

## IONIC STRUCTURE IN MINERAL WATERS. A CONDUCTOMETRY STUDY

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Accepted 9 September, 2015

Mineral waters are non-ideal solutions, with complex electrolytes composition and mechanisms of ionic conductivity. An overview of theoretical models aiming to explain the departures from ideality in solutions of electrolytes starting with the Debye-Hückel theory and including subsequent sophisticated developments, shows that theories could not explain in all details the behavior of non-ideal solutions on wide domains of ionic strength, but limited agreement could be obtained on restricted domains. We measured the conductivity of 15 Romanian and international mineral waters as a function of their ionic strength based on their nominal composition. A nonlinear dependence was found, and the data could be fitted with two distinct curves in the lower and higher ionic strength domains. Thus two distinctive classes of mineral waters were identified, with a third class having intermediate properties. The estimated average Debye radius was significantly smaller for the mineral waters in the higher ionic strength domain. The latter contained also higher concentrations of the kosmotropic ions  $Mg^{2+}+Ca^{2+}$ , which suggest that they have a more ordered structure of water molecules. Our study could provide a basis for further physical chemistry studies of conductivity mechanisms in mineral waters as well as for thorough investigations of clinical differences between the identified classes of mineral waters.

*Keywords:* mineral water, Debye-Hückel radius, Davies equation, ionic strength, conductivity.

### INTRODUCTION

Mineral waters are used since centuries and even millennia for their health benefits in stress, asthma and digestive symptoms<sup>1</sup> relief, as well as in weight loss and convalescence. They demonstrated a benefic influence by reducing cholesterol levels and the risk of cardiovascular problems in post-menopausal women<sup>2</sup>, by regulating troubled glucidic metabolism<sup>3</sup> and even by showing anti-aging capabilities and increased life expectancy in humans and metazoans<sup>4</sup>. However, the healing capabilities of mineral waters are not completely understood. Their therapeutic action has been associated to their dissolved chemical constituents such as the bicarbonate ion<sup>1,2</sup>, sodium<sup>2</sup> or lithium<sup>4</sup>. 2011]. Both  $Li^+$  and  $Na^+$  are ions of alkaline metals of the first main group in the periodic table of elements and, therefore, have chemically similar properties. However, it is interesting to note that, as shown by hydration entropy and viscosity

measurements, the  $Li^+$  and  $Na^+$  ions increase order in the water structure, while their chemical homologs  $K^+$ ,  $Rb^+$  and  $Cs^+$  decrease it<sup>6,7</sup>. In this connection one can note that the  $K^+$  ion, with a high concentration in tumors and a de-structuring effect on water, causes the highest value of water's spin-lattice relaxation time in NMR<sup>8</sup> (and thus yielding histopathologic contrast in the NMR tomography). At the same time the  $Li^+$  and  $Na^+$  ions classify in the central zone of the Hofmeister or lyotropic series of cations; this gives a classification of ions in order of their effects on the solubility of proteins and on the stability of secondary and tertiary structure of the later, as well as on many other properties of their solutions in water, such as surface tension<sup>9</sup>. In mineral waters,  $Na^+$  and  $Li^+$  coexist with other cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Mn^{2+}$ ) and anions ( $HCO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ) with synergic or opposed properties. Therefore it should be useful to look after a global or average characteristic of such complex aqueous solutions (as the mineral waters are). With this aim, it might be interesting to define a sequencing parameter of the

mineral waters, able for instance to rank them in a Hofmeister-type series. But theoretically this seems to be a very difficult, if not impossible task, as the Hofmeister effect is still an unsolved mystery<sup>9</sup>. However, other properties of mineral waters<sup>10</sup> and other global characteristics of aqueous solutions of inorganic ions are at hand. Such is the ionic strength, easy to evaluate from the nominal ionic composition of mineral waters, and the electrical conductivity of the respective aqueous solution, readily measurable with a simple portable instrument; moreover these two parameters correlate straightforwardly. In a previous study we measured the electrical conductivity of some commercial still mineral waters<sup>11</sup>. We now extend this study by examining the correlations between two physical quantities, conductivity and ionic strength of the analyzed waters. The results are discussed from the perspectives of a new criterion for the classification of mineral waters and of possible biological implications.

#### WATER, IONS, ELECTROLYTE SOLUTIONS. A BRIEF CONCEPTUAL PICTURE

Mineral waters are characterized by their dissolved ions, in fact they are aqueous electrolyte solutions<sup>12-14</sup>. These ions are charge carriers and the mineral waters are good conductors of electric current. They are characterized by conductivity and by ionic strength, and by a relationship between these two quantities.

**Ionic strength.** The ionic strength of a solution is a measure of its concentration of ions and is one of the main characteristics of a solution with dissolved electrolytes. Most important, the ionic strength,  $I$ , of a solution is a function of the concentration of *all* ions present in that solution.

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2, \quad (1)$$

where  $c_i$  is the molar concentration of ion  $i$  (M, mol/L),  $z_i$  is the charge number of that ion, and the sum is taken over all ions in the solution. The ionic strength is thus a global parameter of the solution, and this is an essential aspect for mineral waters which are a complex mixture of dissolved ions. For a 1:1 electrolyte such as sodium chloride, the ionic strength is equal to the concentration, but

for  $\text{MgSO}_4$  the ionic strength is four times higher. Generally multivalent ions contribute strongly to the ionic strength.

Because ions of opposite charge attract each other due to electrostatic forces, while ions of the same charge repel each other and, ions are not randomly distributed throughout the electrolyte solution, as they would be in an ideal solution. Thus mineral waters are non-ideal solutions. In such solutions volumes are no longer strictly additive, and it is preferable to work with molality  $b_i$  (mol/kg{H<sub>2</sub>O}) rather than molarity  $c_i$  (mol/L). Hence the ionic strength is defined as:

$$I = \frac{1}{2} \sum_{i=1}^n b_i z_i^2. \quad (2)$$

Mineral waters have a non-zero ionic strength due to the presence of dissolved salts; also they have characteristic conductivities. Ionic strength plays a central role in the theories that describe the strong deviations from ideality typically encountered in ionic solutions, like the Debye-Hückel theory<sup>15</sup> which will be discussed further. These theories provide also the basis for connecting ionic strength and conductivity.

