

A CASE STUDY OF CONDUCTIVITY IN MINERAL WATER

Eugen A. PREOTEASA^a and Constantin IONESCU-TIRGOVISTE^{b*}

^a“Horia Hulubei” National Institute for Physics and Nuclear Engineering, P.O. Box MG-6, 077125 Bucharest-Magurele, Romania, E-mail: eugenpreoteasa@gmail.com

^b“Nicolae C. Paulescu” National Institute of Diabetes, Nutrition and Metabolic Diseases, Ion Pavel Diabetes Center, 12 I.L. Caragiale St., Bucharest, Romania, E-mail: cit@paulescu.ro

*Correspondence: cit@paulescu.ro.

Received

Conductometry studies evidenced non-ideal electrolyte solution properties of mineral waters. They classified themselves in two groups with an intermediate domain between. Keia is a high purity water at the junction of the two main groups. It shows the highest concentration in Ca^{2+} – thus the main charge carrier – followed by Mg^{2+} , Na^+ and SO_4^{2-} . Low HCO_3^- results in a pH slightly more alkaline than blood plasma. Although formation of ionic associations ($\text{Ca}^{2+}\text{SO}_4^{2-}$, $\text{Mg}^{2+}\text{SO}_4^{2-}$) limit the Debye-Huckel theory, the Davies plot shows two straight lines, with Keia at their intersection. A histogram of ionic strength is irregular, and Keia is placed towards lower values, pointing to large limits of the intermediate group. The histogram of measured conductivity supports a Gaussian fit, with Keia placed within the (mean \pm SD) interval, hosting ~67 % of the mineral waters; they may show thus similar charge transport mechanisms. For Debye radius fit attempts of the histogram failed, and Keia was close to the mean value. Outside the corresponding volume of Debye spheres the water molecules interact by hydrogen bonds forming clusters, as sustained also by the mean value of the ordering, kosmotropic, total $\text{Ca}^{2+}+\text{Mg}^{2+}$ ions. The possible role of water clusters in homeopathy is discussed.

Keywords: Mineral water, Debye-Hückel radius, Davies equation, ionic strength, conductivity, Keia.

INTRODUCTION

In previous studies we investigated comparatively 15 mineral waters by conductometry aiming to evaluate the potential of this simple and convenient method for characterizing them and to elaborate a picture of their structure at the ionic and molecular level^{1,2}. These mineral waters have a large variety of complex ionic composition, with ionic strength between ~1 and ~14 mM, and showed a ionic conductivity covering a range of values as large as almost two decades, from below 10^2 to above 10^3 $\mu\text{S}/\text{cm}$. They evidenced pronounced properties of non-ideal electrolyte solutions. This means that ions are not randomly distributed throughout the solution, because ions of opposite charge attract each other, while ions of the same charge repel each other. Accordingly the thermodynamic properties of the solution are not additive and the activity coefficient of each component are is not equal to one. The departures from ideality in solutions of electrolytes was described first by the classical Debye-Hückel

theory³ and by many subsequent models, of which the Davies equation⁴ is particularly convenient for analyzing experimental data. In our case, it showed that the investigated mineral waters classify themselves in two groups with distinct properties, towards low and, respectively, high ionic strength values². Due to their specific character, the mineral waters of the two domains were carefully examined. However, there is an intermediate domain between the two aforementioned, where the mineral waters could evidence interesting properties, as it happens frequently at boundaries. We illustrate now this domain by the case study of the mineral water Keia which was located almost exactly at the junction of the two domains. The present perspective focused on individual details is complementary to the previous one intended to release a sketch of the big picture.

THEORETICAL BACKGROUND

Mineral waters are aqueous electrolyte solutions characterized by conductivity and by ionic strength, and by the relationship between these two

quantities⁵⁻¹¹. The ionic strength of a solution is a measure of its concentration of ions is a function of the concentration of *all* dissolved ions:

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

where c_i is the molar concentration of ion i (M, or 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. Concentrations c_i are usually expressed in a molar base (M, or mol/L) but, because mineral waters are non-ideal solutions where volumes are no longer strictly additive, it is preferable to work with molality b_i (mol/kg{H₂O}) instead of c_i . As charge transport in electrolyte solutions takes place by ions, conductivity depends on ionic strength. we have to deal on one side with the 'measured conductivity', χ , which is the reciprocal of solution's resistivity ρ , and on the other with the 'molar conductivity', Λ_m , defined as the ratio of the measured conductivity χ to the molar concentration c of the electrolyte, $\Lambda = \chi/c$. Note that the molar conductivity is a difficult concept for an aqueous solution of a complex mixture of dissolved ions in different proportions. However the basic notions are defined for a single dissociated electrolyte^{10,11}. In such a solution the measured conductivity is proportional to the activity a of a dissolved ion

$$\chi \sim a, \quad (2)$$

which is proportional to concentration c ; the proportionality constant is known as an activity coefficient, γ :

$$a = \gamma c \quad (3)$$

The mean activity coefficient of a fully dissociated electrolyte of formula $A_n B_m$ is given by

$$\gamma_{\pm} = (\gamma_A^n \gamma_B^m)^{1/(n+m)}. \quad (4)$$

In an ideal electrolyte solution the activity coefficients of all the ions are equal to one, while in non-ideal solutions the activity coefficients are different of one due to the interactions between ions and to their non-uniform distribution. Activity coefficients are themselves functions of concentrations (eq. 4) as the amount of inter-ionic interactions increases as the concentrations of the electrolytes increases.

Debye-Hückel theory³ allows single ion activity coefficients – and associated properties like

conductivity – to be calculated. The principal assumption is that each ion is surrounded by ions of opposite charge which form a fuzzy spherical cloud and which can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach. The solvent is described as a uniform medium of constant relative dielectric constant, without structure. It is also assumed that the solute is a strong electrolyte completely dissociated and that ions are spherical and are not polarized by the surrounding electric field. Solvation of ions by water can be ignored except insofar as it determines the effective sizes of the ions and there is no electrostriction.

The molal activity coefficient of ions A^+ and B^- in the Debye-Hückel theory³ is:

$$\log_{10} \gamma_{\pm} = -A z_j^2 \frac{\sqrt{I}}{1 + B a_0 \sqrt{I}} \quad (5)$$

$$A = \frac{e^2 B}{2.303 \times 8 \pi \epsilon_0 \epsilon_r k T} \quad (5')$$

$$B = \left(\frac{2 e^2 N}{\epsilon_0 \epsilon_r k T} \right)^{1/2}, \quad (5'')$$

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 $B = 3.29 \text{ nm}^{-1} \text{ mol}^{-1/2} \text{ dm}^{3/2}$. Also ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant, k is the Boltzmann constant, T is the absolute temperature, N_A is the Avogadro number, and e is the elementary charge.

The Debye-Hückel equation gives a satisfactory agreement with experimental measurements of the activity coefficient for solutions of 1:1 electrolytes (e.g. Na⁺Cl⁻) at sufficiently low concentrations (less than 10⁻³ mol/L). 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. Ca²⁺, Mg²⁺, SO₄²⁻, etc., which are present in mineral waters) deviations from the theoretical predictions occur. This is particularly relevant for the Keia water which is dominated by Ca²⁺ and contains also lower concentrations of Mg²⁺ and SO₄²⁻ (see below). 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 Debye-Hückel equation one or more terms

describing aspects of the phenomena ignored in the original theory. The semi-empirical model due to Davies⁴ is of major interest from this perspective.

Using the **Davies equation**⁴ one can calculate activity coefficients of electrolyte solutions at relatively high concentrations. The equation was refined by fitting to experimental data. The final form of the equation gives the mean molal activity coefficient, γ_{\pm} , of an electrolyte which dissociates into ions having charges z_1 and z_2 as a function of ionic strength, I .

$$-\log \gamma_{\pm} = \frac{1}{2} z_1 z_2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.15I \right). \quad (6)$$

The first term is similar to the Debye–Hückel equation. 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 for 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. For electrolytes that dissociate into ions with higher charges and if there is association between the ions, with the formation of ion-pairs, such as $\text{Mg}^{2+}\text{SO}_4^{2-}$, the calculations become less precise^{12,13}. Once again, such are phenomena to be expected in the Keia mineral water.

Debye length¹⁴. 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 and outside of which charges are electrically screened.

In an electrolyte or a colloidal suspension, the Debye length¹⁴ for a monovalent electrolyte, usually denoted with symbol κ^{-1} (and with χ^{-1} by some authors, not to be confounded with the reciprocal of conductivity) is given by:

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 kT}{2N_A e^2 I}}. \quad (7)$$

Alternatively, it may be expressed by making use of the *Bjerrum length*¹⁴:

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

where λ_B , the Bjerrum length of the medium, 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. In standard units, the Bjerrum length is given by

$$\lambda_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B}, \quad (9)$$

where e is the elementary charge, ε_r is the relative dielectric constant of the medium and ε_0 is the vacuum permittivity. For water at room temperature, $T \sim 300$ K, $\varepsilon_r \sim 80$, so that $\lambda_B \sim 0.7$ nm.

