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Application of Classical Thermodynamics to the Conductivity in Non-polar Media: Experimental Confirmation

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Abstract

We previously proposed (Gourdin-Bertin, S.; Chassagne, C. *J. Chem. Phys.* **2016**, *144*(24), 244501) a simple theoretical model to account for the evolution of the conductivity with the dielectric permittivity, in non-polar media. In this article, we validate experimentally the theory for the case of an ionogenic species kept at constant chemical potential (i.e. in equilibrium with a non dissolved salt, in contrast to previously published conductivity measurements done as function of various fully dissolved salt concentrations). To our knowledge, it is the first time that this type of experiments has been done explicitly.

1 Introduction

An impressive amount of work on conductivity in non-polar medium has been done in the 1930s, especially by Fuoss and Kraus who published a series of 53 articles all entitled " Properties of electrolytic solutions", see for instance [1]-[3]. They measured the conductivity of various solvents or mixtures of solvents as function of small and dissolved quantities of added salt. They found that the specific conductivity varies with the concentration and decreases with added salt, at low salt concentrations. They attributed this behavior to the formation of ion pairs, a concept that had previously been introduced by Bjerrum in the 1920s [5]. They proposed a graphical method (so-called "Fuoss plot" [2]) to determine the associated equilibrium constant, in various solvents. They also measured the equilibrium constant for mixtures of solvents [3] and found a dependence of the equilibrium constant on the dielectric permittivity. Twenty years later, they adequately gave the results as a linear plot of the logarithm of the equilibrium constant as a function of the inverse of the permittivity [4].

Recently, there has been a growing interest for the conductivity of surfactants in non-polar medium [6][7][8] and for the conductivity of mixtures of pure solvents [9][10][11]. In some cases, the chemical potential of the ionogenic species is not affected by the creation of ions or of ion-pairs. We have recently proposed a theory for the conductivity of these systems based on classical thermodynamics [12]. We refer to this article for further details about the derivations and discussions about the applicability of alternative theories. However, we were not able to confirm experimentally this theory, as we did not know the nature of the conducting species in most relevant experiments.

In order to confirm this theory, we here present experimental studies done with ionogenic species of constant chemical potential, which generate known conducting ions. The experiments are done in a non-polar medium with varying permittivity. To the best of our knowledge, it is the first time that such an experiment is carried out. In the literature, one can only find studies in which the chemical potential of the ionogenic species is changed, and not the permittivity (for real ionic surfactants, which may undergo disproportionation, see [13]). The permittivity is varied by changing the composition of a mixture of solvents. Here, we use an excess of potassium chloride in a mixture of n-dodecanol and toluene or heptane. Even though thermodynamic data are available for ions in mixed solvent [14], they are for mixtures with water, and we found no data about ions in heavy alcohols.

The article is organized as follows: first, the materials and methods are presented. In a second part, the results are given and discussed. A short conclusion ends the article.

Part I

Material and methods

Chemicals

Dodecanol (>98%, ACS reagent), toluene (>99.5%, ACS reagent) heptane (>99%, Reag. Ph. Eur.) and potassium chloride (99,9995%, TraceSELECT) were purchased at Sigma-Aldrich, and used without further purification. Dodecanol was used as it yields a conductivity within the range of our conductimeters. Toluene and heptane were chosen for their low toxicity and the fact that they have the same number of carbon atoms, but are chemically different (aromatic versus aliphatic compounds).

Labware

New beakers in Teflon and stainless steel were used, with new magnetic stirrers in teflon. No special cleaning treatment of the beakers was applied prior the rinsing procedure given below in "Method". Ordinary watch glasses were used to cap the beakers.

Conductimeters

Two Emcee 1153 conductimeters were used, in a $\times 1$ and $\times 100$ configuration, which corresponds to a theoretical range of [1 pS/m - 2000 pS/m] and [100 pS/m - 200000 pS/m] respectively. The manufacturer states that accuracy of the measurements is about 10% for both ranges. For higher conductivities, the electrical impedance was measured using a 4194A impedance/gain-phase analyzer from Hewlett-Packard with a home-made cell [16].