**Conductivity.** In the case of electrolyte solutions we have to deal on one side with the, “measured conductivity”,  $\chi$ , which is the reciprocal of solution’s resistivity  $\rho$ , and on the other with the “molar conductivity”,  $\Lambda_m$ . This is defined as the ratio of the measured conductivity  $\chi$  to the molar concentration  $c$  of the electrolyte<sup>16,17</sup>:

$$\Lambda = \chi/c. \quad (3)$$

The measured conductivity’s SI unit is 1 mho/m = 1 S/m (Siemens/m), but in practice the traditional unit of  $\mu\text{S/cm}$  is used (1  $\mu\text{S/cm}$  =  $10^{-4}$  S/m). The molar conductivity SI unit is  $\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$ . The electrical conductivity of a solution is measured by determining the resistance between two electrodes separated by a fixed distance, using an alternating voltage at typical frequencies in the range 1–3 kHz in order to avoid electrolysis<sup>18</sup>. The dependence on the frequency is usually small<sup>19</sup>, but may become appreciable at very high frequencies, an effect known as the Debye-Falkenhagen effect<sup>20-23</sup>.

**Non-ideal electrolyte solutions.** Mineral waters are complex, non-ideal aqueous electrolyte

solutions and, accordingly, the corresponding theory [e.g., ref. 12] is necessary in order to understand some of their characteristics – in particular, to find a relationship between ionic strength and conductivity. In chemistry, an *ideal solution* shows thermodynamic properties analogous to those of a mixture of ideal gases, which include the lowering of vapor pressure, the elevation of boiling point, the depression of freezing point, and the osmotic pressure (the so-called colligative properties) and has an activity coefficient of each component (which measures deviation from ideality) equal to one<sup>13</sup>. In *non-ideal electrolyte solutions* particular aspects of these thermodynamic properties and “anomal” activity coefficients show that ions are not randomly distributed as expected in an ideal solution.

The starting point for the explanation of departures from ideality in solutions of electrolytes was given by the Debye-Hückel theory<sup>15</sup> which assumes an extremely simplified model of the electrolyte solution but nevertheless gives accurate predictions of mean activity coefficients for ions in sufficiently dilute solution. To make things even more complicated, the mineral waters have concentrations of ions much higher than the limit of the Debye-Hückel theory applicability. However, the Debye-Hückel model introduces the basic concepts and we must rely on its picture of electrolyte solution; subsequent developments only refined the same picture. We refer below mainly to classical models and thus our overview has some historical character too.

The properties of a solution are proportional the so-called activity  $a$  of a dissolved ion, which is proportional to concentration  $c$ ; the proportionality constant is known as an activity coefficient,  $\gamma$ :

$$a = \gamma c. \quad (4)$$

In general, the mean activity coefficient of a fully dissociated electrolyte of formula  $A_nB_m$  is given by

$$\gamma_{\pm} = (\gamma A^n \gamma B^m)^{1/(n+m)},$$

$$I = \frac{1}{2} \sum_{i=1}^n b_i z_i^2. \quad (5)$$

In an ideal electrolyte solution the activity coefficients of all the ions are equal to one. Non-ideality arises principally (but not exclusively)

because ions of opposite charge attract each other due to electrostatic forces, while ions of the same charge repel each other. In consequence the distribution of ions in solution is not uniform, as it would be in an ideal solution. Activity coefficients are themselves functions of concentration as the amount of inter-ionic interaction increases as the concentration of the electrolyte increases.

**Debye-Hückel theory** allows single ion activity coefficients – and associated properties like conductivity – to be calculated; it also provides a suggestive yet realistic picture of the electrolyte solution structure.

The principal assumption is that each ion is surrounded more closely by ions of opposite charge than by ions of like charge which form a fuzzy cloud. Individual ions surrounding a “central” ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach. The electrostatic interactions between ions are mediated by Coulomb’s law through the solvent, described as a uniform medium, without structure. It is also assumed that: the solute is a strong electrolyte completely dissociated; ions are spherical and are not polarized by the surrounding electric field; the solvent plays no role other than providing a medium of constant relative dielectric constant; solvation of ions by water can be ignored except insofar as it determines the effective sizes of the ions; there is no electrostriction.

The Debye-Hückel theory<sup>15</sup> was based in the essence on the assumption that each ion was surrounded by a spherical “cloud” made up of ions of the opposite charge. Thus each cation is surrounded by a spherically symmetric cloud of other ions. The cloud has a net negative charge. Similarly each anion is surrounded by a cloud with net positive charge.

The molal activity coefficient of ions  $A^+$  and  $B^-$  in the Debye-Hückel theory is:

$$\log_{10} \gamma_{\pm} = -Az_j^2 \frac{\sqrt{I}}{1 + Ba_0 \sqrt{I}}, \quad (6)$$

$$A = \frac{e^2 B}{2.303 \times 8\pi \epsilon_0 \epsilon_r kT}, \quad (6')$$

$$B = \left( \frac{2e^2 N}{\epsilon_0 \epsilon_r kT} \right)^{1/2}, \quad (6'')$$

where  $I$  is the ionic strength and  $a_0$  is a parameter that represents the distance of closest approach of ions. For aqueous solutions at 25 °C  $A = 0.51 \text{ mol}^{-1/2} \text{ dm}^{3/2}$  and  $B = 3.29 \text{ nm}^{-1} \text{ mol}^{-1/2} \text{ dm}^{3/2}$ . The notations are as usual:  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the dielectric constant,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $N_A$  is the Avogadro number,  $e$  is the elementary charge.