Expressing the Debye length in cm one obtains the equation¹¹:

$$\kappa^{-1}(\text{cm}) = 1.988 \cdot 10^{-10} \sqrt{\frac{\varepsilon_r T}{I(\text{M})}}. \quad (10)$$

At room temperature (25 °C), for 1:1 electrolytes (e.g. Na^+Cl^-) in water, one can consider the simplified expression for the Debye length:

$$\kappa^{-1}(\text{nm}) = \frac{0.304}{\sqrt{I(\text{M})}}, \quad (10')$$

where κ^{-1} is expressed in nanometers (with the relative dielectric constant of water $\varepsilon_r = 78.6$); this expression evidences most clearly the inverse square root relationship between Debye radius and ionic strength.

EXPERIMENTAL

The KeiaTM bottled mineral water was extracted from an underground water deposit located at Cheia, Izvorul Zaganului in the Ciucas Mountains natural park, Romania¹⁵. Conductivity measurements were performed in standard conditions¹⁶ as previously described² using a Romanian instrument with alternating voltage in the kHz range in order to avoid electrolysis¹⁷, with a standard cell of 1 cm width between electrodes at 26 °C. The dependence on the frequency is usually small¹⁸, but may become appreciable at very high frequencies, an effect known as the Debye–Falkenhagen effect^{19–21}. 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 composition as specified by the manufacturers¹⁵.

Only strong electrolytes have been considered. Nominal values of ionic concentrations in mg/L, converted in mmol/L, were used for calculating the ionic strength expressed in mmol/L (mM). The contribution of the weak electrolytes HCO_3^- and H_2PO_4^- 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 ($0.75 \cdot 10^{-2}$), respectively⁵. The approximate Debye radius κ^{-1} valued were estimated from the ionic strength values using eqs. ($10, 10^7$) valid for 1:1 electrolytes, neglecting possible discrepancies due to ions with electric charge higher than one present in the samples. The results obtained before for Keia and other 14 mineral waters² were used for locating Keia in an overall picture.

Table 1

The nominal ionic composition of Keia still mineral water*

Ion	Concentration, nominal (mg/L)
Ca^{2+}	40.73–44.85
Mg^{2+}	2.87–2.90
Na^+	2.2
K^+	0.6
Cl^-	< 4.0
HCO_3^-	149
PO_4^{3-}	< 0.04
SO_4^{2-}	5.8
Ionic Fe	0.022
Ionic Mn	0.01
Ionic Pb	0.0005
Total dry residue	142–147
pH	7.83

*As specified by the producer [21].

CHEMICAL COMPOSITION

The ionic composition of Keia mineral water¹⁵ is given in Table 1 and their role is discussed below.

The ionic conductivity in the Keia mineral water is due to four cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and four anions (Cl^- , HCO_3^- , PO_4^{3-} , SO_4^{2-}). The highest

concentrations are shown by Ca^{2+} followed by Mg^{2+} and Na^+ , and by HCO_3^- , of which Ca^{2+} is probably the most important charge carrier. The bicarbonate concentration was among the lowest in the investigated 15 mineral waters; anyway, the bicarbonate has very low dissociation constants and is a weak electrolyte, which implies only a small contribution to conductivity and to other properties. Probably the strong electrolytes like SO_4^{2-} play more important roles, in spite of their relatively lower concentration. We note that Keia was the only mineral water containing PO_4^{3-} , also a weak electrolyte. It did not contain neither the NO_3^- ion nor dispersed SiO_2 particles¹⁵, showing thus a high purity, an aspect which most probably is medically relevant.

This water is among the few investigated which contained ions of transition metals such as Fe and Mn. They may have multiple valence states and no further specification is given on this aspect important in principle for charge transport, but their contribution can be neglected due to very low concentrations. The later ions may play an useful role as cofactors in the active centers of some metabolically important enzymes. Moreover it contained very low traces of Pb, about 0.5 ppb; this concentration is more than one order of magnitude below the maximum allowed concentration of 15 ppb in drinking water²², and thus it did not represent any biological risk in spite of lead toxicity. The total dry residue of 142 mg/L was among the lowest in the investigated mineral waters which showed values in the range of 50–1700 mg/L; therefore Keia can be considered a weakly mineralized water. The pH of 7.83 is associated in part to the low value of bicarbonate (147–149 mg/L)¹ and is slightly more alkaline than the blood plasma; the alkaline nature of this water is probably of substantial clinical relevance, as a prophylactic action of drinking alkaline liquids is widely accepted. Keia does not contain detectable concentrations of B, NH_4^+ , F^- and NO_2^- ; moreover the measured radioactivity level is extremely low (0.004 Bq/L global alpha activity and 0.17 Bq/L global beta activity)¹⁵.