Method

Beakers were rinsed as follows: 5 times with hot water, 5 times with demineralized water, 2 times with ethanol (technical grade), 2 times with methanol (technical grade), 2 times with acetone (technical grade) and then air-dried. Dodecanol and one of the hydrocarbons were poured in the same beaker. The massic concentration was determined by weighting the beaker before and after each addition and the total mass of solvent was between 120 and 150 g for all experiments. The beaker was capped by a watch glass, and stirred for 5 minutes, at room temperature. The conductimeter was rinsed as follows after each measurement: 3 times with ethanol (technical grade), then 3 times with methanol (technical grade), 3 times with acetone (technical grade) and then air-dried. The conductivity was determined from a few subsequent measurements with the same conductimeter. Each data point represents the measurement with only one sample. The experiment was repeated only if it seemed needed. For one sample, a mean value was determined before the point was integrated in the result plot, to avoid any bias of data selection. A large excess of KCl (1 or 2 g) was then added to the mixture, and the solution was stirred for 20 hours, at room temperature. Note that the temperature at which the experiments are done may vary of a few degrees, between 296 and 299 K, as the set-up was not thermostated. Conductivity was then measured following the same procedure, and mass and temperature were often checked.

Validation of the method

- Evolution of the conductivity with time, with or without KCl, has been checked. Some hydrocarbon solvent was lost, due to evaporation. This loss may change the relative concentration of up to 2% in absolute value for a capped system after 24 hours.

- Water may be absorbed and increase the conductivity [11]. (0.5% of absorption by mass, and + 50% of conductivity after 24 hours for pure dodecanol in an uncapped beaker). This effect is however negligible for a capped system but it prevents to change the concentration of hydrocarbons by uncapped evaporation, so an experiment yields the conductivity at only one concentration.

- Influence of the type of beaker (teflon or stainless steel) was evaluated. The influence was found to be negligible in experiments with added salt. The type of beaker affected slightly the result for experiments without added salt, for times longer than 15 minutes.

- Influence of the rinsing procedure was checked with different rinsing cycles, and no significant change in the results was observed.

In conclusion, a medium reproducibility of the results was achieved, with $\pm 20\%$ in the case of added salt, and $\pm 50\%$ for the case without added salt. As written above, the relative concentration of

dodecanol is known with a 2% accuracy. Although the accuracy is not perfect, it is enough to check the validity of the theory, as we proceed to show.

Part II

Results and discussion

The conductivity of a mixture of a hydrocarbon with dodecanol, as a function of the mass fraction of dodecanol, without added salt is given in Fig.1. The conductivity increases sharply with the mass concentration of alcohol. This sharp increase was first shown by Dukhin et al. in a recent series of articles [9][10][11].

<Fig 1. Conductivity, in pS/m, of mixtures of hydrocarbons (toluene: blue squares, heptane: red circles) as a function of the mass fraction of dodecanol, without added salt.>

Conductivity is higher with toluene than with heptane, which may be linked to the higher dielectric permittivity of toluene (2.38 for toluene and 1.924 for heptane, the permittivity of dodecanol being 6.24). This effect is also present in the data of Dukhin et al. [11]. This conductivity is likely due to impurities, since it is too high to be caused by autoprotolysis of the alcohol. Indeed, conductivity of pure dodecanol is here in the order of 10^5 pS/m, therefore the concentration of free ions is on the order of 10^{-7} M (the specific conductivity of ions in dodecanol is likely to be more than 10 times lower in dodecanol than in water, since dodecanol has a viscosity of 16 cP), and an autoprotolysis constant could be in the order of 10^{-14} to account for. However, the autoprotolysis constant for a linear alcohol is generally under 10^{-19} [15], so this explanation is unlikely.

The conductivity of the same systems in the presence of added salt, displayed on Fig.2, is also higher than without added salt. The ratio of these conductivities is between 6, for pure dodecanol, and 60, for a half-half mixture, by weight. This means that the conductivity in systems with added salt is mostly due to the partial dissolution of the salt. Therefore, we assume that the conductivity in this case is totally due to potassium and chloride free ions.

<**Fig.2.** Conductivity, in pS/m, of mixture of hydrocarbons (toluene: blue squares, heptane: red circles) with dodecanol as a function of the mass fraction of dodecanol, with an excess of KCl.>

The conductivity is still higher with toluene than with heptane, which still may be linked to the differences in permittivity.

Our theory [12] is based on the the Born model for solvation and Gibbs thermodynamics. The main assumption is that the Born energy for an already solvated (with the first shell) ion accounts for all the variation of the concentration of free ions in mixture of a polar and a non polar liquid, with free ions at a fixed chemical potential. The check is an adequate plot, which should give a straight line. This theory was not developed before due to the lack of experiment for conductivity in non-polar media with ions at fixed chemical potential, with a varying permittivity.

