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Application of classical thermodynamics to the conductivity in non-polar media

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Electrical conductivity in non-polar media is a subject which recently regained interest. If most of experiments and theoretical developments were done more than 50 years ago, new experiments and theories have been recently published. As the electrical conductivity describes, at low field, the equilibrium state of a system, it is natural to apply theories based on equilibrium thermodynamics. In this article, well-established classical thermodynamics and solvations models are applied to recently published data. This enables to get a new insight in intriguing phenomena, such as the linear dependence of the conductivity on the concentration of ionic surfactant and the evaluation of conductivity for the mixture of two miscible fluids, such as alcohol and alcane, which have very different conductivities. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4954046>]

I. INTRODUCTION

Conductivity in non-polar medium has been studied extensively. Pioneer work has been done by Fuoss and Onsager, between 1930 and 1950, on the conductivity of salt in non-polar medium.^{1,2} A large amount of work has subsequently been done by Kraus and co-workers with over 50 papers on the topic, see, e.g., Refs. 3–5. In their experiments, salts were added to different solvents, and, among other things, conductivity was measured. These authors introduced the concept of ion-pair and ion-association and determined the associated equilibrium constants. They found that either neutral or charged species are formed by association. Formation of charged species is out of this scope of the article. Formation of neutral species is reflected in a decrease of equivalent conductivity. The formation of ion-pair is enhanced in low-permittivity solvents, due to coulombic attraction. In high-permittivity solvents, ion-pair formation become significant only at high concentrations. Ions remain dissociated at low concentrations.

Recently, the topic of ions-pairing in non-polar solvent has regained interest. An extended review on ion, ion-pair, and inverse micelles in non-polar media has been done by Dukhin and Parlia.⁸ In a following article, Dukhin *et al.*⁹ state that the formation of ion-pair decreases the conductivity in the case of surfactant in non-polar solvent, by analogy with the work of Onsager, Fuoss, and Kraus. However, this analogy is questionable as we will discuss in the present article. In two subsequent articles, Dukhin, Bombard, and Parlia^{10,11} study the conductivity of mixtures of alcohols and hydrocarbons without added ionogenic substance. The conductivity varies non-linearly, by several orders of magnitude, with the composition of the mixture. The authors develop a theory based on ion-pair formation, which enables them to fit the data, but the hypotheses they make are disputable due to their lack of compatibility with classical thermodynamics. We would here like to propose different hypotheses that are compatible with thermodynamical laws.

In the present article, two cases, corresponding to two different thermodynamic conditions, will be distinguished. These cases are explicitated in the first part of the article. Each case is illustrated using data taken from literature. In a second part, systems consisting of mixtures of non-polar liquids will be analysed. In the last part, a system consisting of microemulsions will be discussed.

II. PART I: QUALITATIVE EFFECT OF THE FORMATION OF ION-PAIR ON THE CONDUCTIVITY, IN A GIVEN SOLVENT

Ion-pair formation was first described by Bjerrum¹² in the case of dissolved salt in various solvents. If the dielectric permit of the solvent is low enough, or if ions are charged enough, the attraction between anion and cation can lead to the formation of ion pairs. Three kind of ion pairs exist, for symmetric salts: ion pairs without shared solvation layer, ion pairs with shared solvation layer, and ion pairs with contact between ions. In a given solvent, the three kinds of ion-pairs can be treated with only one equilibrium constant, which is the sum of the three equilibrium constants of ion-pairing. Several models have been proposed for determining the equilibrium constant of ion pairs.^{13–16} In this first part, the effect of the formation of ion pair on the number of free ions and hence on the conductivity (as the conductivity is proportional to the number of free ions, at low enough concentration of free ions) will be discussed for two thermodynamically different cases.

Case I: This case corresponds to the one in which the ionic species formation is limited by the quantity of added salt. The salt is therefore assumed to be totally dissolved.

Case II: This case corresponds to the one in which the ionic species formation is limited by the chemical potential of a non-ionic species or an excess of salt, in equilibrium with the free ionic species.

Each case is illustrated by experimental data from the literature.

A. Case I

In this case, it has been established that the creation of ion-pair decreases the concentration of free ions and thus decreases the conductivity.¹⁷

A simple way to describe the formation of ion-pairs in this case is to consider them as a chemical species, where a law of mass action can be applied. We note C^+ the cationic species, with a charge +1. We note A^- the anionic species, with a charge -1. We note AC the ion-pair, and we suppose that only neutral AC species exists (no species like ACA^- or CAC^+ are considered). If the solution is dilute enough, the chemical activity is proportional to the molar concentration and we may write

$$[A^-, C^+]c_0/[A^-][C^+] = K_{AC}, \quad (1)$$

where c_0 is a concentration of 1 mol/l, for the sake of homogeneity of the equation. A dimensioned constant, $K_{AC}^* = K_{AC}/c_0$, may be defined, for practical use.

Existence of three types of neutral ion-pair does not change the thermodynamics. As said above, one may still consider them as only one chemical species and use an effective equilibrium constant which is the sum of the three separate ones.

If there is only C^+ and A^- as ionic species, due to electroneutrality,

$$[C^+] = [A^-]. \quad (2)$$

We have three unknowns ($[A^-]$, $[C^+]$, and $[AC]$) and two equations: a third equation is required.

