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Journal of Electroanalytical Chemistry xxx (2006) xxx–xxx

Journal of
Electroanalytical
Chemistry

www.elsevier.com/locate/jelechem

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

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Received 1 September 2004; received in revised form 17 December 2004; accepted 5 January 2005

8 Abstract

9 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”.
10 These surfactants “solvate ions” in non-polar liquids by building protective shells around them, similar to the hydration layers of water
11 around ions in aqueous solutions. The number of ions, and consequently the conductivity, correlates with amount of the solvating sur-
12 factant. This is a unique situation in which “solvation” controls the number of ions. It is exactly opposite to the situation in most aque-
13 ous systems for which the solvating agent (the water molecules) is in excess and the number of ions correlates instead with the amount of
14 the dissociating agent. In order to determine the size of these “sterically stabilized” ions we use a combination of conductivity and elec-
15 troacoustic measurements. This approach was successfully used fifty years ago by Zana and Yeager to determine the size of hydrated ions
16 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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19 *Keywords:* Ions; Surfactants; Solvating; Non-polar liquid; Electroacoustics; Conductivity
20

21 1. Nature of ions in non-polar liquids

22 In order for ions to exist in a fluid they must have a suf-
23 ficiently large size, otherwise coulombic attraction, which
24 increases as the ions approach each other, would over-
25 power the thermal motion that keeps these ions apart. This
26 coulombic attraction, in the absence of some balancing
27 force, would otherwise pull the ions together to form neu-
28 tral entities. In water, ions can effectively enlarge their size
29 by building a protective solvation shell, thus isolating
30 themselves from the very polar water molecules. Such a
31 construction is impossible in non-polar liquids because
32 the molecules do not possess a sufficient dipole moment
33 to facilitate this construction. Adding to the difficulty in
34 non-polar liquids, the critical ion radius at which coulom-
35 bic attraction balances thermal motion, is much larger as

compared to water. This so-called Bjerrum radius [1] is 36
proportional to the dielectric constant [2] of the liquid. 37
Consequently it is equal to 28 nm in non-polar liquids, 38
whereas in water it is only 0.7 nm. 39

These two factors, the large Bjerrum radius and the lack 40
of dipole moments for the solvent molecules, create a very 41
unfriendly environment for ions in non-polar liquids. As a 42
result, few ions exist, which it turns leads to the very low 43
conductivity of such non-polar liquids, typically five orders 44
of magnitude less than that of pure water. 45

This short description tells us that we must create pro- 46
tective solvating shells around ions if we want to increase 47
and control the ionic concentration and conductivity of a 48
non-polar liquid. The idea of “steric stabilization” of ions 49
has been around for a long time [2–5]. Oil-soluble surfac- 50
tants can perform this function because they have a polar 51
lyophilic part with a significant dipole moment. Interaction 52
of ions with the polar parts of these surfactant molecules 53
creates the desirable protective shell as ions are encapsu- 54
lated into large structures, usually called “inverse micelles”. 55

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

68 We obtained the first confirmation of this idea with sim-
69 ple conductivity measurements of various non-ionic surfac-
70 tants, as listed in Table 1. Actually, it has long been known
71 that such non-ionic surfactants have a surprisingly large
72 conductivity [3]. However, little attention is paid to this
73 curious fact, with only some mention of ionic impurities
74 [3] as a possible cause of this conductivity anomaly. There
75 has been no explanation, or even discussion, as to why ions
76 exist in these liquids with a dielectric constant in the range
77 of 3–12 [4], but do not exist in many other non-aqueous
78 fluids.

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

85 Ion pairs are rather “loose” objects. Ions can one
86 moment briefly dissociate under thermal stress, only to be
87 pulled back a moment later by coulombic attraction. An
88 applied electric field shifts this association/dissociation bal-
89 ance towards dissociation. Surfactants, including non-ion-
90 ics, can do the same.

