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How non-ionic “electrically neutral” surfactants enhance electrical conductivity and ion stability in non-polar liquids

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Abstract

We show that it is possible to control the electrical conductivity of non-polar liquids such as kerosene using substances that are normally presumed to be non-dissociating and electrically neutral. This assumption is reflected even in the name “non-ionic surfactants”. These surfactants “solvate ions” in non-polar liquids by building protective shells around them, similar to the hydration layers of water around ions in aqueous solutions. The number of ions, and consequently the conductivity, correlates with amount of the solvating surfactant. This is a unique situation in which “solvation” controls the number of ions. It is exactly opposite to the situation in most aqueous systems for which the solvating agent (the water molecules) is in excess and the number of ions correlates instead with the amount of the dissociating agent. In order to determine the size of these “sterically stabilized” ions we use a combination of conductivity and electroacoustic measurements. This approach was successfully used fifty years ago by Zana and Yeager to determine the size of hydrated ions in water. In the present case, these surfactants create anions and cations having quite different sizes, 30 and 1 nm, respectively.

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1. Nature of ions in non-polar liquids

In order for ions to exist in a fluid they must have a sufficiently large size, otherwise coulombic attraction, which increases as the ions approach each other, would overpower the thermal motion that keeps these ions apart. This coulombic attraction, in the absence of some balancing force, would otherwise pull the ions together to form neutral entities. In water, ions can effectively enlarge their size by building a protective solvation shell, thus isolating themselves from the very polar water molecules. Such a construction is impossible in non-polar liquids because the molecules do not possess a sufficient dipole moment to facilitate this construction. Adding to the difficulty in non-polar liquids, the critical ion radius at which coulombic attraction balances thermal motion, is much larger as

compared to water. This so-called Bjerrum radius [1] is proportional to the dielectric constant [2] of the liquid. Consequently it is equal to 28 nm in non-polar liquids, whereas in water it is only 0.7 nm.

These two factors, the large Bjerrum radius and the lack of dipole moments for the solvent molecules, create a very unfriendly environment for ions in non-polar liquids. As a result, few ions exist, which it turns leads to the very low conductivity of such non-polar liquids, typically five orders of magnitude less than that of pure water.

This short description tells us that we must create protective solvating shells around ions if we want to increase and control the ionic concentration and conductivity of a non-polar liquid. The idea of “steric stabilization” of ions has been around for a long time [2–5]. Oil-soluble surfactants can perform this function because they have a polar lyophilic part with a significant dipole moment. Interaction of ions with the polar parts of these surfactant molecules creates the desirable protective shell as ions are encapsulated into large structures, usually called “inverse micelles”.

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Many publications discuss the steric stabilization of ions, but it is curious that all of them discuss only ionic surfactants that themselves can dissociate into ions in non-polar liquids. It is clear that the ability of a surfactant to dissociate in oil is an extra feature, which is not required for building a protective shell. Non-ionic surfactants can solvate ions as well as ionic surfactants. This leads us to the somewhat *paradoxical idea that non-ionic, non-dissociating substances can be used to control the conductivity and ionic composition of non-polar liquids*. This idea opens a completely new way to control the electrical properties and ionic composition of these liquids.

We obtained the first confirmation of this idea with simple conductivity measurements of various non-ionic surfactants, as listed in Table 1. Actually, it has long been known that such non-ionic surfactants have a surprisingly large conductivity [3]. However, little attention is paid to this curious fact, with only some mention of ionic impurities [3] as a possible cause of this conductivity anomaly. There has been no explanation, or even discussion, as to why ions exist in these liquids with a dielectric constant in the range of 3–12 [4], but do not exist in many other non-aqueous fluids.

It is well-known that there are always ionogenic impurities in non-polar liquids. It follows, for instance, from that fact that electric field of sufficient strength can generate electric conductivity. This phenomenon was first analysed by Onsager [6] who explained it by the break-up of “ion pairs” into separate free ions at high field strength.

Ion pairs are rather “loose” objects. Ions can one moment briefly dissociate under thermal stress, only to be pulled back a moment later by coulombic attraction. An applied electric field shifts this association/dissociation balance towards dissociation. Surfactants, including non-ions, can do the same.