Ions originates from the dissociation of a neutral specie at a fixed chemical potential, or from the dissolution of a salt present in exces. The concentration of free ions c is linked to the dissociation or dissolution constant K^{diss} by $c^2 \sim K^*$, in the case of monovalent ions. At a given dissociation constant, creation of ions-pairs do not change the concentration of free ions, it only changes the total concentration of ions (free or paired). As the conductivity is proportionnal to the concentration of free ions and not to the total concentration of ions, ion-pairing do not change the conductivity and should not be included in conductivity theory with ions at a fixed chemical potential (of course, ion-pairing decrease the conductivity in which a total concentration of ions, free or paired, is added). This dissociation constant is linked to the standard Gibbs energy of dissociation $\Delta_r^{diss}G^0$ by :

$$K^* = \exp\left(-\frac{\Delta_r^{diss}G^0}{kT}\right) \quad (1)$$

With k the Boltzmann constant, and T the temperature in Kelvin. The Gibbs energy is the enthalpy freed from entropy, and we assume that most of the dependance of Gibbs energy to the dielectric constant is the enthalpic part. The enthalpy of dissolution is the sum of three terms :

$$\Delta_r^{diss}H^0 = \Delta_r^{chemical}H^0 + \Delta_r^{solvation}H^0 + \Delta_r^{electrostatic}H^0 \quad (2)$$

$\Delta_r^{chemical}H^0$ is for chemical bonds which are broken or created during the dissociation, so it does not vary with the permittivity. $\Delta_r^{solvation}H^0$ is for the creation of the first layer of solvation, so it does not vary with the dielectric constant under the following assumption: the first shell of solvation is due to the polar molecule, so it is the same for any composition of a mixture made of a non-polar and a polar liquid. This assumption seems reasonable in most cases. $\Delta_r^{electrostatic}H^0$ is the electrostatic energy associated to an object with the size and charge of a solvated ion in a medium with a permittivity ϵ_r . A modified Born model for the solvation of ions, in which the electrostatic distance d_{el} is the radius of the solvated ion, seems reasonable for this electrostatic enthalpy. (The "modified" Born model is in opposition to the "traditional" one, in which the electrostatic distance is the crystallographic radius of the ion [17].) l_B is the Bjerrum length in vacuum (corresponding to 56 nm).

$$\Delta_r^{electrostatic}H^0 = \frac{l_B}{\epsilon_r d_{el}} \quad (3)$$

Therefore, the dependance of the standard Gibbs energy of dissociation with the permittivity is (A has no specific meaning here) :

$$\Delta_r^{\text{diss}} G^0 = A + \frac{l_B}{\epsilon_r d_{el}} \quad (4)$$

The concentration of free ions is therefore linked to the permittivity by :

$$c^2 \sim K^* \sim \exp\left(\frac{-l_B}{\epsilon_r d_{el}}\right) \quad (5)$$

The conductivity depends linearly on the concentration of free ions only if inter-ionic interactions (such as hydrodynamic coupling and electrostatic relaxation) are negligible and if the viscosity is constant. As the concentrations in our system are low, inter-ionic interactions are likely to be negligible. However, the viscosity varies by a factor 40 between pure heptane (3.9×10^{-4} Pa.s) and pure dodecanol (1.61×10^{-2} Pa.s). To remove the effect of viscosity, we use a Walden-like product [18], which states that the product of the conductivity σ by the viscosity η is proportional to the concentration:

$$\sigma\eta \sim c \quad (6)$$

We therefore decided to plot a Walden-like product $\sigma\eta$ as function of $1/\epsilon_r$ in a semilog plot, which is reminiscent of the "Fuoss plot" (the association constant as function of $1/\epsilon_r$ in semilog plot). Both the viscosity and the permittivity are needed for the plot, for mixtures of dodecanol with heptane or toluene. We could only find these data in literature for mixtures of dodecanol and heptane [19][20], so we will not comment further about the case of dodecanol and toluene. If our theory is correct, the plot should be a straight line (A B C or D have no specific meaning here)

$$\ln(\sigma\eta) = B + \ln(c) = C + \frac{1}{2} \ln(K^{\text{diss}}) = D - \frac{\Delta_r^{\text{diss}} G^0}{2kT} = D - \frac{A}{2} - \frac{l_B}{2d_{el}} \frac{1}{\epsilon_r} \quad (7)$$

We find that indeed, without added salt, for a mixture of dodecanol and heptane, a straight line is obtained, see Fig.3. This confirms the role of electrostatics on the conductivity of mixtures of solvents.