This third equation is the conservation of mass, which links the concentration of ionic species to the concentration of ion-pairs,

$$[A^-] + [A^-, C^+] = C_m. \quad (3)$$

C_m being the concentration of added salt. It would be the concentration of A^- or C^+ without formation of ion-pairs. Combining the three equations and solving the resulting second-order equation yield the classical textbook result

$$[A^-] = [C^+] = (\sqrt{1 + 4K_{AC}^* \times C_m} - 1)/2K_{AC}^*. \quad (4)$$

Two limits can be distinguished.

If $K_{AC}^* \times C_m \gg 1$,

$$[A^-] = [C^+] = \sqrt{C_m/K_{AC}^*}. \quad (5)$$

[As one can easily see, taking $K_{AC}^* \times C_m \gg 1$ and $[A^-, C^+] \simeq C_m$ in the action of mass law will lead to the same result.]

If $K_{AC}^* \times C_m \ll 1$,

$$[A^-] = [C^+] = C_m - K_{AC}^* \times C_m^2. \quad (6)$$

[As one can easily see, taking $K_{AC}^* \times C_m \ll 1$ and $[A^-] \simeq C_m$ in the action of mass law will lead to the same result.] Eq. (6) agrees with the Debye-Huckel-Onsager (or Fuoss-Onsager) expression.⁷ Dukhin *et al.*, on the other hand, found a different relation, which reads $[A^-] = [C^+] = C_m - 2K_{AC}^* \times C_m^2$.^{8,9} Dukhin *et al.* attribute this difference to the definition of K_{AC}^* . However, the difference is due to an

error in the Taylor expansion of a square root.⁹ From Eqs. (1) and (6) we can also deduce that

$$[A^-, C^+] = K_{AC}^* \times [A^-]^2 \simeq K_{AC}^* \times C_m^2. \quad (7)$$

From these results, we may conclude that for systems in case I, below the solubility limit, at any given C_m , ion-pairs formation (thus the formation of $[A^-, C^+]$) decreases the concentration of free ion (A^- and C^+) and therefore decreases the conductivity see Fig. 1.

There are countless experiments on the conductivity of fully dissolved salt in low polar solvent. The series of articles "Properties of Electrolytic Solutions," by Fuoss, Kraus *et al.*, published over 20 years, contains more than 50 articles on the topic. These authors found a decrease in the conductivity with the increase in concentration, and a method to find the limiting specific conductivity and the equilibrium constant of ion-pair formation from the conductivity measurements.⁶ They also found, for some systems, an increase of the specific conductivity at high concentration, which they attributed to the formation of triple-ion species ($A^-C^+A^-$ or $C^+A^-C^+$). The creation of these species is out of scope of this article.

B. Case II

This case corresponds to several situations as follows.

(a) An excess of salt, which remained undissolved: the chemical potential of the neutral species does not depend of the creation of ion pair.

When an excess of salt is added to a solution, some salt remains undissolved. In such a case, the chemical potential of the salt is constant. It creates a second law of mass action,

$$[A^-][C^+] = K_{dissAC} \times c_0^2 = K_{dissAC}^*. \quad (8)$$

Together with the first law of mass action,

$$[A^-, C^+]/[A^-][C^+] = K_{AC}^*, \quad (9)$$

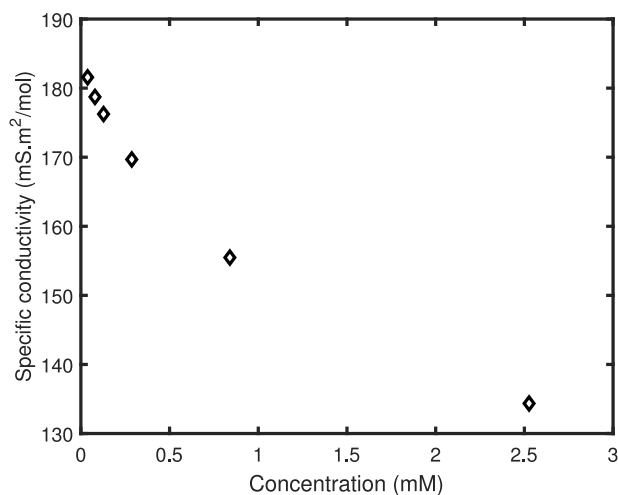


FIG. 1. Specific conductivity of tetra-*n*-butylammonium nitrate in acetone as a function of the concentration. The decrease is due to both ion-pairing and corrective forces. Data taken from Ref. 6.

and with the electroneutrality,

$$[A^-] = [C^+], \quad (10)$$

we find

$$[A^-, C^+] = [A^-][C^+]K_{AC}^* = K_{AC}^* \times K_{dissAC}^* \\ [A^-] = [C^+] = \sqrt{K_{dissAC}^*}. \quad (11)$$

In this case, as the chemical potential of the salt is kept constant, ion-pairs' formation does not change the concentration of free ions. So ion-pair formation does not change the conductivity.

It is not possible to measure the effect of ion-pair formation in the case of an excess of salt in a solvent. As the experiment is done at one concentration, it is not possible to study the evolution of the conductivity with the concentration.

(b) Autoprotolysis ($2AH \rightarrow A^- + AH_2^+$): the constant is low enough to ensure no variation of the concentration and therefore of the chemical potential of the neutral species. The same holds for autoprotolysis as for an excess of salt: in a pure solvent, there is no parameter to change, and thus no evolution to see.