If surfactant molecules appear at just the right moment and at the right place they can squeeze between the ions at the brief moment of dissociation. This action would thwart the subsequent association act. Ions thus become solvated by the surfactant and free.

The concentration of ions and the resulting electrical conductivity depends on two factors:

1. the concentration and properties of the ions pairs;
2. the concentration and properties of the solvating surfactants.

In a given situation, one of these two factors might be dominant.

The first factor might be dominant in the case of a pure surfactant liquid, where the concentration of ions pairs is the limiting factor because surfactant molecules are present in excess. This explains why the conductivity of various surfactants, as shown in Table 1, does not correlate with surfactant properties such as HLB number or dielectric permittivity.

The second factor would be dominant when the concentration of surfactant is not sufficient to solvate all of the available ion pairs. In practice, a surfactant solution added to a non-polar liquid might often represent this case. All non-polar liquids contain some ion pairs and to this we must add a supply of ion pairs that come into the solution along with the surfactant. We may not know much about the chemical nature or concentration of these ion pairs, but this information actually becomes somewhat irrelevant in this case. If the total number of ion pairs substantially exceeds the solvating capacity of the added surfactant, we are led to the interesting conclusion that the *electrical conductivity of this non-polar liquid becomes a function of the added concentration of a non-ionic, non-dissociating substance*.

There is a simple way to verify this hypothesis. We need only measure the conductivity of a non-polar liquid as function of the concentration of an added non-ionic surfactant. This experiment is presented in the next section and confirms our idea.

An important use for conductivity measurements is an estimate of the ion concentration. In order to perform this calculation, one needs information about the diffusivity, or size, of the ions. This presents a problem for non-polar liquids, because the size of the “surfactant solvating ions” is unknown. To resolve this question, we employed an electroacoustic technique similar to that used, successfully by Zana and Yeager [7–10] fifty years ago to characterize the size of solvated ions in water. This study applies this technique for characterizing the size of ions in a set of non-ionic surfactants in kerosene. *It will be shown that the size of the cations and anions are very different*. In the present case, only the anion is solvated. The cation remain small, practically the same size as in water. We have not found any reference considering this possibility. It is usually claimed that ions in non-polar liquids must be large. Actually, this statement has to be applied to just one type of ion, either the anions or cations. The other ion can

Table 1
Properties of non-ionic surfactants

Surfactant	HLB No.	Viscosity, cStokes	Dielectric permittivity	Conductivity, 10^{-10} (S/m)
SPAN 20, Spectrum Co.	8.6	2703 ± 316	7.2	25,000
SPAN 20 Aldrich	8.6	3166 ± 299	6.6	14,300
SPAN 80	4.3	1006 ± 45	4.7	3550
Arlacel 83	3.7	1133 ± 94	4.9	12,500
SPAN 85	1.8	220 ± 17	3.7	102

remain small; it simply would not have a partner with which to build an ion pair.

The situation in which just one type of ion is solvated is easier to understand as compared to the case when both are solvated. An ion attracts the dipole moment of the polar part of the surfactant. Oppositely charged ions would attract this dipole moment with a different orientation. In turn, this would require a different orientation of the surfactant molecules in the micelles that are built around cations or around anions. It is hard to imagine how the same surfactant molecules could construct micelles with a very different structure. We will show that only the anion becomes solvated due to the preferential polarization of the non-ionic surfactants.

Investigation of these peculiar properties of non-ionic surfactants might have particular relevance to environmental concerns in industrial applications because these surfactants "...are much less harmful than ionic ones and thus can be considered for food, pharmaceutical and cosmetic applications ..."

2. Conductivity of non-polar liquids with non-ionic surfactants

For conductivity measurements we used Models 627 and 645 of Conductivity Meter by Scientifica. Model 627 operates at 18 Hz with an applied voltage of about 5 V rms. The measurement range is from 20 to 20,000 picosiemens/cm. Model 645 operates at higher conductivities range of nano-siemens/cm.