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

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

- 98 1. the concentration and properties of the ions pairs;
- 99 2. the concentration and properties of the solvating
- 100 surfactants.
- 101

In a given situation, one of these two factors might be 102
dominant. 103

The first factor might be dominant in the case of a pure 104
surfactant liquid, where the concentration of ions pairs is 105
the limiting factor because surfactant molecules are present 106
in excess. This explains why the conductivity of various 107
surfactants, as shown in Table 1, does not correlate with 108
surfactant properties such as HLB number or dielectric 109
permittivity. 110

The second factor would be dominant when the concen- 111
tration of surfactant is not sufficient to solvate all of the 112
available ion pairs. In practice, a surfactant solution added 113
to a non-polar liquid might often represent this case. All 114
non-polar liquids contain some ion pairs and to this we must 115
add a supply of ion pairs that come into the solution along 116
with the surfactant. We may not know much about the 117
chemical nature or concentration of these ion pairs, but this 118
information actually becomes somewhat irrelevant in this 119
case. If the total number of ion pairs substantially exceeds 120
the solvating capacity of the added surfactant, we are led 121
to the interesting conclusion that the *electrical conductivity*
122 *of this non-polar liquid becomes a function of the added con-*
123 *centration of a non-ionic, non-dissociating substance.* 124

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

130 An important use for conductivity measurements is an
131 estimate of the ion concentration. In order to perform this
132 calculation, one needs information about the diffusivity, or
133 size, of the ions. This presents a problem for non-polar liq-
134 uids, because the size of the “surfactant solvating ions” is
135 unknown. To resolve this question, we employed an elec-
136 troacoustic technique similar to that used, successfully by
137 Zana and Yeager [7–10] fifty years ago to characterize
138 the size of solvated ions in water. This study applies this
139 technique for characterizing the size of ions in a set of
140 non-ionic surfactants in kerosene. *It will be shown that*
141 *the size of the cations and anions are very different.* In the
142 present case, only the anion is solvated. The cation remain
143 small, practically the same size as in water. We have not
144 found any reference considering this possibility. It is usu-
145 ally claimed that ions in non-polar liquids must be large.
146 Actually, this statement has to be applied to just one type
147 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

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

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

162 Investigation of these peculiar properties of non-ionic
163 surfactants might have particular relevance to environmen-
164 tal concerns in industrial applications because these surfac-
165 tants "...are much less harmful than ionic ones and thus
166 can be considered for food, pharmaceutical and cosmetic
167 applications ..." [12].

168 2. Conductivity of non-polar liquids with non-ionic 169 surfactants

170 For conductivity measurements we used Models 627 and
171 645 of Conductivity Meter by Scientifica. Model 627 oper-
172 ates at 18 Hz with an applied voltage of about 5 V rms. The
173 measurement range is from 20 to 20,000 picosiemens/cm.
174 Model 645 operates at higher conductivities range of
175 nano-siemens/cm.

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

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

186 Fig. 1 shows the conductivity of kerosene with added
187 amounts of the various surfactants. It is important to
188 note that the conductivity generated by added amounts
189 of the two SPAN 80 surfactants is the same, in spite
190 of the fact that the conductivity of these two surfactants
191 by themselves was quite different. A similar situation is
192 observed in comparing the effect of the SPAN 80 and
193 Arlcel 83, which have similar HLB number (4.3 vs.
194 3.7). Although the conductivity of the Arlcel 83 is four
195 times that of the SPAN 80 it is only slightly more effec-
196 tive in increasing the conductivity of the kerosene
197 solution.

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

202 We think that these data confirm our hypothesis that the
203 observed conductivity is related to the solvation of ions cre-
204 ated after breaking up of the ions pairs.