(c) A dissociation of a weak acid ($AH = A^- + H^+$) with an equilibrium constant K_{AH}^* , and ($A^- + H^+ = A^-, H^+$) with a constant K_{AC}^* . A new equilibrium constant between neutral species (AH and A^-, H^+) and free ionic species may be written, with a value of $1/(1/K_{AH}^* + K_{AC}^*)$. The effect on the free ion concentration depends on the product of the constant K_{AH}^* and K_{AC}^* and of the concentration. If the dissociation is almost complete, effect of ion-pairing in this case is the same as in the case of fully dissolved salt. If the dissociation is very small, the ion-pairing is likely to have no effect, as it should not change the equilibrium constant too much between neutral species and free ions.

(d) A disproportionation of micelles ($2M = M^+ + M^-$), see Ref. 30. The constant is low enough to ensure no variation of the chemical potential of the neutral species. This last system is of interest for studying the effect of the formation of ion-pair at a constant chemical potential, as the conductivity of micelles as function of ionic surfactant can be measured: it has been found that the conductivity is linearly dependent on ionic surfactant solution in a non-polar medium.²⁴⁻²⁶ One can see from Fig. 2 that the curve is somewhat convex. In case that ion-pair has an effect on conductivity, one would expect a concave (sublinear) curve. The convexity is likely due to the increase of the permittivity of the system.

Dukhin⁸ rose an interesting question, about the effect of ion pair formation on the conductivity: "This is surprising conclusion requesting explanation why the electrostatic attraction between inverse micelles cations and anions does not lead to the formation of the ion-pairs. There is currently no clear answer to this question. Many authors use disproportionation model that predicts linear conductivity dependence as such answer. However, disproportionation model simply ignores ion-pairing. It does not provide any reason explaining why it does not occur." Dukhin did not find a convincing explanation for the absence of ion-pairing in the available literature and hypothesized that

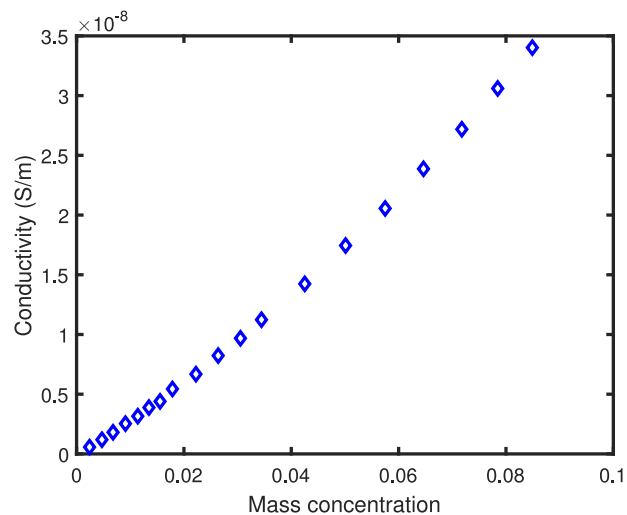


FIG. 2. Conductivity of a ionic surfactant, AOT, in heptane, as a function of the mass concentration of AOT. Data taken from Ref. 8.

the phenomena might be linked to the size of micelles.⁹ He concludes by saying that more experiments are needed to confirm this hypothesis. There is however a simple explanation.

One strong hypothesis of the disproportional model is that the shape of the formed micelles, or their sizes, or any other properties do not change with micelle concentration. We will use this hypothesis, as all others authors do. As there is a condition of fixed chemical potential, ion pairs' formation has no effects on the conductivity. This does not mean that there is no ion-pairs formation. Indeed, the concentration of charged micelles is linked to the concentration of the neutral ones $[M]$ by a law of mass action. The disproportionation model reads, in terms of chemical equation,



which implies

$$[M^+][M^-]/[M]^2 = K_{dispr}. \quad (13)$$

Due to electroneutrality, $[M^+] = [M^-]$. The conductivity is proportional to $[M^+]$, therefore it is proportional to $\sqrt{K_{dispr}}[M]$.

Formation of ion-pairs M^+M^- does not change the concentration of free charged micelles, as this concentration is fixed by K_{dispr} . The concentration of ion pairs is proportional to $[M^+][M^-]$ so it is proportional to $[M]^2$. As long as this concentration is low compared to $[M]$, which should be the case because the creation of charged species is not favored in a low polarity solvent, it does not change the conductivity or the concentration of free charged micelles.

For all the cases (a)-(d), the creation of ion-pair does not change the chemical potential of the ionogenic species. Therefore it does not change the chemical potential of free ionic species and thus their concentration. As a consequence, the conductivity is not changed by the formation of ion-pairs.

III. PART II: MIXTURES OF NON-POLAR LIQUIDS AND THE EFFECT OF DIELECTRIC PERMITTIVITY

By mixing two solvents with different permittivities, it is possible to create a new solvent with an adjustable dielectric permittivity, as it was done by Fuoss.³¹ If the dielectric permittivity ϵ_r varies, the equilibrium constant K_{AC} becomes a function of the dielectric permittivity.

This dependence of the equilibrium constant may be calculated. We here calculate the modification of equilibrium constant for the ion-pairs formation. The method extends straightforward to the dissociation or disproportionation reactions.

According to classical thermodynamics,

$$-RT \ln K_{AC} = \Delta_r G_{AC}^0, \quad (14)$$

with $\Delta_r G_{AC}^0$ the standard free enthalpy of reaction, and R the constant of ideal gases and T the absolute temperature.