The properties of the five different surfactants used in this study are given in Table 1. We used SPAN 20 from two different manufactures; the one produced by Spec-

trum Chemical was more than ten years old. We did not apply any additional purification. All surfactants were used as received from manufacturer. These surfactants have different polar groups. The value of the so-called HLB number (hydrophobic–lyophilic balance) reflects this polarity; the larger HLB number corresponds to a greater polarity.

Fig. 1 shows the conductivity of kerosene with added amounts of the various surfactants. It is important to note that the conductivity generated by added amounts of the two SPAN 80 surfactants is the same, in spite of the fact that the conductivity of these two surfactants by themselves was quite different. A similar situation is observed in comparing the effect of the SPAN 80 and Arlacel 83, which have similar HLB number (4.3 vs. 3.7). Although the conductivity of the Arlacel 83 is four times that of the SPAN 80 it is only slightly more effective in increasing the conductivity of the kerosene solution.

Fig. 2 shows the conductivity for kerosene and six other high purity non-polar liquids as a function of added concentration of SPAN 80. There is again an almost linear dependence of conductivity with added surfactant.

We think that these data confirm our hypothesis that the observed conductivity is related to the solvation of ions created after breaking up of the ions pairs.

We do not know the chemical nature of these ion pairs, or their concentration. Actually this information is not very important because the electrodynamic properties of these non-polar liquids are controlled by the solvating agents, not by dissociating ones. There is a deficit of solvating agent and it is their concentration that determines the concentration of ions.

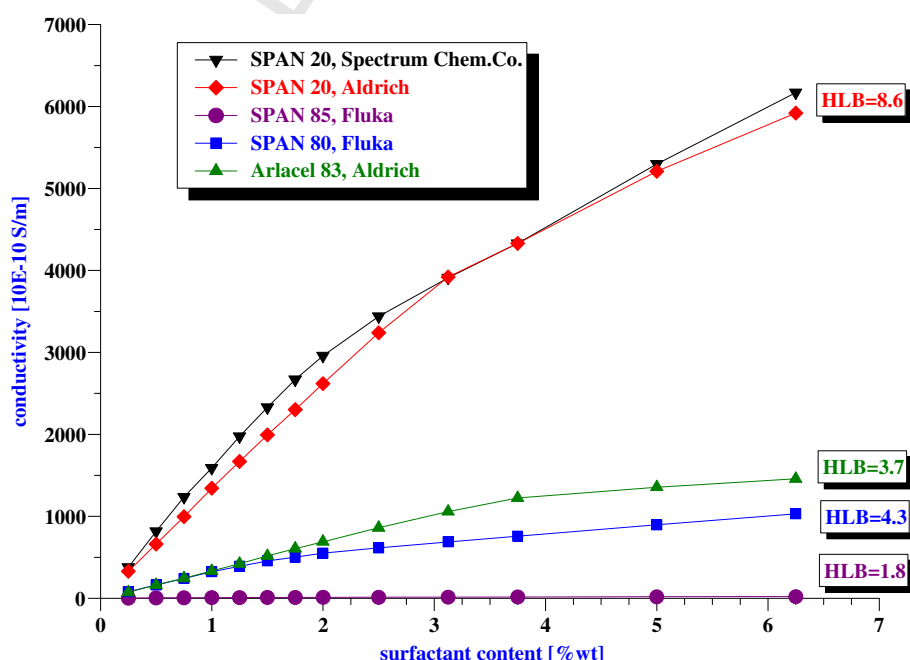


Fig. 1. Conductivity of the kerosene solutions with various non-ionic surfactants.

