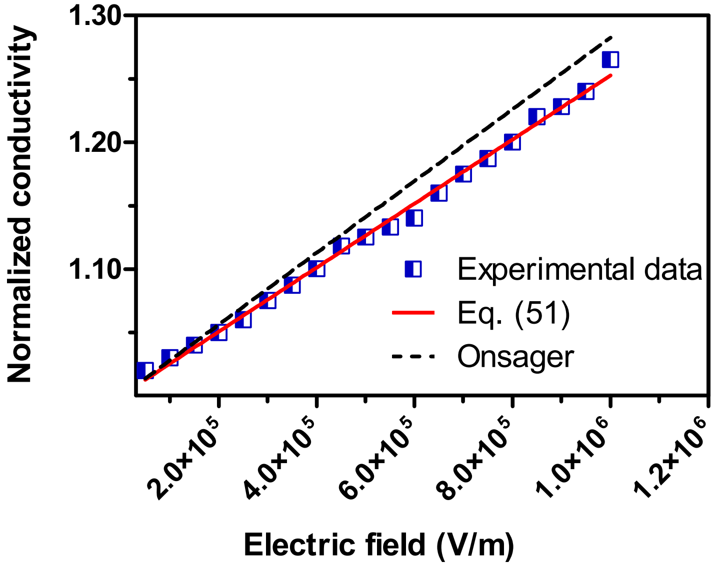


Figure 9 The normalized experimental conductivity data of 1 wt% span 85/dodecane against the applied electric field strength from the Figure 4 of the literature [53]*. The same data are fitted with Eq. (51) and Onsager's equation expressed as* $\sigma/\bar{\sigma} = 1 + \gamma E$ *(see literature* [53]*), where* $\sigma/\bar{\sigma}$ *is the normalized conductivity,* γ *is a constant,* $\gamma = \frac{e^3}{16\pi\varepsilon_m k_B^2 T^2} = 2.82 \times 10^{-7}$ *m/V for dodecane. The fitting quality with Eq. (51) in term of* R^2 *is 0.9953, a perfect fit.*

VI. Discussions

The disproportionation model is relatively favored in literature [22,34], and is now demonstrated in this article that the corresponded conductivity equation cannot predict the correct relationship between the conductivity and the concentrations of inverse micelles and cannot explain why non-ionic surfactants can be charged in non-aqueous systems. Apparently, one of the major drawbacks of the disproportionation model is that it doesn't lead to a conclusion that the conductivity is also dependent on the applied electric field.

The electric field induced charge mechanism predicts that the conductivity may increase with volume fractions linearly at the beginning, exponentially in the middle, and peak in the relatively high concentrations. A qualitative physical picture could be like this: since the inverse micelles are formed by the surfactant molecules, the high surfactant concentrations could produce more charged inverse micelles, resulting in linear increase at the beginning; When more charged micelles are created, those charged micelles will impose electric fields to neighboring inverse micelles, making them charged, too. This chain-reaction like charging process leads to an exponential increase of conductivity at relatively higher concentrations due to the large number of charged inversed micelles. In the meanwhile, if the concentrations of surfactant are too high and too many charged inverse micelles are produced, the collisions between the inverse micelles may slow down the motions of inverse micelles under an electric field, resulting in a lower conductivity and create a conductivity peak against the concentrations. The surprising conductivity decrease at high concentrations of inverse micelles shown in Figure 2, 4, and 6 is easily understandable. As speculated earlier, the locally concentrated inverse micelles may prevent charged inverse micelles from moving easily due to the spatial crowdedness and reduced free volumes. In addition, the intimate contacts or collisions between neighbored inverse micelles may increase the competitiveness of charge transfers, slowing down the charge movements, too. All those factors may contribute to low mobility of charged inverse micelles, thus resulting in low conductivity.

The electric-field-induced charging mechanism immediately looks awkward to the author, once such a conclusion has to be reached. Intuitively, the charged entities should carry charges intrinsically without relying on external driving forces. On the other hand, since charged entities may generate almost 30 times stronger electric fields locally in non-aqueous systems, they definitely have the capability to polarize the neighboring neutral inverse micelles; the electric-field-induced charge separation thus becomes possible and plausible. The electric fields that either comes from internal neighboring charging entities or from the externally applied sources could be the only reason responsible for polarizing inverse micelles, separating charges, and keeping them apart stably. Both the ion pair dissociation and the disproportionation mechanisms including the fluctuation theory are unable to provide a reasonable explanation on how the separated charges are stabilized in non-aqueous systems; Physically, oppositely charged entities in non-aqueous systems tend to preferentially bond together due to almost 30 times stronger Coloumbic attractive forces. Intuitively, the conductivity of inverse micelle systems should be controlled by ionic transportation and those ions likely are the charged inverse micelles.