By definition,

$$\Delta_r G_{AC}^0 = \Delta_r H_{AC}^0 - T \Delta_r S_{AC}^0, \quad (15)$$

where $\Delta_r H_{AC}^0$ is the standard enthalpy of reaction and $\Delta_r S_{AC}^0$ is the standard entropy of reaction. Free enthalpy is therefore enthalpy, freed from entropy. We assume that standard entropy of reaction does not depend strongly on the dielectric permittivity. Standard enthalpy of reaction may be split in three terms as follows:

$$\Delta_r H_{AC}^0 = \Delta_r^{chemical} H_{AC}^0 + \Delta_r^{solvation} H_{AC}^0 + \Delta_r^{electrostatic} H_{AC}^0. \quad (16)$$

The first term, $\Delta_r^{chemical} H_{AC}^0$, is the due to destruction and creation of chemical bounds during the reaction. For ion pairs, this term is zero. The second term, $\Delta_r^{solvation} H_{AC}^0$, is due to the modification of the solvation shell. We assume that the solvation shell does not depend on the composition of the liquid, which is true if one species is polar and the other non-polar. Indeed, polar species will build the solvation shell, as long as they are in non-negligible quantities. This term is zero for ion-pair formation when ions keep their solvation shell. It is non-zero in the case of ion-pair with shared solvent or when there is contact between ions. However, it does not depend strongly on the dielectric permittivity. Only the third term, $\Delta_r^{electrostatic} H_{AC}^0$, depends strongly on the dielectric permittivity. It is the coulombian energy, therefore we find, for ion-pair formation,

$$\Delta_r^{electrostatic} H_{AC}^0 = -\frac{N_a e^2}{4\pi\epsilon_0\epsilon_r d_{AC}}, \quad (17)$$

with d_{AC} the distance between anion and cation in an ion-pair, e the elementary charge, ϵ_0 the permittivity of vacuum, ϵ_r is the relative permittivity of the medium, and N_a the Avogadro number.

Effect of decreasing the dielectric permittivity of a medium (e.g., by addition of hydrocarbon to an alcohol) depends on the system. Two cases are of particular interest. The first one, where ionic species are due to a dissolved salt. The second one, where it comes from an excess of salt or from a dissociating species.

A. Case I

In this case, the equilibrium constant for ion-pairs varies with the dielectric permittivity as

$$K_{AC}^* \sim \exp\left(+\frac{N_a e^2}{4\pi\epsilon_0 d_{AC} RT \epsilon_r}\right). \quad (18)$$

If ions are already in majority in ion-pairs form, free ion concentration varies as $\sqrt{C_m/K_{AC}^*}$, as will the conductivity.

If ions are mostly free, free-ion concentration varies as Eq. (6): $[A^-] = C_m - K_{AC}^* \times C_m^2$. The variation of the conductivity as function of the dielectric permittivity is quite smooth as long as the equilibrium constant is small compared to $1/C_m$.

Caution is needed when handling these equations, especially if ions are dissolved in liquid A, at a constant concentration, and liquid A is then mixed with liquid B. In this case, C_m varies linearly with the proportion of liquid A.

The variation of the equilibrium constant with the permittivity was studied by Fuoss, for tetraisoamylammonium nitrate in mixture of water and dioxane.⁵ The data are reproduced Fig. 3, and the fitting distance is 0.66 nm, which is a realistic value for this distance, as the sum of radii is equal to 0.60-0.72 nm depending on the radius chosen.^{18,19}

B. Case II

In this case, the equilibrium constant varies with the dielectric permittivity as

$$K_{AC}^* \sim \exp\left(+\frac{N_a e^2}{4\pi\epsilon_0 d_{AC} RT \epsilon_r}\right). \quad (19)$$

For K_{dissAC}^* , we use the same reasoning as above. Most of the dependence in dielectric permittivity lies in the term: $\Delta_r^{electrostatic} H_{dissAC}^0$. According to the model of Born,²⁰ the

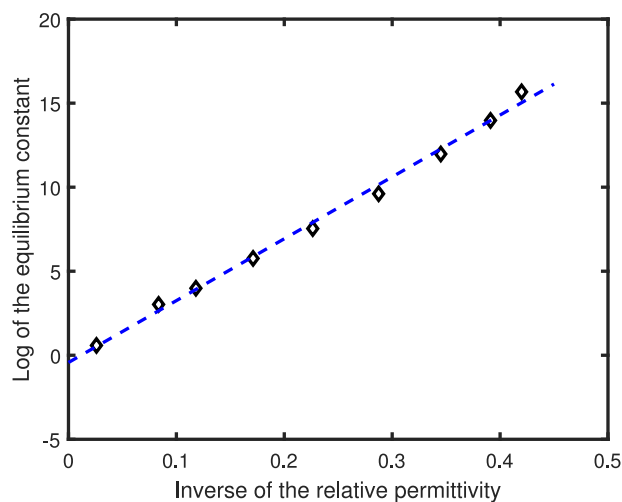


FIG. 3. Dependence of the equilibrium constant on the relative permittivity, for tetraisoamylammonium nitrate in water-dioxane mixtures. The blue curve is a fit corresponding to a distance between ions of 0.66 nm. Data taken from Ref. 5.