A significant aspect of this result is the prediction that the mean activity coefficient is a function of *ionic strength* rather than the electrolyte concentration. For very low values of the ionic strength the value of the denominator in the expression above becomes nearly equal to one,  $1 + Ba_0 I^{1/2} \sim 1$ . In this situation the mean activity coefficient is proportional to the square root of the ionic strength,  $\log \gamma \sim I^{1/2}$ . This is known as the Debye-Hückel limiting law.

This theory Debye-Hückel equation gives a very satisfactory agreement with experimental measurements of the activity coefficient for solutions of 1:1 electrolytes (e.g. Na+Cl-) at sufficiently low concentrations (typically less than  $10^{-3} \text{ mol dm}^{-3}$ ). The limit of applicability of the Debye-Hückel theory is for solutions with a ionic strength not higher than 0.1 M. At higher concentrations and with electrolytes that produce ions of higher charges (e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , etc., which are present in mineral waters) deviations from the theoretical predictions occur.

The limitations of the Debye-Hückel theory are due to many neglected aspects of the complex phenomena in solution and which have to be taken into account. Most important is the solvation of ions. The solvent is not a structureless medium but is made up of molecules. The water molecules in aqueous solution are both dipolar (dipole moment  $d = 0,387 \text{ eÅ} = 1,84 \text{ D}$ ) and polarizable. Both cations and anions have a strong primary solvation shell and a weaker secondary solvation shell. The first solvation shell of a sodium ion dissolved in water is formed by 6  $\text{H}_2\text{O}$  molecules. The oxygen atoms are arranged at the vertices of an octahedron with the sodium ion at its centre. Also many ions such as the nitrate ion,  $\text{NO}_3^-$ , are manifestly not spherical. Ions are polarized, and especially polyatomic ions are polarizable.

**Conductivity in Debye-Hückel theory. Strong electrolytes.** Notwithstanding all its limitations, the D-H theory allows a consistent explanation of the conductivity at low ionic strength. When an electric field is applied to an electrolyte solution, the dissolved ions together with their charge cloud are acted upon by an electrostatic force which moves them along the field lines. Moreover the electric field causes the distortion of the charge cloud from its spherical symmetry. The movement is opposed by friction forces due to the viscosity of the solution, as well as by electrophoretic retardation forces. Experimentally, when conductivity is measured the system is subject to an oscillating external field due to the application of an AC voltage to electrodes immersed in the solution; this imparts an oscillating character to the charge cloud deformation. Based on the postulates of Debye-Hückel theory and taking into account the charge cloud distortion together with viscosity and electrophoretic effects, Lars Onsager derived a theoretical expression<sup>24-26</sup> to account for the empirical relation known as Kohlrausch's Law, for the molar conductivity,  $\Lambda_m$ :

$$\Lambda_m = \Lambda_m^0 - K\sqrt{c}. \quad (7)$$

$\Lambda_m^0$  is known as the limiting molar conductivity,  $K$  is an empirical constant and  $c$  is the electrolyte concentration. ("Limiting" here means "at the limit of the infinite dilution"). Onsager's expression is

$$\Lambda_m = \Lambda_m^0 - (A + B\Lambda_m^0)\sqrt{c}, \quad (8)$$

where  $A$  and  $B$  are constants that depend only on temperature, the charges on the ions and the dielectric constant and viscosity of the solvent. This is known as the Debye-Hückel-Onsager equation. However, this equation only applies to very dilute solutions and has been largely replaced by other equations<sup>24-26</sup>.

Both Kohlrausch's law and the Debye-Hückel-Onsager equation break down as the concentration of the electrolyte increases above a certain value. The reason for this is that as concentration increases the average distance between cation and anion decreases, so that there is more inter-ionic interaction. Various attempts have been made to extend Onsager's treatment to more concentrated solutions<sup>27</sup>. Whether ion-association occurs is a controversial point, however, often cations and

anions interact to form an ion-pair. Formation of ion-triplets has been suggested also<sup>28,29</sup> and this suggestion has received some support recently<sup>30-31</sup>.

**Weak electrolytes.** A weak electrolyte is never fully dissociated (*i.e.* there are a mixture of ions and complete molecules in equilibrium). Typical weak electrolytes are weak acids and weak bases. In mineral waters the high concentration of  $\text{HCO}_3^-$  ion especially emphasizes the importance of weak electrolytes. The concentration of ions in a solution of a weak electrolyte is less than the concentration of the electrolyte itself. For acids and bases the concentrations can be calculated when the value(s) of the acid dissociation constant(s) is(are) known. The solution becomes ever more fully dissociated at weaker concentrations, and for low concentrations of weak electrolytes, the degree of dissociation of the weak electrolyte becomes proportional to the inverse square root of the concentration.

For a monoprotic acid, HA, obeying the inverse square root law, with a dissociation constant  $K_a$ , an explicit expression for the conductivity as a function of concentration,  $c$ , known as Ostwald's dilution law, can be obtained

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{\Lambda_m c}{K_a (\Lambda_m^0)^2}. \quad (9)$$

**Debye length in an electrolyte.** In electrolytes the *Debye length* (also called *Debye radius*), is the measure of a charge carrier's net electrostatic effect in solution, and how far those electrostatic effects persist. A *Debye sphere* is a volume whose radius is the Debye length, in which there is a sphere of influence, and outside of which charges are electrically screened.

In an electrolyte or a colloidal suspension, the Debye length<sup>32</sup> for a monovalent electrolyte, usually denoted with symbol  $\kappa^{-1}$  (and with  $\chi^{-1}$  by some authors) is given by:

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 kT}{2N_A e^2 I}} \quad (10)$$

or, for a symmetric monovalent electrolyte like NaCl,

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 RT}{2F^2 c_0}}, \quad (10')$$

where  $R$  is the universal gas constant,  $N_A$  is the Avogadro number,  $F$  is the Faraday constant, and  $c_0$  is the molar concentration of the electrolyte.