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

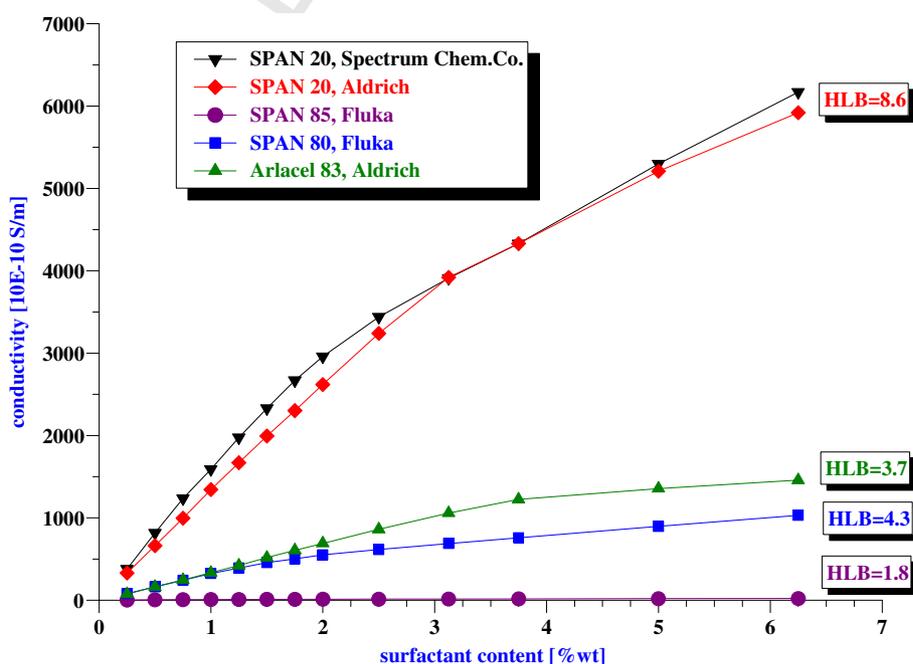


Fig. 1. Conductivity of the kerosene solutions with various non-ionic surfactants.

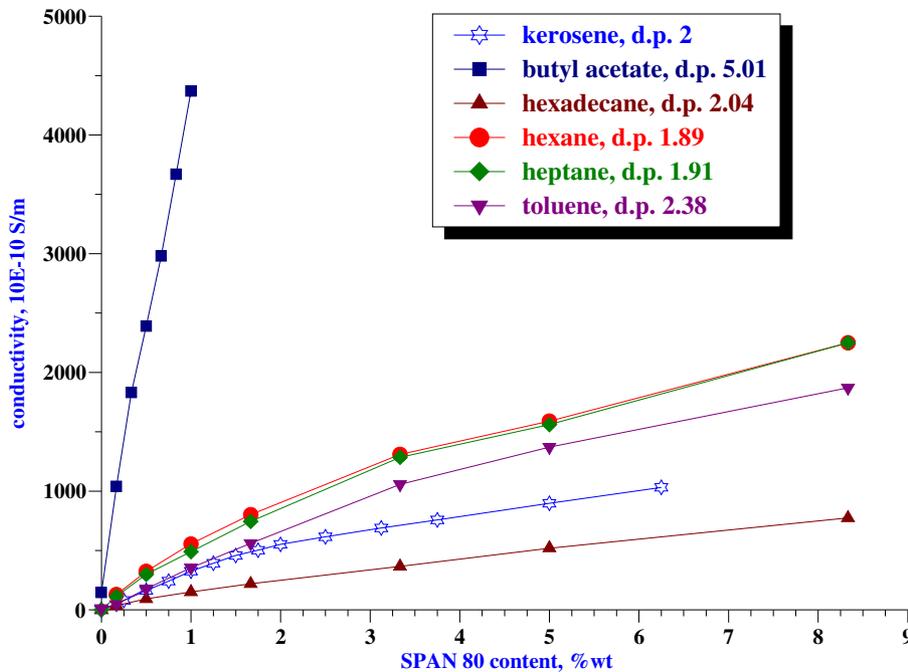


Fig. 2. Conductivity of the various non-polar liquids with SPAN 80. Abbreviation d.p stands for dielectric permittivity of the liquid.

212 3. Conductivity measurement combined with adsorption on 213 alumina surface

214 There is a simple way to learn the properties of cations
215 and anions separately. We can add small solid particles to
216 the kerosene/surfactant mixture. We propose that the par-
217 ticles will adsorb either the positive or negative ions, but
218 not both. We will verify this assumption later with an inde-
219 dependent measurement of the surface charge on the parti-
220 cles. The other ion, not adsorbed, would remain in
221 solution and still contribute to the conductivity.