<Fig. 3. Walden-like product (fs.Pa.s/m) as a function of the inverse of the permittivity, for mixture of dodecanol and heptane, without added salt.>

With added salt, Fig.4 is obtained. Two different regimes can be observed, each corresponding to a straight line.

<Fig.4. Walden-like product (fS.Pa.s/m) as a function of the inverse of the permittivity, for mixture of dodecanol and heptane, with an excess of KCl.>

As the Walden-like product (or the conductivity) is far higher with an excess of potassium chloride than without added salt, we assume that the conductivity is only due to chloride and potassium ions. The first line, at low $1/\epsilon_r$, is attributed to the saturated solution. The potassium and chloride ions are in equilibrium with the excess of potassium chloride, and thus eq.(7) holds. From the slope, here -32, we get an estimate of the electrostatic distance $d_{el} = 0.88$ nm. Using the Born model, which seems reasonable here, we identify the electrostatic distance with the radius of a solvated ion. As the dodecanol is the only polar specie in the system, ions are likely solvated by dodecanol, even at moderate dodecanol concentration, with polar heads in contact with ions, and tails giving an excluded volume of given radius. This radius should therefore be close to the length of a dodecanol molecule, which is between 0.77 nm (mean diameter, see [21]) and 1.7 nm when fully extended. The distance of 0.88 nm is therefore within the expected range.

The second line, at high $1/\epsilon_r$, may be related to the kinetic of dissolution. Even after 20 hours, the solution is not saturated in the case of low dielectric permittivity. This was checked, by monitoring the conductivity during 72 hours. Taking evaporation into account, the conductivity increased for points at high $1/\epsilon_r$, and not at low $1/\epsilon_r$. This means that the time to reach equilibrium increases when $1/\epsilon_r$ increases. As this time is linked to the ratio between the equilibrium concentration and the kinetic constant of dissolution, this suggests that this constant decreases more than the equilibrium concentration when the permittivity is decreased. This could be linked to the role of the permittivity in the rate-limiting step of the dissolution reaction. The Walden product is still applicable in this range, however the concentration is now proportional to the kinetic dissolution constant, k_{dis} . We have:

$$c \sim k_{dis} \sim \exp\left(\frac{-l_B}{\epsilon_r d_{el}}\right) \quad (8)$$

The energy in this case is the electrostatic contribution (excluding dodecanol molecules at contact with ions) to the activation energy of the dissolution reaction. The electrostatic distance, calculated from the second slope using eq.(8), is found to be $d_{el} = 0.84$ nm. Note that for the first slope, one used $c \sim \exp(-l_B/(2\epsilon_r d_{el}))$. As the found d_{el} are very close, on the plots this corresponds to a factor 2 between the slopes of the first and the second line. The fact that the found d_{el} are very close could be linked to Hammond's postulate, even though we have no proof for it.

Estimation of the electrostatic length for the case without added salt (see Fig.3) yields $d_{el} = 0.65$ nm. This value is significantly different from 0.88 nm, so we can infer that ions have different origins in this case, which is expected. We do not know which ions are conducting in the case without added salt, except that they are not created by auto-protolysis.

2 Conclusion

In [12] a theory on the conductivity in non-polar medium was proposed. This theory predicted the dependence of the conductivity on the dielectric permittivity. In the present article, the theory was confirmed in the case of ionogenic species at fixed chemical potential. We found a simple linear relationship between a Walden-like product and the inverse of the permittivity, as expected from the theory. In the case of mixtures of alcohols and hydrocarbons, without added salt, it is still not known which ionic species is conducting and which ionogenic species generated it. To determine if a given ionogenic species, such as a carboxylic acid, is a likely candidate, one can monitor the evolution of the electrostatic length by varying its concentration in solution. Using high-purity and high-polarity aprotic solvent may also be interesting, to avoid any interference of auto-protolysis and to simplify the system.

Another interesting approach would be to evaluate the solvent influence on the electrostatic distance, for example by using an alcohol containing an hydroxyl group in the middle of the carbon chain. An other study could be done on the kinetic of dissolution, by recording the evolution of the conductivity with time. One could then try to find the physical meaning of the electrostatic length in this case.