electrostatic energy of creation of one ion depends on

$$\frac{N_a e^2}{8\pi\epsilon_0 a_{ion} \epsilon_r}, \quad (20)$$

with a_{ion} the radius of an ion. Since the dissociation of one neutral molecule creates two ions, the electrostatic energy involved depends on

$$\frac{2N_a e^2}{8\pi\epsilon_0 a_{ion} \epsilon_r}, \quad (21)$$

if both ions have the same radius, as, for example, alcoholate and alcoholium ions, we get

$$K_{dissAC}^* \sim \exp\left(+\frac{N_a e^2}{4\pi\epsilon_0 a_{ion} RT \epsilon_r}\right). \quad (22)$$

This expression thus differs by a factor up to two in the exponential from the ion-pair formation constant K_{AC}^* as $d_{AC} = 2a_{ion}$ if the solvation shell is kept in the ion-pairs. A factor of two in an exponential means that the variation of the dissociation constant is the square of the variation of the ion-pair formation constant.

As the free salt concentration and thus the conductivity are proportional to $\sqrt{K_{dissAC}^*}$, the dependence on the dielectric permittivity is given by the factor $\exp(-N_a e^2 / (8\pi\epsilon_0 a_{ion} RT \epsilon_r))$.

Let us consider the case of auto-protolysis of an alcohol mixed with hydrocarbon.

For the sake of argument, we assume that the mixture is ideal, so the activity of alcohol depends on the logarithm of its concentration. This hypothesis is strong and is likely to be crude. However, more advanced models, such as regular solutions or an Ising-like model, require more calculations, but the changes in conductivity are likely to be small compared to the changes due to the dielectric permittivity. We also assume that ions created are solvated in the same way in pure alcohol and in mixtures, which is likely to be true, as the polar alcohol tends to bind to the charged species. Under these hypothesis, the concentration of ions varies as $[\text{alcohol}] \times \sqrt{K_{dissAC}^*}$. Therefore, as the dielectric permittivity changes, the concentration of ions varies dramatically.

C. Discussion about recent experimental findings

There was, up to this date, no experimental data on this case. Recently, experimental work has been published on mixture of alcohol and hydrocarbons by Dukhin and co-workers.^{10,11} On these mixtures, only one other publication can be found, on the conductivity of mixtures of ethanol and gasoline.³²

In the first article,¹⁰ written by Dukhin and Bombard, the conductivity of a mixture of *n*-octanol and an alkane (PAO) of similar viscosity was measured. The authors found a very non-linear dependence (almost an exponential dependence) of the conductivity on the fraction of alcohol. They explained it by a first theory¹⁰ that they retracted one year later.¹¹ On the two curves of the article, we choose the one obtained by Dukhin, as there is currently no theory explaining the one of Bombard. According to Dukhin *et al.* the differences between the two set of experimental data are due to the differences in octanol used.

In the second article,¹¹ Dukhin and Parlia measure the conductivity and electric permittivity of mixtures of alcohol and toluene, for 8 alcohols. They again find a very non-linear dependence of the conductivity on the fraction of alcohol, at low alcohol content. For some alcohols (methanol, ethanol, propanol, and butanol), they find a quite linear relation between the conductivity and the alcohol content, at high alcohol content.

We show the data for a mixture of ethanol and of heptanol with toluene in Fig. 4. An important question is the nature of the free ions in the system. There are a few possibilities. The ions may be created by: a dissolution of salt or a dissociation of strong acid (both correspond to Case I), autoprotolysis or by the dissociation of a weak acid (both correspond to Case II). We can safely rule out the case where an excess of salt remains undissolved. Note that we do not discard the fact that there might be other possibilities.

One strong hypothesis required to interpret the data is that the ion creation process is the same for the eight alcohols.

Dukhin *et al.*¹¹ assumed that ions were created by autoprotolysis. As the conductivity is roughly proportional to the free ions concentration, as the free ions concentration is proportional to the square root of the autoprotolysis

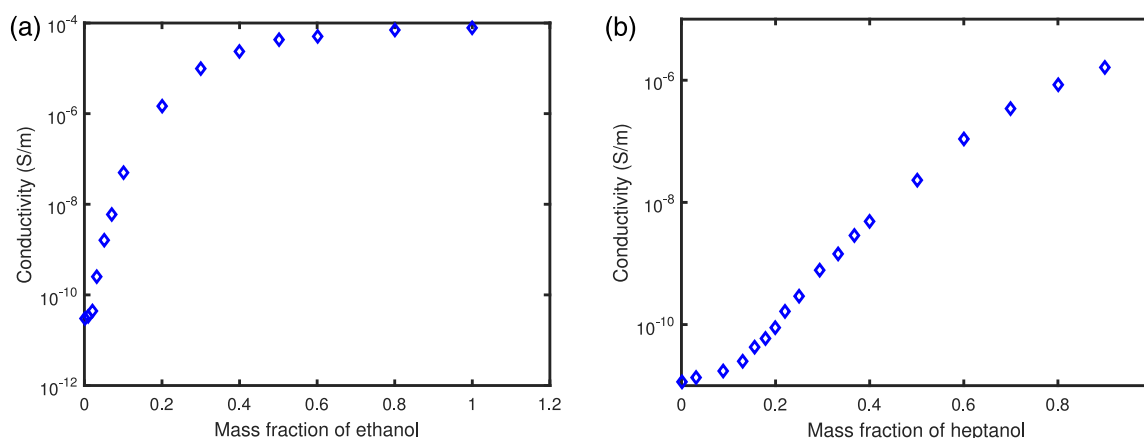


FIG. 4. Conductivity of a mixture of alcohol and toluene, as a function of the mass fraction of alcohol, log/lin. (a) Left: ethanol. (b) Right: heptanol. Data taken from Ref. 11.