Alternatively,

$$\kappa^{-1} = \frac{1}{\sqrt{8\pi \lambda_B N_A I}}, \quad (11)$$

where  $\lambda_B$  is the Bjerrum length of the medium. This Bjerrum length is the separation at which the electrostatic interaction between two elementary charges is comparable in magnitude to the thermal energy scale,  $kT$ . For water at room temperature,  $\lambda_B \approx 0.7$  nm. At room temperature (25 °C), in water for 1:1 electrolytes (*e.g.* NaCl) one can consider the simplified expression for the Debye length<sup>33</sup>:

$$\kappa^{-1}(\text{nm}) = \frac{0.304}{\sqrt{I(\text{M})}}, \quad (12)$$

where  $\kappa^{-1}$  is expressed in nanometers (with the relative dielectric constant of water  $\epsilon_r = 78.6$ ). Expressing the Debye length in cm and allowing more generally for the temperature and the dielectric constant of the solvent, one obtains<sup>17</sup>,

$$\kappa^{-1}(\text{cm}) = 1.988 \cdot 10^{-10} \sqrt{\frac{\epsilon_r T}{I(\text{M})}}. \quad (12')$$

The predictions of the Debye-Hückel theory and implicitly the Debye-Hückel-Onsager or Kohlrausch equations are not accurate at higher ionic strength, therefore we have to look for a more accurate theory of electrolyte solutions outside the low ionic strength domain. This can be done by adding to the result of the Debye-Hückel theory one or more terms describing aspects of the phenomena ignored in the original theory. In order to extend the validity domain of the model, various formulae have been developed both empirically and theoretically. Two semiempirical models due to Davies and to Bromley are of major interest.

The **Davies equation**<sup>34</sup> is an empirical extension of Debye-Hückel theory<sup>15</sup> which can be used to calculate activity coefficients of electrolyte solutions at relatively high concentrations [Davies]. The

equation was refined by fitting to experimental data. The final form of the equation gives the mean molal activity coefficient,  $\gamma_{\pm}$ , of an electrolyte which dissociates into ions having charges  $z_1$  and  $z_2$  as a function of ionic strength,  $I$ .

$$-\log \gamma_{\pm} = \frac{1}{2} z_1 z_2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.15I \right). \quad (13)$$

The second term,  $0.15 I$ , goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye-Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye-Hückel equation. For 1:1 electrolytes the difference between measured values and those calculated with this equation is about 2% of the value for 0.1 M solutions. The calculations become less precise for electrolytes that dissociate into ions with higher charges. Further discrepancies will arise if there is association between the ions, with the formation of ion-pairs, such as  $\text{Mg}^{2+}\text{SO}_4^{2-}$ .

The **Bromley equation**<sup>35</sup> also was developed [Bromley 1973] with the objective of calculating activity coefficients for aqueous electrolyte solutions whose concentrations are above the range of validity of the Debye-Hückel equation. The Bromley equation is essentially an empirical equation. Bromley observed that experimental values of  $\frac{1}{z_+ z_-} \log \gamma_{\pm}$  were often approximately proportional to ionic strength. Accordingly he developed the equation, for a salt of general formula  $M_p^{z_+} M_q^{z_-}$ :

$$\log \gamma_{\pm} = \frac{-A_{\gamma} |z_+ z_-| \sqrt{I}}{1 + \rho \sqrt{I}} + \frac{(0.06 + 0.6B |z_+ z_-| I)}{\left(1 + \frac{1.5}{|z_+ z_-|} I\right)^2} + BI. \quad (14)$$

At 25 °C  $A_{\gamma}$  is equal to 0.511 and  $\rho$  is equal to one. The  $B$  parameters are relatively easy to determine. Bromley noted that the equation gave satisfactory agreement with experimental data up to ionic strength of 6 molal, though with decreasing accuracy when extrapolating to very high ionic strength. As with other equations, it is not satisfactory when there is ion-association as, for example, with divalent metal sulfates. Bromley also proposed extensions to multicomponent solutions

and for the effect of temperature change. A modified version of the Bromley equation has been suggested and used extensively<sup>36</sup>. For some complex electrolytes, Ge *et al.* (2008) obtained a new set of Bromley parameters using up-to-date measured or critically reviewed osmotic coefficient or activity coefficient data.

#### Specific ion Interaction Theory (SIT theory).

This is one of the two main theoretical approaches used to estimate single-ion activity coefficients in electrolyte solutions at relatively high concentrations. It takes into consideration *interaction coefficients* between the various ions present in solution. Interaction coefficients are determined from equilibrium constant values obtained with solutions at various ionic strengths.

SIT theory was first proposed by Brønsted<sup>38</sup> and was further developed by Guggenheim<sup>39</sup>. The **Guggenheim equation** can be written, in its simplest form for a 1:1 electrolyte, MX, as:

$$\log \gamma_{\pm} = \frac{-A_{\gamma} \sqrt{I}}{1 + \sqrt{I}} + \beta b. \quad (15)$$

$\gamma_{\pm}$  is the mean molal activity coefficient. The first term on the right-hand side is the Debye-Hückel term; in the second term,  $\beta$  is an interaction coefficient and  $b$  the molality of the electrolyte. As the concentration decreases so the second term becomes less important until, at very low concentrations, the Debye-Hückel equation gives a satisfactory account of the activity coefficient. Further developments extended the SIT theory<sup>40-42</sup> to allow the interaction coefficients to vary with the ionic strength. In this way  $I^{1/2}$  may appear at a higher power in the second term.