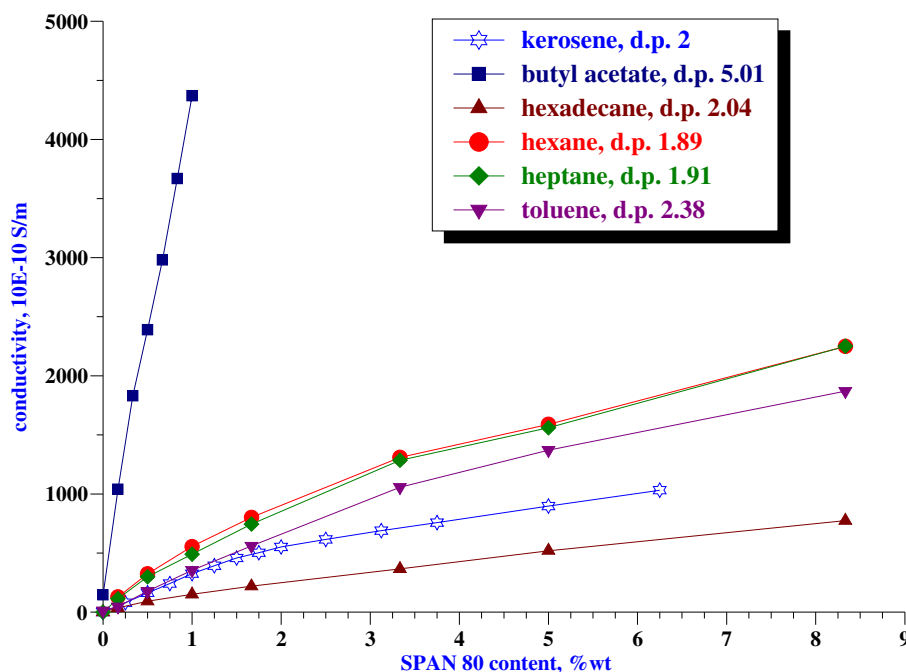


Fig. 2. Conductivity of the various non-polar liquids with SPAN 80. Abbreviation d.p stands for dielectric permittivity of the liquid.

3. Conductivity measurement combined with adsorption on alumina surface

There is a simple way to learn the properties of cations and anions separately. We can add small solid particles to the kerosene/surfactant mixture. We propose that the particles will adsorb either the positive or negative ions, but not both. We will verify this assumption later with an independent measurement of the surface charge on the particles. The other ion, not adsorbed, would remain in solution and still contribute to the conductivity.

We made such tests using a well-dried alumina, Sumitomo AKP-30, having a nominal diameter of $0.3\ \mu\text{m}$ [13]. We measured the size distribution of a 5%v/v dispersion in kerosene using a Dispersion Technology DT-1200 Acoustic Spectrometer [14]. In kerosene the alumina is slightly aggregated and the measured diameter was about $1\ \mu\text{m}$.

Fig. 3 shows the conductivity vs. surfactant concentration for both plain kerosene and for kerosene with added 5%v/v alumina particles. The reduction in conductivity with added alumina particles reflects the adsorption of ions by the alumina particles. There are two possible explanations

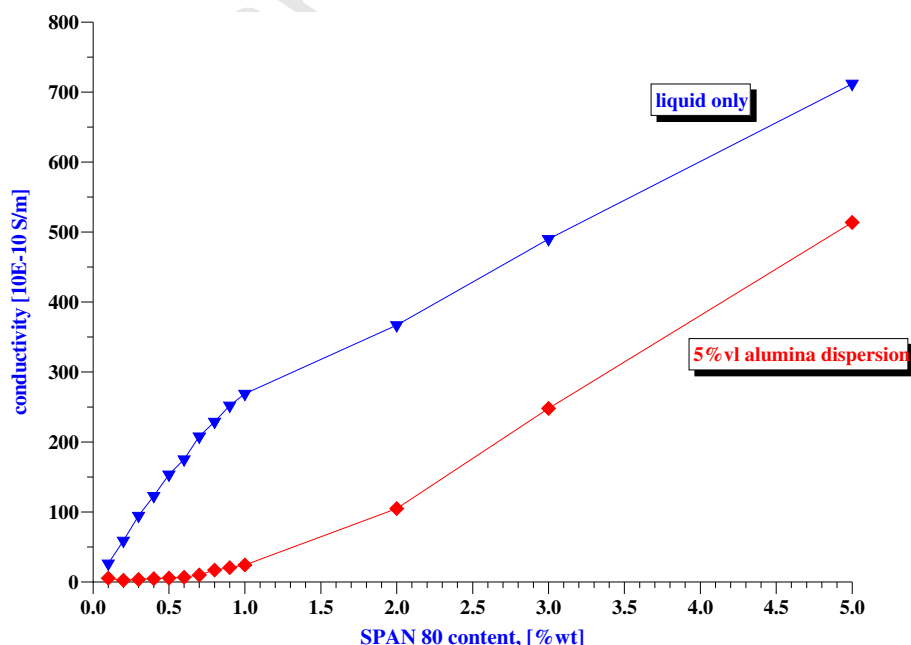


Fig. 3. Conductivity of the SPAN 80 in kerosene solutions with and without alumina AKP-30 particles at 5%v/v.

for this decrease: (1) both anions and cations are being adsorbed or (2) just anions or cations but not both are adsorbed. The first possibility will be ruled out later by measurements of the electric surface charge on the particles, induced by the ions adsorption.