constant, as the autoprotolysis constant changes dramatically with dielectric permittivity, the conductivity should depend strongly on it. As can be seen in Fig. 4, for mixture of ethanol and toluene, the conductivity does not depend strongly on the concentration of alcohol as it is more than 60%. It depends linearly, which suggests a dilution effect. For three other alcohols, methanol, propanol, and butanol, the behaviour is the same. Therefore, autoprotolysis may be ruled out. It would be contrary to the classical thermodynamics to assume that the auto-protolysis constant does not vary with the dielectric permittivity as done in Ref. 11. Moreover, the experimental values of conductivity imply high concentrations of charged species. The found related auto-protolysis constants in Ref. 11 are higher by 9 orders of magnitude than the IUPAC ones.³³

There is currently no way to find the nature of ionic species in these systems, however it is possible to make a reasonable guess. We assume that there is a small apparent conductivity of the alcane, σ_{PAO} . In practice, this apparent conductivity might be the true alcane conductivity, but it might also be related to the limit of detection of the measurement device. The value of σ_{PAO} is given by the measured conductivity of pure alcane. The octanol conductivity, σ_{oct} , is the one measured with “pure” octanol (not mixed with the alcane). In the octanol/alcane mixture, the conductivity depends on the content of octanol (x). The dissociation of a neutral species (which might be a weak, carboxylic, acid) or the separation of ion-pairs is determined by the content of octanol x . We suppose that the dissociating neutral species or the ion-pairs are present only in the “pure” octanol and not in the pure alcane. Thus, the concentration of dissociating species is proportional to the octanol content x . We also suppose that this neutral species or these ion-pairs are mostly non-dissociated in pure octanol. The total conductivity is thus

$$\sigma = \sigma_{PAO} + x\sigma_{oct} \exp\left(+\frac{N_a e^2}{8\pi\epsilon_0 d R T} \left(\frac{1}{\epsilon_r(x)} - \frac{1}{\epsilon_r(x=1)}\right)\right). \quad (23)$$

We may check that for $x = 1$, i.e., for “pure” octanol, $\sigma = \sigma_{PAO} + \sigma_{oct} \simeq \sigma_{oct}$. All terms such as absolute concentration of dissociating species and non-electrostatic contributions to the free enthalpy of dissociation are included in σ_{oct} . To apply Eq. (23), we use σ_{PAO} and σ_{oct} , found from experiments. These two experimental parameters have to be measured, as they depend on the alcane and of the octanol chosen. The remaining unknowns are the function $\epsilon(x)$ what we call the electric distance d which is a parameter to be found. For estimating d we assume that the ion has only one solvation layer and that this solvation layer is made of octanol molecules.

To determine if it is most likely a dissolved salt or a weak acid, we do the following hypothesis:

- Ions pair are solvent separated, and so we do not consider shared solvent or contact ion-pair. Shared solvent or contact ion pair will yield a result very close to the one of a weak acid. We assume that these ions, with solvation, have the same size than alcohol molecule.

- The weak acid is of the size of the alcohol, it is reasonable if the weak acid is derived from the alcohol (octanoic acid in octanol, or heptanoic acid in heptanol).

If ions-pair are solvent separated, we can assume a distance d which is the double of the size of an alcohol molecule. If it is the dissociation of a weak acid, the size of ions is the size of the alcohol molecule. The size of octanol is 0.685 nm, according to Marcus, and the size of heptanol is extrapolated to 0.655 nm.

For $\epsilon(x)$, the relative permittivity of alcane/octanol mixture, we use the Maxwell-Garnett formula

$$\frac{\epsilon(x) - \epsilon_{PAO}}{\epsilon(x) + 2\epsilon_{PAO}} = x \frac{\epsilon_{oct} - \epsilon_{PAO}}{\epsilon_{oct} + 2\epsilon_{PAO}}. \quad (24)$$

Therefore, the mixture of alcane and octanol is considered as an inclusion of octanol in alcane. As in alcohol the polar head is small, even for high concentration of alcohol, it is possible that the approximation will not be too bad.

To simplify the analysis, we study the case of a mixture of toluene and heptanol, and the case of a mixture of octanol and an oil. As octanol and oil have the same viscosity, the viscosity is likely to be independent of x for this mixture. For mixture of heptanol and toluene, we use the formula $\eta(x) = \eta^x(1)\eta^{1-x}(0)$, a common approximation since Arrhenius.³⁴

The agreements between the theory presented above and Dukhin's data are very good (see Fig. 5) when we assume that the dissociating species in the alcohol is the related carboxylic acid, i.e., with $d = 0.685$ nm for octanol mixture and $d = 0.655$ nm for heptanol. However, this good agreement is not enough to prove all our main assumptions:

- (1) there is dissociation of a neutral species;
- (2) this neutral species is the related carboxylic acid;
- (3) this neutral species is present only in alcohol and not in the alcane;
- (4) the Maxwell-Garnett equation is valid.