The activity coefficient of the  $j$ th ion in solution is written as  $\gamma_j$  when concentrations are on the molal concentration scale and as  $y_j$  when concentrations are on the molar concentration scale. (The molality scale is preferred in thermodynamics because molal concentrations are independent of temperature). The theory generalizes the above equation for more dissolved ions; the activity coefficient can be expressed as

$$\log \gamma_j = -z_j^2 \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k \epsilon_{jk} m_k \quad (16)$$

(molalities) or

$$\log y_j = -z_j^2 \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}} + \sum_k b_{jk} m_k \quad (16')$$

(molar concentrations) where  $z$  is the electrical charge on the ion,  $I$  is the ionic strength,  $\epsilon$  and  $b$  are interaction coefficients and  $m$  and  $c$  are concentrations. The summation extends over the other ions present in solution. The first term in these expressions comes from Debye-Hückel theory<sup>15</sup>. The second term shows how the contributions from "interaction" are dependent on concentration. Thus, the interaction coefficients provide corrections to Debye-Hückel theory when concentrations are higher than the region of validity of that theory.

**Virial theorem<sup>43</sup> and Pitzer equation<sup>44-46</sup>.** In the above developments one can make an analogy to the virial equation of state for a real gas.

$$PV = RT + BP + CP^2 + DP^3 \dots \quad (17)$$

where  $P$  is the pressure,  $V$  is the volume,  $T$  is the temperature and  $B, C, D \dots$  are the virial coefficients. (The virial theorem relates the average over time of the total kinetic energy, of a stable system of many particles bound by potential forces, with the average of the total potential energy.) The first term on the right-hand side is for an ideal gas. The remaining terms quantify the departure from the ideal gas law with changing pressure,  $P$ <sup>43</sup>. In the case of the above developments for electrolyte solutions,  $P$  should be substituted by  $I$ <sup>1/2</sup> retaining only the first terms. By contrast the **Pitzer equation** is an approach inspired by the virial theorem which is based on rigorous thermodynamics. The parameters of the Pitzer equations are linear combinations of parameters, of a virial expansion of the excess Gibbs free energy, which characterise interactions amongst ions and solvent. The determination Pitzer parameters is more laborious. Whilst the Bromley and SIT approaches are based on pair-wise interactions between oppositely charged ions, the Pitzer approach also allows for interactions between three ions. The Pitzer theory is more rigorous than the equations of specific ion interaction theory (SIT theory), but Pitzer parameters are more difficult to determine experimentally than SIT parameters. For a simple electrolyte  $M_pX_q$ , at a concentration  $m$ , made up of ions  $M^{+}$  and  $X^{-}$ <sup>44</sup>:

$$\ln \gamma_{\pm} = |z_+ z_-| f_{\gamma} - m \left( \frac{2pq}{p+q} \right) B_{MX}^{\gamma} + m^2 \left[ 2 \frac{(pq)^{3/2}}{p+q} \right] C_{MX}^{\gamma} \quad (18)$$

These equations were applied to an extensive range of experimental data at 25 °C with excellent agreement to about 6 mol kg<sup>-1</sup> for various types of electrolyte<sup>45</sup>. The treatment can be extended to mixed electrolytes and to include association equilibria<sup>46</sup>.

In a comparison of Bromley, SIT and Pitzer models, little difference was found in the quality of fit<sup>47</sup>.

**Overview.** In brief, the mineral waters are very complicated non-ideal electrolyte solutions made up by a complex mixture of electrolytes, not only of strong but also of weak ones and including divalent ions which will favour association, with the formation of ion-pairs, such as Mg<sup>2+</sup>SO<sub>4</sub><sup>2-</sup> (and possibly ion-triplets); all these characteristics favour discrepancies and accuracy of simple models like the Debye-Hückel theory is improbable. The models of progressive mathematical complexity presented above evidence the puzzle nature of the conductivity mechanisms in such non-ideal electrolyte water solutions. Because of the complex phenomena involved, it is beyond the scope of this study to obtain a refined theoretical description of the experimental data. Rather, some empiric approximations are searched for in hope of qualitatively understanding the mechanisms of electrical charge conduction in mineral waters and of proposing plausible classification criteria. To this end we retain the notion of charge cloud characterized approximately by the Debye length and Bjorom length which suggestively underlines the heterogeneous structure of the solution. The above models and concepts proved important for the understanding of the behaviour of ions in natural waters such as rivers, lakes<sup>48,49</sup> and sea-water<sup>50</sup>. We can expect that they will be useful for mineral waters, too.

## EXPERIMENTAL

Fifteen commercial mineral waters were analyzed. Conductivity measurements were performed with a Romanian instrument, with a standard cell of 1 cm width between electrodes at 26 °C. NaCl solutions of known concentration were used as standards. The relative errors were of 8–10 %. The approximate ionic strength was evaluated from the nominal compositions as specified by the manufacturers. Only strong electrolytes have been considered. The contribution of the weak electrolytes HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> to the ionic strength

has been neglected because the acidity (dissociation) constants are very low for carbonic acid ( $K_1 = 0.45 \cdot 10^{-6}$ ) and low for phosphoric acid ( $0.75 \cdot 10^{-2}$ ), respectively<sup>51</sup>; although the later has a larger acidity constant, it is totally or almost absent in mineral waters. The approximate Debye radius  $\kappa^{-1}$  valued were estimated from the ionic strength values using eqs. (12–12') valid for 1:1 electrolytes, neglecting possible discrepancies due to ions with electric charge higher than one present in the samples.

Nominal values of ionic concentrations in mg/L, converted in mmol/L, were used for calculating the ionic strength expressed in mmol/L (mM) for the inorganic ions resulted by dissociation of strong electrolytes.