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References

- [1] Copenhafer, D. T.; Kraus, C. A. Properties of Electrolytic Solutions. LIII. Molecular Weight of Salts in Benzene by the Cryoscopic Method1. *JACS* **1951**, *73*(10), 4557-4561.
- [2] Fuoss, R. M.; Kraus, C. A. Properties of Electrolytic Solutions. II. The Evaluations of Λ_0 and of K for Incompletely Dissociated Electrolytes. *JACS* **1933**, *55*(2), 476-488.
- [3] Fuoss, R. M.; Kraus, C. A. Properties of Electrolytic solutions. III. The Dissociation Constant. *JACS* **1933**, *55*(3), 1019-1028.
- [4] Fuoss, R. M.; Kraus, C. A. Ionic Association. II. Several Salts in Dioxane-Water Mixtures. *JACS* **1957**, *79*(13), 3304-3310.
- [5] Bjerrum, N. Kgl. Danske Videnskab. **1926** *Selskab* 7.
- [6] Dukhin, A. S.; Goetz, P. J. . How Non-Ionic “electrically neutral” Surfactants Enhance Electrical Conductivity and Ion Stability in Non-Polar Liquids. *J. Electroanalytical Chem.* **2006**, *588*(1), 44-50.
- [7] Guo, Q.; Singh, V.; Behrens, S. H. Electric Charging in Nonpolar Liquids because of Nonionizable Surfactants. *Langmuir* **2009**, *26*(5), 3203-3207.
- [8] Beunis, F.; Strubbe, F.; Karvar, M.; Drobchak, O.; Brans, T.; Neyts, K. Inverse Micelles as Charge Carriers in Nonpolar Liquids: Characterization with Current Measurements. *COCIS* **2013**, *18*(2), 129-136.
- [9] Bombard, A. J.; Dukhin, A. Ionization of a Nonpolar Liquid with an Alcohol. *Langmuir* **2014**, *30*(15), 4517-4521.
- [10] Dukhin, A.; Parlia, S. Ion-Pair Conductivity Theory Fitting Measured Data for Various Alcohol-Toluene Mixtures across Entire Concentration Range. *J. Electroanalytical Chem.* **2015** *162*(4), H256-H263
- [11] Parlia, S.; Dukhin, A.; Somasundaran, P. Ion-Pair Conductivity Theory: Mixtures of Butanol with Various Non-Polar Liquids and Water. *J. Electrochemical Soc.* **2016**, *163*(7), H570-H575.

- [12] Gourdin-Bertin, S.; Chassagne, C. Application of Classical Thermodynamics to the Conductivity in Non-Polar Media. *J. Chem. Phys.* **2016**, *144*(24), 244501.
- [13] Hsu, M. F.; Dufresne, E. R.; Weitz, D. A. Charge Stabilization in Nonpolar Solvents. *Langmuir* **2005**, *21*(11), 4881-4887.
- [14] MARCUS, Y. *Ions in Solution and their Solvation*. John Wiley & Sons, 2015.
- [15] Rondinini, S., et al. Autoprotolysis Constants in Non-Aqueous and Aqueous Solvents *Pure & Appl. Chem* **1987**, *59*, 12.
- [16] J. Van der Ploeg, M. Mandel, *Meas. Sci. Technol.* **1999**, *389*, 389–395.
- [17] Born, M. Volumen und Hydratationswärme der Ionen. *Zeit. Physik A* **1920**, *1*(1), 45-48.
- [18] Walden, P. Über organische Lösungs-und Ionisierungsmittel. III. Teil: Innere Reibung und deren Zusammenhang mit dem Leitvermögen. *Z. Phys. Chem.* **1906** *55*, 207-246.
- [19] Sastry, N. V.; Valand, M. K. Dielectric Constants, Refractive Indexes and Polarizations for 1-Alcohol+ Heptane mixtures at 298.15 and 308.15 K. *Ber. Bunsenges. Phys. Chem.* **1997**, *101*(2), 243-250.
- [20] Sastry, N. V.; Valand, M. K. Viscosities and Densities for Heptane+ 1-Pentanol,+ 1-Hexanol,+ 1-Heptanol,+ 1-Octanol,+ 1-Decanol, and+ 1-Dodecanol at 298.15 K and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*(6), 1426-1428.
- [21] MARCUS, Y. *The Properties of Solvents*. Chichester : Wiley, 1998.