The use of other hypotheses could yield a good agreement between theory and experiment, e.g., we could suppose that small ions form a contact pair. The theory only proves the role of electrostatics on the conductivity of such a mixture, which is quite obvious.

There is still a problem. To account for the conductivity of light alcohol, such as ethanol, a concentration of free ions about 0.01 mM is needed. As the conductivity does not depend too much on the fraction of ethanol, the weak acid should be mostly dissociated, which means that the concentration of undissociated acid is under 0.01 mM. It implies an acidity constant greater than 10^{-5} . It would be acceptable in water, but not in alcohol, as acidity constants are typically 100 000 smaller in alcohol than in water.²⁷ Moreover, it has been recently shown that the conductivity of ethanol depends on the material of the beaker in which it is measured, with a conductivity varying from 2 to 250 $\mu\text{S/m}$ for the same sigma-aldrich ethanol.²⁸ Therefore, it is logical to assume that the conductivity of ethanol mixed with toluene depends on the material of the glassware in which they have been mixed. In water, the pyrex glassware releases sodium and dihydrogenosilicate ions,²⁹ maybe it releases sodium and

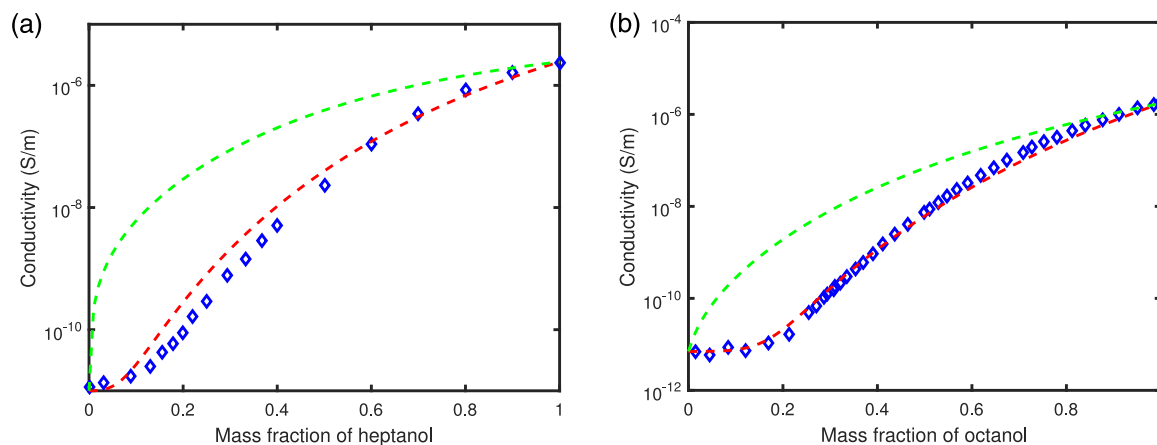


FIG. 5. Conductivity of mixture of alcohol and hydrocarbons. (a): Left heptanol with toluene. (b) Right: octanol with PAO. Blue: experimental point. Green: theoretical curve, with an electrostatic distance of two length of an alcohol molecule. Red: theoretical curve, with an electrostatic distance of one length of an alcohol molecule. Data taken from Ref. 10 and from Ref. 11.

trihydrogenosilicate ions in ethanol. Which kind of ion-pairs these ions are likely to create? Are these ions responsible of the conductivity of both ethanol and octanol? We do not know.

The only firm conclusion we can make is that the conductivity of mixture of alcohol and hydrocarbons is not due to autoprotolysis of alcohol. Other experiments are clearly needed on this topic, especially at constant chemical potential of known dissociating species in alcohol or with an excess of salt. One should also work with special beakers and labware to prevent release of ions from the instruments. When precise experiments will be available, the theory may be expanded to account for the variation of the entropy of dissociation and will enable a better computation of the enthalpy of dissociation.

Note: During the reviewing process, a new article on the subject as been published by Dukhin *et al.*²¹ This new article is on the conductivity of butanol mixed with toluene, heptane, or hexane. The conclusion states: “Thus the theoretical model based on the ‘auto-dissociation of alcohol,’ which had been previously been applied to binary mixtures of various alcohols with toluene, applies to mixtures containing hexane and heptane as well.” The discussion of this section therefore applies to this article as well. We notice a numerical error in Eq. (5) of the same article. Moreover, the “dissociation constant” defined by Eq. (4) is not defined as is usually done in chemistry.

IV. PART III: MICROEMULSIONS: THEORY AND DISCUSSION

Microemulsions of interest are small droplets of water in an oil phase, stabilised by a surfactant. Their conductivity is due to the charge of the droplets. Eicke²² published in 1989 a model to predict the conductivity of such microemulsions, based on statistical mechanics, more precisely on equipartition of energy. He thus assumed that the mean Born energy for a droplet is half the thermal energy,

$$\frac{\langle (ze)^2 \rangle}{8\pi\epsilon_0\epsilon_r a_{droplet}} = \frac{RT}{2N_a}, \quad (25)$$

with $\langle (ze)^2 \rangle$ the mean square charge of a droplet. The main assumption is that $e^2/8\pi\epsilon_0\epsilon_r a_{droplet}$ is small enough compared to the thermal energy. It is equivalent to require that the radius $a_{droplet}$ is big enough compared to a characteristic length, which is the Bjerrum length. Using statistical mechanics Hall,²³ in 1990, shows that $a_{droplet}$ should be at least one sixth or one seventh of the Bjerrum length. If droplets are smaller than one seventh of the Bjerrum length, the creation of charge is too costly energetically and is reduced. If droplets have a size of one sixth of the Bjerrum length, the mean square charge of a droplet computed with the equipartition of energy is 1.8 time the mean square charge computed without. For one eighth of the Bjerrum length, this ratio is 2.8.