## RESULTS AND DISCUSSIONS

The ionic strength  $I$  values calculated from the nominal compositions of mineral waters, the measured conductivity  $\chi$  values and the Debye radius  $\kappa^{-1}$  values estimated by eqs. (12–12') are presented in Table 1. The ionic strength of mineral waters, generally in the range of 1–10 mM, is below the limit of applicability of the Debye-Hückel theory (100 mM) and thus is not a setback, but it is outside the optimal domain for the theory (typically less than 1 mM). We are compelled to use the measured conductivity  $\chi$  as we cannot use the molar conductivity  $\Lambda$ . This is because the mineral waters are complex mixtures of various electrolytes and, therefore, defining a molar concentration  $c$  characteristic of the whole mineral water (and thus the molar conductivity  $\Lambda = \chi/c$ ) is not a simple matter. For the measured conductivity  $\chi$  of a single electrolyte dissociating in monovalent ions, assuming that the Debye-Hückel-Onsager equation would still be valid, one could write the equation:

$$\chi = \Lambda_0 I - (A + B\Lambda_0) I^{3/2}. \quad (19)$$

But such a simple equation cannot be written for a complex solution like the mineral waters and, therefore, we could not fit the function (19) to the data points. However, it suggests that in logarithmic coordinates the slope of the  $\chi$  versus  $I$  relationship could be included somewhere between 1 and 3/2.

The  $\chi$  versus  $I$  double logarithmic plot is shown in Figure 1. It evidences a repartition of the points

with a rather high statistical spread, in an apparently nonlinear pattern, but which can be linearized on restricted value domains of  $I$ . Apparently, two interpretations are possible: 1) by two distinct linear regressions, with slopes of  $1.14 \pm 0.10$  and  $0.58 \pm 0.15$ , which intersect around  $I = 3$  mM and yield two curves A and B of the form:

$$\chi = \sigma I^\lambda, \quad \lambda = 0.58 \pm 0.15 \text{ (A)}, \\ 1.14 \pm 0.10 \text{ (B)} \quad (20)$$

and 2) by an unique nonlinear curve with continuously decreasing slope (and which might reach even a maximum or saturation at very high ionic strengths, where the slope could approach zero).

Note that the slope 1.14 of the regression line in the lower ionic strength domain is close to 1, similarly to the first (linear) term of eq. (18). At the same time the slope 0.58 of the second line is close to 1/2, being formally similar to eqs. (6–16) which contain  $I^{1/2}$ , and far of 3/2 like in eq. (19), which excludes a fit with a function of the later form (19). However, a fit of the whole examined ionic strength domain with an arbitrary single function of the form:

$$\chi = \alpha - \beta(1 - \gamma I^{0.5}) / I^{0.5} \quad (21)$$

might be possible, but finding the parameters  $\alpha$ ,  $\beta$ ,  $\gamma$  for a good fit is difficult and this hypothesis requires further examination. Therefore we favor the two-curve hypothesis. Its main result is the identification of two distinctive classes of mineral waters: A) at higher ionic strength and with higher conductivity (San Benedetto, Borsec, Evian, Zizin, Vittel, Perla Covasnei and, somewhat more excentric, Dorna); and B) at lower ionic strength and showing lower conductivity (Bucovina, Izvorul Minunilor, Hera). In between there is an intermediate domain of ionic strength and conductivity where a number of mineral waters share characteristics of both classes A and B (including Izvorul Zanelor, Keia, Herculane, Calipso and Roua). It is plausible that the water and ions have different structures and sustain different conductivity mechanisms in the classes A and B and intermediate characteristics in the A+B zone. This suggests that the medical properties of mineral waters might also be differentiated in the A and B groups and, possibly, in the A+B group they might show joined physiological action, but an extended analysis based on clinical data is needed to check this conjecture.



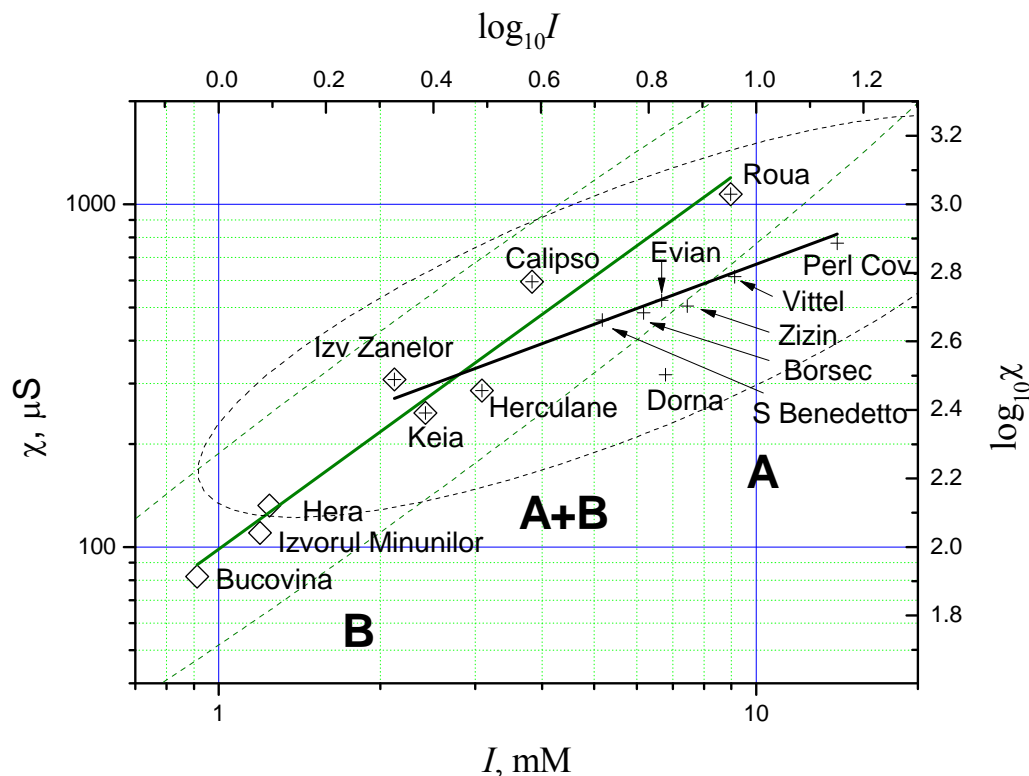


Figure 1. Double logarithmic plot of measured conductivity as a function of ionic strength of the investigated still mineral waters.