222 We made such tests using a well-dried alumina, Sumi-
223 tomo AKP-30, having a nominal diameter of 0.3 μm [13].
224 We measured the size distribution of a 5%v/l dispersion in
225 kerosene using a Dispersion Technology DT-1200 Acoustic
226 Spectrometer [14]. In kerosene the alumina is slightly
227 aggregated and the measured diameter was about 1 μm .

228 Fig. 3 shows the conductivity vs. surfactant concentra-
229 tion for both plain kerosene and for kerosene with added
230 5%v/l alumina particles. The reduction in conductivity with
231 added alumina particles reflects the adsorption of ions by
232 the alumina particles. There are two possible explanations

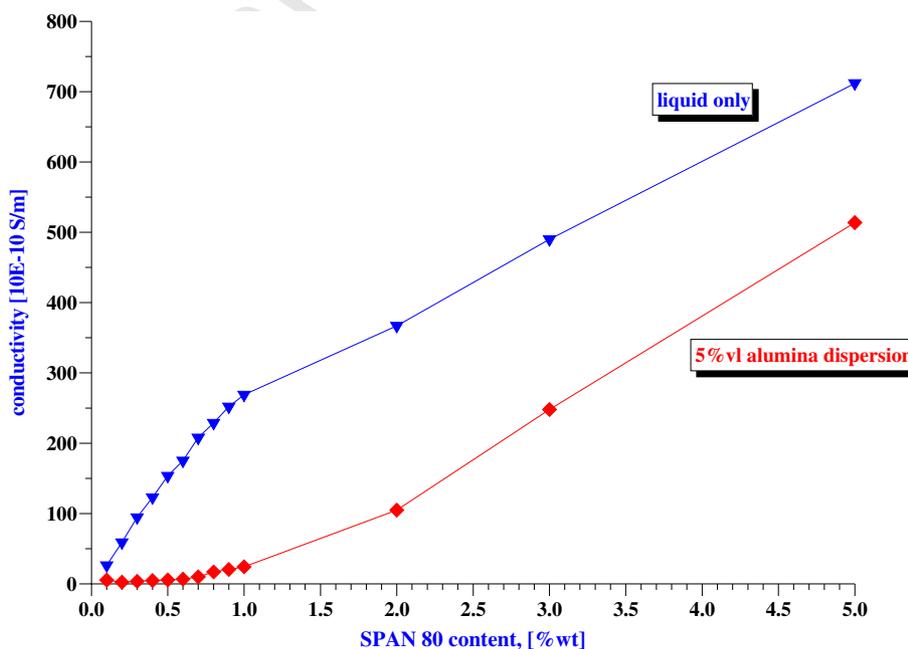


Fig. 3. Conductivity of the SPAN 80 in kerosene solutions with and without alumina AKP-30 particles at 5%v/l.

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

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

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

253 This conclusion of unequal ion size is rather new for this
254 field; the assumption of equal ion sizes is most widely used
255 [2]. In order to determine whether the adsorbed ions are the
256 anions or cations, and finally the size of the ions, we
257 employed electroacoustic measurement as described in
258 the next section.

259 4. Electroacoustic measurements

260 Debye [15] first predicted an electroacoustic effect sev-
261 enty years ago. In either electrolyte solutions or disper-
262 sions, the effect is related to a coupling between