In the second case, there are two more possibilities: the anions and cations are the same size or they are quite different in size. The equal-size possibility can be ruled out by noting that the conductivity is drastically reduced with the addition of the alumina particles, whereas if the ions were of similar size we should expect that the conductivity would be reduced only by a factor two. This leaves us with the conclusion that the anions and cations are quite different in size.

So we can conclude that at low surfactant concentrations below 1%, the alumina adsorbs practically all ions of one type. These adsorbed ions had originally made a large contribution to the conductivity, but their removal from the solution by adsorption leads to a dramatic decrease in conductivity. This indicates that these adsorbed ions are much more mobile than the ions that remain in solution.

This conclusion of unequal ion size is rather new for this field; the assumption of equal ion sizes is most widely used [2]. In order to determine whether the adsorbed ions are the anions or cations, and finally the size of the ions, we employed electroacoustic measurement as described in the next section.

4. Electroacoustic measurements

Debye [15] first predicted an electroacoustic effect seventy years ago. In either electrolyte solutions or dispersions, the effect is related to a coupling between

electrodynamic and mechanical phenomena. For instance, the transmission of ultrasound through an electrolyte solution or dispersion generates a current, which is usually referred to as an Ion/Colloid Vibration Current. There are commercial instruments for measuring this effect with the purpose of determining the electrokinetic potential of dispersed particles in liquids. In this study we use a Dispersion Technology DT-300 [14]. One can find a detailed description of this instrument in our book published two years ago by Elsevier [16].

With regard to non-polar liquids, this electroacoustic technique allows us to calculate the electric charge of the particles, knowing nothing about the ionic composition or ion properties of the liquid. This was shown recently by Shilov in a new electroacoustic theory [17] applicable to non-polar dispersions that takes into account double layer overlap between particles. Fig. 4 shows the surface charge (calculated using Shilov's new theory) of the alumina particles as a function of the surfactant concentration for the same dispersion as used in the previous section and described by Fig. 3.

The surface charge was positive as also confirmed by microelectrophoresis.

There is an interesting relationship between the conductivity data shown in Fig. 3 and electroacoustic data of Fig. 4. When the surface charge reaches a saturation level at a surfactant concentration of 1–2%, the conductivity of the alumina dispersion begins to increase at the same rate as that for the plain liquid. This occurs because at higher doses the smaller cations are no longer adsorbed, but remain in the solution and thereafter contribute to the conductivity.