Since the droplets are in oil, the relevant Bjerrum length is the one of oil, which is 28 nm, and not the one of water, as Dukhin and Parlia assumed.⁸ Indeed, they stated the following:

“In the case if Bjerrum length for ions in water would be much smaller than water droplet radius then ions electrostatic field would remain inside of the droplets in the sense that electrostatic interaction beyond the droplets borders would be weaker than thermal motion. Basically, water inside of the microemulsion core screens electrostatic interaction. Consequently, Bjerrum length of microemulsions depends on the dielectric permittivity of water, and not oil.”

However, this reasoning is not compatible with the Maxwell-Gauss equation. Indeed, with a spherical symmetry, the radial electric field depends only on the charge, the radius, and the local permittivity, and thus not on the permittivity in any other point. Therefore, droplets of water must be larger than 4-5 nm to use the Eicke model for microemulsions. Data, taken from Ref. 8, on conductivity of microemulsions are reproduced in Fig. 6. It can be seen on this figure that there is a deviation between data and theory at a weight fraction of 0.05 which corresponds to a radius of 4 nm.

This is coherent with the limit of Eicke’s model, which is valid for droplets larger than one seventh of the Bjerrum length of the continuous phase, here oil. At 4-5 nm, one expects a factor two between theory and experiments. Here the agreement between data and theory is better as Dukhin and Parlia fitted the size of the droplet using the conductivity data. These authors explained the limitations of the Eicke model

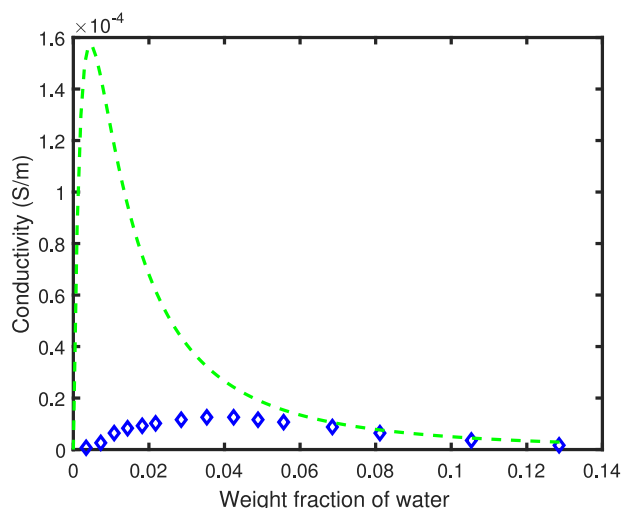


FIG. 6. Conductivity of mixture of AOT, water, and heptane as a function of the weight fraction of water. Data and fit taken from Ref. 8.

by stating the interactions between droplets are important, because the size of droplets is close to the Bjerrum length of water. Since droplets are in an oil phase, their interactions depend on the permittivity of oil and not of the permittivity of water. They state the following.

“There are 3 different types of electrostatic interactions in these systems.

1. Electrostatic attraction between the cation and anion inverse micelles (microemulsion droplets) which leads to the formation of the ion-pairs, according to the work of Bjerrum, Onsager, and Fuoss.
2. Electrostatic interactions between cations and anions formed due to the breakup of the ionic surfactant molecule inside of the inverse micelle (microemulsion droplet) core.
3. Ion-dipole interactions between the ion inside of the inverse micelle (microemulsion droplets) and the dipole moments of the surfactant molecules in the solvating layer polar parts.

All these interaction are suppressed for microemulsions with the large droplet size. All these interactions become important for microemulsion droplets with smaller size and, eventually, inverse micelles.”

Their questions and objections linked to the size of droplets need to be answered by a more general and sophisticated model than the Eicke one. However, the breakdown of the Eicke model for 4-5 nm droplets is primarily due to the hypothesis of equipartition of energy, not due to the missing interactions between or inside droplets, although these missing interactions are likely to modify the conductivity.

V. CONCLUSION

Based on classical thermodynamics, different behaviors of conductivity in non-polar media, as a consequence of ion-pair formation, are described. As it is known, ion-pairing reduces the conductivity of solutions where the added salt is fully dissolved (Case I in this study). As most experiments

are done by adding a salt, no theoretical development on the effect of ion-pairing on the conductivity in the situation of a fixed chemical potential (Case II) has been done. However, the question has recently been raised, as new data showed the linearity of the conductivity in non-polar media with the concentration of ionic surfactant. The model used to explain the data does not account for the formation of ion-pairs, and it was speculated that it should as it is known that ion-pairs are usually formed in non-polar media. Since including ion-pairing would degrade the quality of the correspondence between model and data, it was concluded that ion-pairs do not form in this case. An explanation for their non-formation has been sought. However, we explain in the present article that the formation of ion-pairs does not change the conductivity in this system.

For the conductivity of mixtures of non-polar liquids, such as alcohol and hydrocarbons, classical thermodynamics also provides some insight into the conductivity mechanisms. However, we conclude that more experimental work is needed to get a final word on it.

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Dedicated to the memory of Professor Pierre Turq.

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