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

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

284 The surface charge was positive as also confirmed by
285 microelectrophoresis.

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

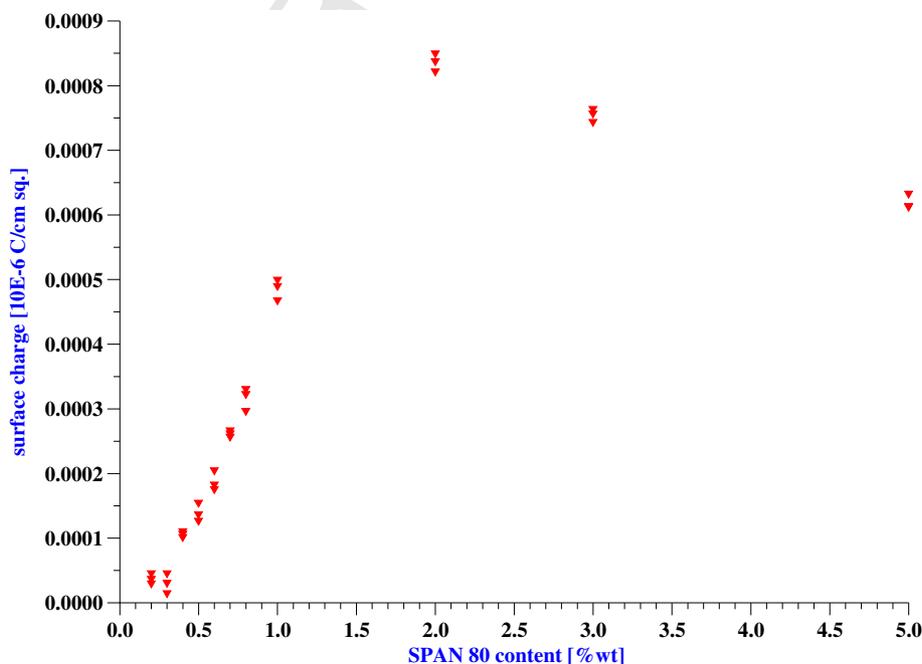


Fig. 4. Surface charge of alumina AKP-30 particles at 5%v/v in kerosene with various concentrations of SPAN 80. Each concentration point is measured three times for showing reproducibility of the method.

295 The decrease in the apparent surface charge at higher
 296 surfactant concentration might be explained, by some lim-
 297 itations of Shilov's theory. This theory is deemed valid
 298 when the Double Layers from neighbouring particles
 299 strongly overlap. This overlap condition is valid for the
 300 lower conductivity measurements, but increases in the con-
 301 ductivity and related ionic strength leads to the collapsing
 302 of the Double Layer and, consequently, a decrease in the
 303 overlap between particles DLs.

304 5. Calculation of the size of anions and cations

305 The combination of conductivity and electroacoustic
 306 data for the alumina dispersion at 1% surfactant content
 307 gives us sufficient data for calculating the size of the ions.
 308 At the 1% surfactant level we can attribute the residual
 309 conductivity of the dispersion (Fig. 3) solely to the anions,
 310 because practically all cations are adsorbed by the alumina
 311 particles. This gives us the following equation for the spe-
 312 cific conductivity K :
 313

$$315 \quad K(\text{at } 1\%) = \frac{F^2}{RT} D^- C_0^- \quad (1)$$

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

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

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

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

$$330 \quad C_0^- = \frac{3\varphi\sigma}{aF} \quad (2)$$

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

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

$$338 \quad D^- = \frac{KRTa}{3F\varphi\sigma} \quad (3)$$

339 At the 1%wt surfactant concentration, we have the fol-
 340 lowing values for the relevant parameters: $K = 10$ pS/cm;
 341 $a = 0.5$ μm ; $RT/F = 0.025$ V; $\sigma = 5 \cdot 10E - 6$ C/m²; and
 342 $\varphi = 0.05$. Accordingly, the computed value for the diffu-
 343 sion coefficient the SPAN 80 anion is:

$$345 \quad D^- \approx 10^{-7} \text{ cm}^2/\text{s} \quad (4)$$

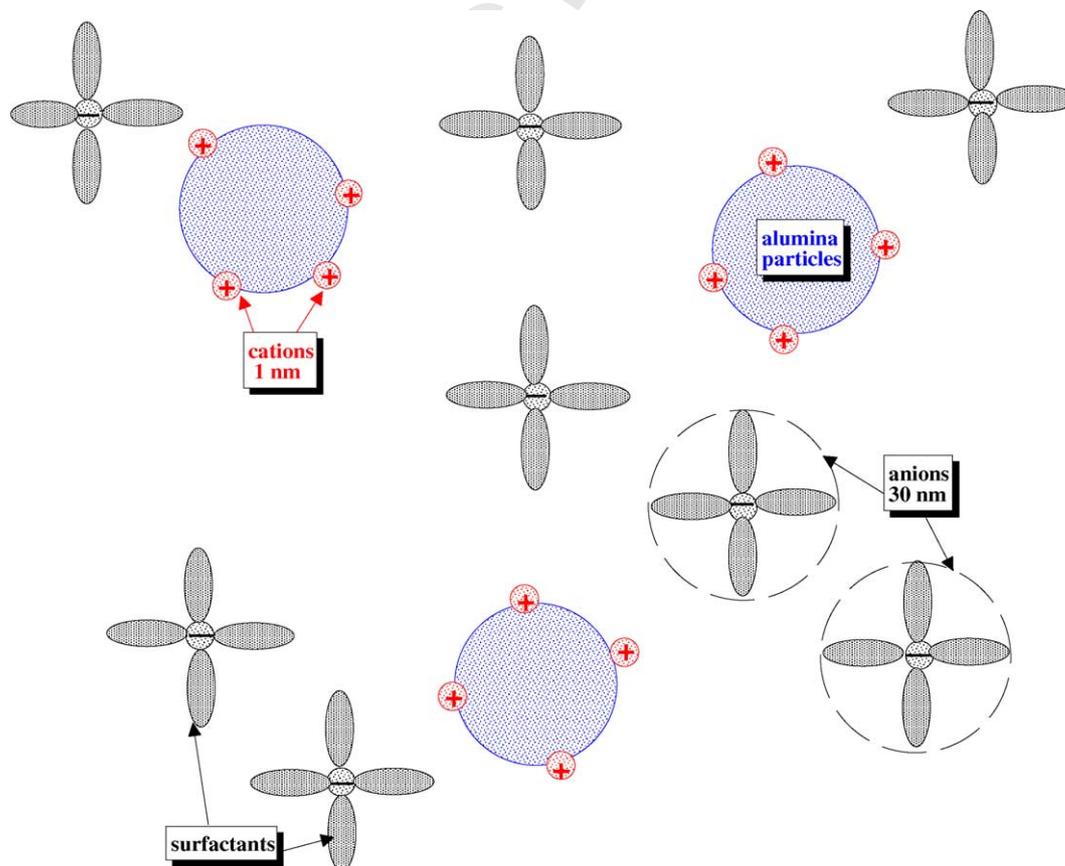


Fig. 5. Cartoon illustrating ions structure and position in the dispersed system described in the text.

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

$$350 \quad D^- = \frac{kT}{6\pi\eta a_i} \quad (5)$$

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

357 To calculate the size of the cations we can use the dif-
 358 ference in conductivity between the plain kerosene and the
 359 alumina dispersion at the same 1%wt of the surfactant
 360 (Fig. 3). At this concentration all of the cations are
 361 deemed adsorbed on the alumina surface, so we can attri-
 362 bute this difference in conductivity solely to the cations.
 363 This difference in conductivity (300 vs. 10 pS) is about
 364 30 times larger than the residual conductivity of the dis-
 365 persion that is associated with anions. This means that
 366 cations are about 30 times smaller than anions, and thus
 367 we can estimate that the size of the cation is only about
 368 1 nm.

369 We can also make an estimate of the ionic strength using
 370 conductivity data of the SPAN 80 solutions without
 371 particles. As an example we would use data at 1 wt%.
 372 The molar concentration C_0 of SPAN 80 at this point is
 373 2.3×10^{-2} mol/L because its molar weight is 428 g/mol.

374 The conductivity of the SPAN 80 solution at this point
 375 is about 300×10^{-10} S/m. In order to calculate concentra-
 376 tion of ions using these conductivity data we should take
 377 into account only cations because their diffusivity is much
 378 higher and they dominate electric conductivity effect. Eq.
 379 (1) yields the following simple expression for calculating
 380 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 assump- 383
 tion about negligible ions interaction. 384

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

6. Uncited reference 388

[11]. 389

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