Table 1

Measured conductivities, Debye length and other parameters of some mineral waters

Still mineral water	Ionic strength, $I$ , <sup>a</sup> mM	Measured conductivity, $\chi$ ( $\mu\text{S}/\text{cm}$ ) <sup>*</sup>	Mean Debye length, $1/\kappa$ , <sup>b</sup> (nm)	Dissolved ions (nominal qualitative composition)	Type of electrolytes	Domain according to $\chi$ versus $I$ relationship
Bucovina	0.913	82	10.3	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{HCO}_3^-$	1:2, 1:1	B
Izvorul Minunilor	1.195	110	8.97	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{HCO}_3^-$	1:2, 1:1	B
Hera	1.243	132	8.79	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{HCO}_3^-$	1:2, 1:1	B
Izvorul Zanelor	2.126	308	6.72	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{HCO}_3^-$	1:2, 1:1	A+B
Keia	2.424	246	6.29	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , $\text{PO}_4^{3-}$ , $\text{Fe}^{2+}$ , $\text{Mn}^{2+}$ , $\text{HCO}_3^-$	1:2, 1:1, 3:2, 3:1	A+B
Herculane	3.091	286	5.58	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{HCO}_3^-$	1:2, 1:1	A+B
Calipso	3.830	595	5,01	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{HCO}_3^-$	1:2, 1:1	A+B
San Benedetto	5.172	460	4,31	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{HCO}_3^-$	1:2, 1:1	A

Table 1  
(continued)

Still mineral water	Ionic strength, $I$ , <sup>a</sup> mM	Measured conductivity, $\chi$ ( $\mu\text{S}/\text{cm}$ )*	Mean Debye length, $1/\kappa$ , <sup>b</sup> (nm)	Dissolved ions (nominal qualitative composition)	Type of electrolytes	Domain according to $\chi$ versus $I$ relationship
Borsec	6.173	482	3.95	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{HCO}_3^-$	1:2, 1:1	A
Evian	6.675	525	3.79	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{SO}_4$ , $\text{NO}_3$ , $\text{HCO}_3$	1:2, 1:1	A
Dorna	6.778	318	3.77	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{NO}_3^-$	1:2, 1:1	A
Zizin	7.447	505	3.61	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{HCO}_3^-$	1:2, 1:1	A
Roua	8.968	1070	3.27	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{HCO}_3^-$	1:2, 1:1	A+B
Vittel	9.120	615	3.25	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$ , $\text{HCO}_3^-$	1:2, 1:1	A
Perla Covasnei	14.158	770	2.61	$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$ , $\text{Fe}^{2+}$ , $\text{SO}_4^{2-}$ , $\text{NO}_3^-$	1:2, 1:1	A

<sup>a</sup>Computed from the nominal ionic compositions, neglecting  $\text{HCO}_3^-$ . <sup>b</sup>Mean radius of hydrated ions.

In the examined ionic strength domain, the non-linearity of the  $\chi$  versus  $I$  data emphasizes the nature of mineral waters as non-ideal electrolyte solutions, irrespective of data interpretation by two intersecting straight lines or by one unique curve. However, while eq. (21) suggests an unique conduction mechanism, eq. (20) is consistent with two distinct mechanisms towards the lower and higher ends of the ionic strength domain, with a smooth passage from one to another or with an overlapping between them in the central domain.

To interpret qualitatively the conductivity results, a possible hypothesis could be suggested in the frame proposed by Onsager, who demonstrated that this kind of behaviour may show *a*) a mass-action equilibrium between neutral pairs and individual ions at low ionic strength and that *b*) at higher concentrations the current is carried mostly by charged aggregates of several ions in mass-action equilibrium with smaller neutral aggregates and simple pairs [O. Nobel p. 283].

We thus see that the results are consistent to the non-uniform distribution of ions and water molecules in the mineral waters, as described in the simplest form by the charge cloud around individual ions of the Debye-Hückel picture. Moreover, larger ionic associations are supposed to occur in mineral waters: neutral pairs, smaller neutral aggregates,

charged aggregates of two or several ions. The co-existence of monovalent (e.g.  $\text{Na}^+$ ,  $\text{Cl}^-$ ) and divalent ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) ions, the complex ionic composition, seem to favour the heterogenous structure in mineral waters.

Even within the simplified Debye-Hückel picture, the ionic atmosphere around the dissolved ions is characterized by the values of the Debye radius  $\kappa^{-1}$  between 2.6 and 10 nm – a remarkable spread in the values of a parameter which describes the heterogeneity in the structure of mineral waters. Noteworthy, the Debye radius is below 5 nm for the class A formed by San Benedetto, Borsec, Evian, Dorna, Zizin, Vittel and Perla Covasnei, as well as for Roua of A+B group, between 5 and 7 nm for most of the ones of class A+B (Calipso, Herculane, Keia, Izvorul Zanelor) and around 9–10 nm in class B (Hera, Izvorul Minunilor, Izvorul Minunilor). This indicates a higher mobility of ions in class A mineral waters as compared to classes A+B and B. Apparently, the smaller estimated average Debye radius for the mineral waters in the higher ionic strength domain seems to disagree with the Onsager's concept of conductivity by charged aggregates of several ions in this domain, as opposed to the current carried by individual ions at low ionic strength. But the mentioned mechanisms were discovered by Onsager and his group in

solutions of big organic complex ions dissolved in solvents of very low dielectric constant. The situation is strongly different in the mineral waters (simple ions, high dielectric constants) and, therefore the Onsager's picture may apply or not in our aqueous solutions containing a complex mixture of inorganic ions. Thus although this image remains inspirational, the problem of detailed conduction mechanisms in mineral waters seems to require further investigation.