The conductivity equation derived on the basis of electric-field-induced charging mechanism shows that the conductivity should linearly increases with the applied electric field strength, and it may increase with the concentrations of inverse micelles as $\sigma \sim \phi^{8/9}$, a almost linear relationship. Comparison with experimental results obtained by different researchers further demonstrates that electric-field-induced charging mechanism works for inverse micelle systems, indeed. It even presents a better fit to the conductivity dependence of the applied electric field than Onsager's theory. Although both Park 53 and Randriamalala [64] confirmed the conductivity dependence on the electric field, they didn't consider the electric field a dominant factor in charging processes; both of those two articles only present a qualitative analysis what may happen in non-aqueous systems and there is no electric-field related conductivity equation proposed.

The relaxation time normally can be considered as a constant, but the relaxation time variation with the electric fields must be taken into account when the applied electric field is high enough. Since the charges of the inverse micelles are induced by electric fields, the dielectric property of non-aqueous systems may be simply controlled by the electrode polarization process, which is well described in literature [6]. The dielectric investigation together with conductivity study may provide more insights on the charging mechanisms of non-aqueous systems.

In this article, all surfactants or called charging agents are assumed to fully soluble in non-aqueous media like organic solvents or oils and enough numbers of inverse micelles are already created. This assumption is very true for many non-aqueous systems containing the charging agents listed in Fig. 1.. There is no solubility issue in non-aqueous systems, quite different from aqueous systems where surfactant solubility and therefore the Kraft temperature is critical to micelle formation, besides the critical micelle concentrations. The temperatures in my equations are nothing to do with the solubility of surfactants but control the mobility of charged inverse micelles.

VII. Conclusions

The charging mechanisms of non-aqueous multiphase surfactant solutions, emulsions, and colloidal suspensions are addressed in this article, with the focus on inverse micelle charging processes that are commonly involved in all three systems. Three types of charging mechanisms available in literature, preferential ion absorption, ion pair dissociation, and disproportionation/fluctuation models, are evaluated; The corresponded conductivity equations are derived on the basis of those mechanisms for comparing with the experimental observations. The preferential ion adsorption charging mechanism predicts that the conductivity is dependent on the concentrations of impurities and independent of inverse micelle concentrations, which conflicts with the experimental results; Both the ion pair dissociation charging mechanism and the disproportionation mechanism predict that the conductivity may non-linearly increase with the concentrations of inverse micelle, and most importantly the predicted conductivity is independent of the applied electric field strength, which conflicts with experimental observations. All those three mechanisms are unable to fully explain observed experimental phenomena. Especially, both ion pair dissociation and disproportionation/fluctuation models suffer a big drawback: the charged entities tend to neutrally stay together rather than separate apart due to much stronger Coloumbic attractive forces in non-aqueous systems.

A new electric-field-induced charging mechanism is proposed to explain how inverse micelles are charged and why charges can be separated and stabilized. It clearly answers why non-ionic surfactants can still be charged in non-aqueous systems. The needed electric fields could come from nearby charging species or from the externally applied sources. The obtained conductivity equation under this charging mechanism shows a complicated relationship with the charges, the electric field, the volume fraction of the charging agent, the relaxation time, and the temperature. The conductivity equation derived on this basis of this mechanism correctly captures four major experimental observations: 1) the conductivity linearly increases with the applied electric field; 2) the conductivity almost linearly increases with concentrations, following $\sigma \sim \phi^{8/9}$; 3) the conductivity deviates from the linear relationship at relatively high concentration region; 4) the conductivity may dramatically drop at very high concentration regions. It fits the experimental data pretty well for both conductivity vs. the concentration of charging agent and conductivity vs. the applied electric field. Our work may shed light on many long time puzzles in non-aqueous multiphase systems, and may potentially have a broad impact in many industrial areas.

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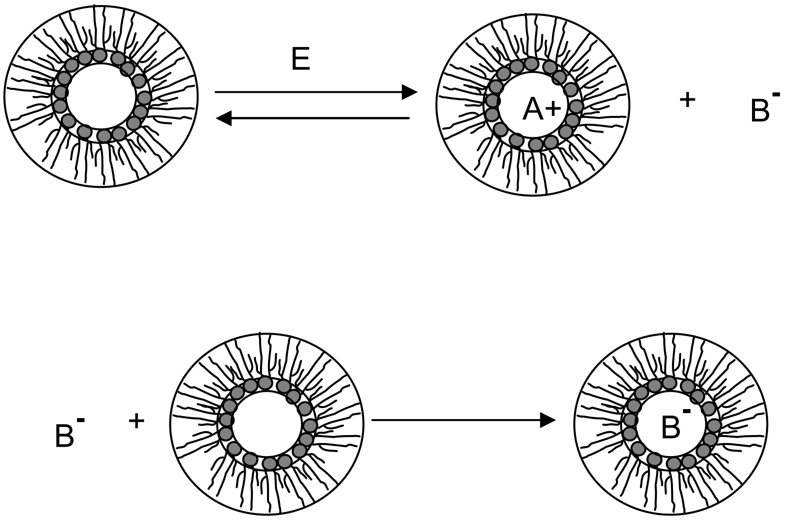
TOC Graphic



Schematic diagram shows charge separation induced and stabilized by an electric field and inverse micelle charged in the end.