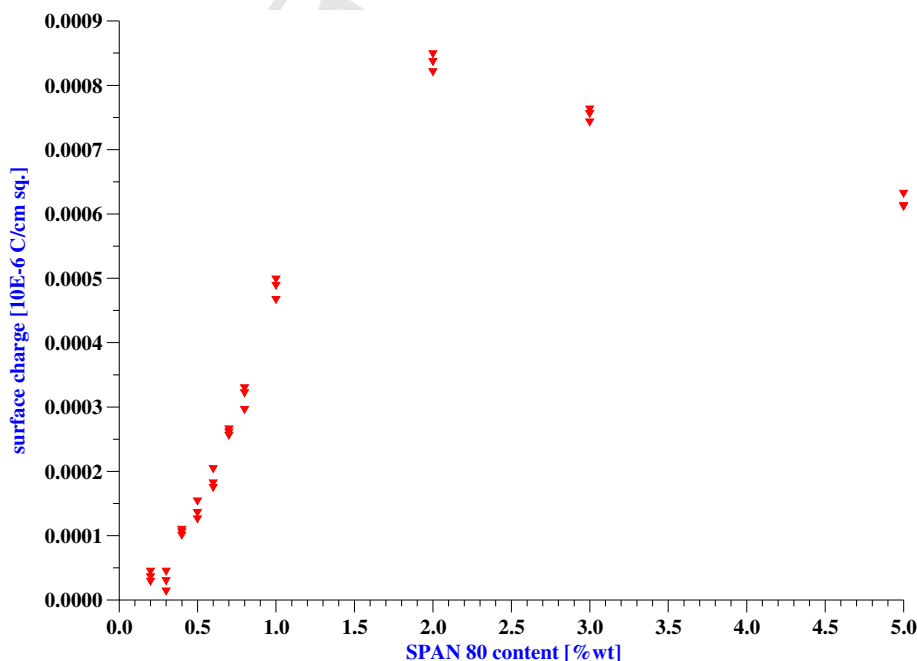


Fig. 4. Surface charge of alumina AKP-30 particles at 5%v/v in kerosene with various concentrations of SPAN 80. Each concentration point is measured three times for showing reproducibility of the method.

The decrease in the apparent surface charge at higher surfactant concentration might be explained, by some limitations of Shilov's theory. This theory is deemed valid when the Double Layers from neighbouring particles strongly overlap. This overlap condition is valid for the lower conductivity measurements, but increases in the conductivity and related ionic strength leads to the collapsing of the Double Layer and, consequently, a decrease in the overlap between particles DLs.

5. Calculation of the size of anions and cations

The combination of conductivity and electroacoustic data for the alumina dispersion at 1% surfactant content gives us sufficient data for calculating the size of the ions. At the 1% surfactant level we can attribute the residual conductivity of the dispersion (Fig. 3) solely to the anions, because practically all cations are adsorbed by the alumina particles. This gives us the following equation for the specific conductivity K :

$$K(\text{at } 1\%) = \frac{F^2}{RT} D^- C_0^- \quad (1)$$

where F is the Faraday constant, R is a gas constant, T is the absolute temperature, D^- is diffusion coefficient of anions having a concentration C_0^- . Eq. (1) ignores any interaction between ions, which is justifiable at the very low

ionic strength in the considered systems. We will estimate this parameter later.

There are two unknown parameters in this equation: D^- and C_0^- .

The concentration of the anions C_0^- can be determined from the value of the particle's surface charge σ , keeping in mind the electro-neutrality condition between the particle surface and the bulk. This leads to the following expression:

$$C_0^- = \frac{3\varphi\sigma}{aF} \quad (2)$$

where φ is volume fraction of the alumina particles, and a is radius of the alumina particles, which are assumed to be monodisperse in size.

Combining these two equations, we obtain the following expression for the diffusivity of the anions, where now all parameters are known:

$$D^- = \frac{KRTa}{3F\varphi\sigma} \quad (3)$$

At the 1%wt surfactant concentration, we have the following values for the relevant parameters: $K = 10$ pS/cm; $a = 0.5$ μm ; $RT/F = 0.025$ V; $\sigma = 5 \cdot 10^{-6}$ C/m²; and $\varphi = 0.05$. Accordingly, the computed value for the diffusion coefficient the SPAN 80 anion is:

$$D^- \approx 10^{-7} \text{ cm}^2/\text{s} \quad (4)$$

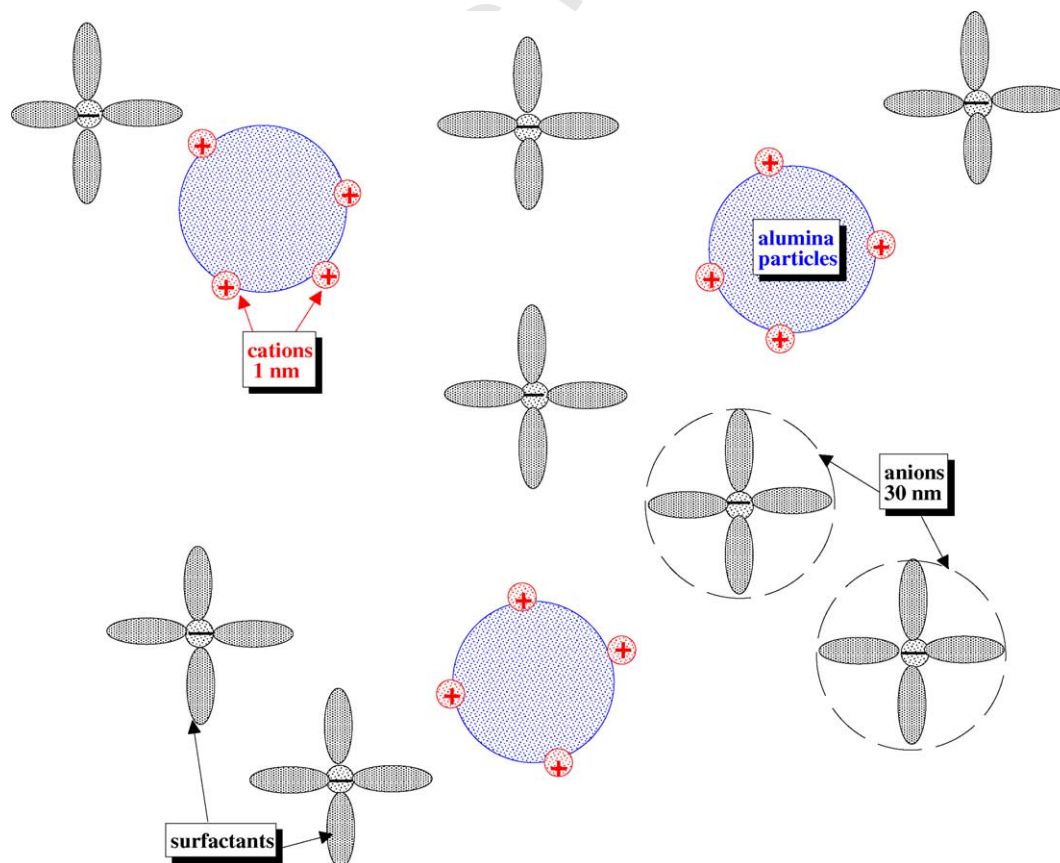


Fig. 5. Cartoon illustrating ions structure and position in the dispersed system described in the text.

Having now the diffusion coefficient for the anion, we can make an approximate estimate of the ion radius a_i using the Einstein expression for the diffusion coefficient:

$$D^- = \frac{kT}{6\pi\eta a_i} \quad (5)$$

where k is Boltzmann constant, and η is dynamic viscosity. Using an approximate viscosity of 1.5 cp, this results in a radius for the SPAN 80 anions in kerosene of 14.6 nm, or a micelle diameter of about 29 nm, which is surprisingly close to the Bjerrum critical diameter of 28 nm computed by Morrison [2].

To calculate the size of the cations we can use the difference in conductivity between the plain kerosene and the alumina dispersion at the same 1%wt of the surfactant (Fig. 3). At this concentration all of the cations are deemed adsorbed on the alumina surface, so we can attribute this difference in conductivity solely to the cations. This difference in conductivity (300 vs. 10 pS) is about 30 times larger than the residual conductivity of the dispersion that is associated with anions. This means that cations are about 30 times smaller than anions, and thus we can estimate that the size of the cation is only about 1 nm.

We can also make an estimate of the ionic strength using conductivity data of the SPAN 80 solutions without particles. As an example we would use data at 1 wt%. The molar concentration C_0 of SPAN 80 at this point is 2.3×10^{-2} mol/L because its molar weight is 428 g/mol.

The conductivity of the SPAN 80 solution at this point is about 300×10^{-10} S/m. In order to calculate concentration of ions using these conductivity data we should take into account only cations because their diffusivity is much higher and they dominate electric conductivity effect. Eq. (1) yields the following simple expression for calculating ions concentration:

$$C_0^+ = C_0^- \approx \frac{KRT}{F^2 D^+} \approx 2.5 \times 10^{-8} \text{ mol/L} \quad 382$$

This low ions concentration justifies our earlier assumption about negligible ions interaction. 383

Finally, Fig. 5 illustrates the ions and the dispersed alumina particles with their approximate sizes as it follows from the described measurements and calculations. 385 386 387

6. Uncited reference 388

[11]. 389

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