In reality the intuitive picture should be even much more complex; other effects not accounted in the Debye-Hückel and subsequent theories – *e.g.* the hydration of ions due to the large dipole moment of water – may contribute to additional heterogeneity in the mineral waters. But on a nanometric scale, outside the Debye sphere around ions, where the electrostatic influences of ions are screened, and water is “pure”, this unique substance so important for life, with its high dipole moment, may form an oscillating ionic plasma<sup>52</sup> or vibronically active water nanoclusters<sup>53</sup> which are consistent to the hypothesis of “quantum coherence” essential to biomolecular function<sup>54,55</sup> as well as to the size and shape of living cells<sup>56</sup>. Implicitly, these more elusive – but biologically important – properties of the “pure” (bulk) water between ions will depend on the distance between them (their density, *i.e.* ionic strength) and on their average Debye radius. In other words, such properties will be different in various mineral waters.

It is plausible that the physical heterogeneity of structure in mineral waters discussed here may influence somehow the structure and functionality of blood plasma and other body fluids and hence the health of the organism – although a physical description of this internal medium containing dissolved proteins, sugars and other biomolecules and floating cells is infinitely much more difficult. By comparison, mineral waters appear simple systems, and only our attempt to a physical description evidenced their complexity. But the above discussion emphasized the importance of mineral waters as possible carriers of heterogeneity' on a nanometric scale, a property worth of further investigation.

As a final note, we resume the discussion from the Introduction about the kosmotropic and chaotropic properties of ions in water and about the Hofmeister series<sup>57</sup>, and this perspective may offer an additional clue. Kosmotropes cause water molecules to favorably interact, which also

stabilizes intramolecular interactions in macromolecules such as proteins<sup>58,59</sup>. A scale can be established if one refers to the Hofmeister series or looks up the free energy of hydrogen bonding of the salts, which quantifies the extent of hydrogen bonding in water<sup>60</sup>. At least for alkali ions, based on calculations of transition energies of a water molecule within the hydration atmosphere, ions have been distinguished according to their tendency to order or to disperse water in their vicinity<sup>7</sup>. Similar calculations of hydration entropies evaluated structure-ordering and structure-disordering effects of alkali ions<sup>6</sup>.

In this context, it is interesting to note that the Romanian mineral waters Borsec, Dorna, Zizin, Perla Covasnei of class A together with Roua of class A+B, as well as with the prestigious waters San Benedetto, Evian and Vittel also of class A have the highest concentrations values of kosmotropic ions. More precisely, they show the sum  $[Ca^{2+}] + [Mg^{2+}]$  in the range 1.6–3.6 mM, in contrast to class B waters Bucovina, Izvorul Minunilor and Hera, with the corresponding parameter in the range 0.25–0.60 mM. Therefore the high kosmotropic ions concentration appears to correlate somehow with the curve showing a 0.58 slope and with the smaller Debye radius. These two parameters appear to concur in identifying mineral waters with special properties.

The previous analysis of conductivity *versus* ionic strength showed that class A waters have higher ionic strength and lower average Debye radius of the ionic atmosphere, suggesting a higher density of heterogeneity centers, but each with a circumjacent influence of a shorter range on the average, and implicitly with a higher mobility. This picture is consistent at the same time to the ordering influence produced by the kosmotropic ions  $Ca^{2+}$  and  $Mg^{2+}$  in their hydration sphere and in the bulk water. The relationship between these physico-chemical properties and the biological and medical value of these waters remain to be investigated.

Nevertheless the San Benedetto, Evian and Vittel waters, as well as Roua and Perla Covasnei, contain also the chaotropic ion  $SO_4^{2-}$ , which is expected to produce disordering of the water structure, in competition with the kosmotropic ions  $Ca^{2+}$  and  $Mg^{2+}$ . This compositional particularity has to be examined from a clinical viewpoint in comparison with waters having similar ionic

strengths and conductivities and Debye radii of the ionic atmosphere.

## CONCLUSIONS

The conductivity of 15 Romanian and international mineral waters was measured as a function of their ionic strength based on their nominal composition, in search of a simple method for a phenomenological characterization. In a double logarithmic plot, a nonlinear dependence was found, showing that mineral waters are non-ideal solutions, with complex electrolytes composition and mechanisms of ionic conductivity. An overview of theoretical models aiming to explain the departures from ideality in solutions of electrolytes starting with the Debye-Huckel theory and including subsequent more sophisticated developments, shows that theories could not explain in all details the behavior of non-ideal solutions on wide domains of ionic strength, however limited agreement theory and experiment could be obtained on restricted domains. Our data could be fitted with two distinct curves in the lower and higher ionic strength domains. Thus two distinctive classes of mineral waters were identified, with a third class having intermediate properties. The estimated average Debye radius was significantly smaller for the mineral waters in the higher ionic strength domain.

To interpret qualitatively the conductivity results, a possible hypothesis could be proposed in the frame of Onsager's theory of current carriers, postulating an equilibrium between neutral pairs and individual ions at low ionic strength and an equilibrium between charged aggregates of several ions, smaller neutral aggregates and simple pairs at higher concentrations. However, this image apparently disagrees with the smaller estimated average Debye radius for the mineral waters in the higher ionic strength domain. Thus the problem of detailed conduction mechanisms in mineral waters requires further investigation.

The mineral waters grouped in the higher ionic strength domain contained also higher concentrations of the kosmotropic ions  $[Mg^{2+}] + [Ca^{2+}]$ , which suggest that they are characterized by a more ordered structure of water molecules. In brief, as compared to the low ionic strength mineral waters, this class of waters show smaller estimated average Debye radius of ions, higher mobility of ions and a more ordered bulk water structure based on favoured hydrogen bonding. However, due to their

complex ionic composition, the nonlinear properties of mineral waters are too complicated to be explained by simplified theoretical models and to suggest straightforward mechanisms of electrical current conduction. Our study could thus provide a basis for further physical chemistry studies of conductivity mechanisms as well as for thorough investigations of clinical differences between the identified classes of mineral waters.

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