Note that due to its high concentration, the presumably important role of Ca^{2+} in the ionic charge transport could be disturbed by the formation of ionic associations between this and other divalent ions, like $\text{Ca}^{2+}\text{SO}_4^{2-}$, $\text{Mg}^{2+}\text{SO}_4^{2-}$, ... which result in departures of conductivity from the theoretical predictions of eqs (5–5'') and (6).

CONDUCTOMETRY. RESULTS AND DISCUSSIONS

The physico-chemical properties relevant for conductivity of the still mineral water Keia are presented in Table 2. They will be discussed in the following.

In our previous study [2] on 15 mineral waters, a comparison of experimental data to the Davies equation (13) has been done in a $\log_{10}\chi$ vs. $I^{1/2}/(1+I^{1/2}) - 0.15I$ plot (Fig. 1). This diagram shows that the investigated mineral waters classify in two

groups A and B, each of them represented by a characteristic linear fit with different slopes and intercepts. The two straight lines intersect and it is remarkable that the datapoint of Keia is located very close to the intersection of linear fit lines. Of the 15 mineral waters, only Keia, Heculane and Izvorul Zanelor are located in this zone of the diagram. This suggests that Keia (and the other two) have properties intermediate to the A and B groups, in a A+B subgroup. And it is precisely for this reason that we pay a particular attention to Keia mineral water.

Table 2

Ionic strength, conductivity and other properties of the Keia still mineral water

Ionic strength, I^a mM	Measured conductivity, χ ($\mu\text{S}/\text{cm}$)*	Mean Debye length, $1/\kappa^b$ (nm)	Dissolved ions (nominal qualitative composition)	Type of electrolytes
2.424 ± 0.021	246 ± 18	6.29 ± 0.03	Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , Fe^{2+} , Mn^{2+} , HCO_3^-	1:2, 1:1, 3:2, 3:1

^a Calculated from the nominal composition as specified by the producer.

^b Estimated from the ionic strength with eq. (10).

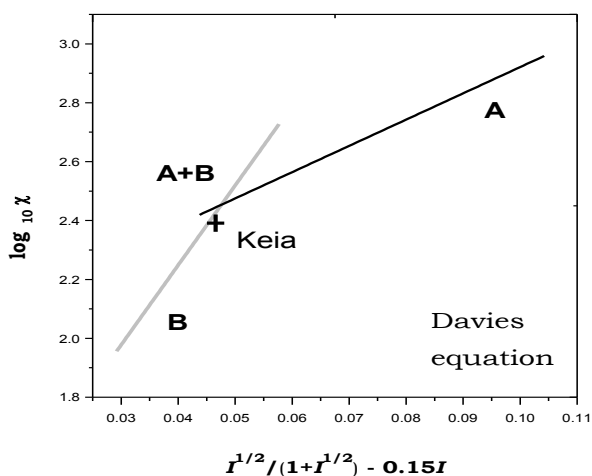


Figure 1. Davies equation (eq. 6) linear fit of the conductivity data of the investigated 15 mineral waters evidencing the two distinctive domains A and B by two straight lines with significantly different slopes. The representative point of Keia mineral water is located close to their intersection, where a domain A+B of mineral waters with intermediate properties is defined. Modified after Ref. [2-Preoteasa and Ionescu-Tirgoviste 2015, in press].

In a histogram of the ionic strength values of the 15 investigated mineral waters, Keia is located in the 2–4 mM interval (Fig. 2), together with Heculane and Izvorul Zanelor [2]. The ionic strength histogram has an irregular shape, suggesting a possible bimodal distribution, but it does not allow fitting with current peak functions e.g. Gaussian,

Poisson). The weigh center of the histogram is at 5.4 mM. The set of ionic strength value has an arithmetic mean and standard deviation of 5.29 ± 3.72 mM, a geometric mean of 3.989 ± 0.003 mM and a median of 5.172 mM. Thus the Keia mineral water ($I = 2.42$ mM) has a ionic strength value in the lower values domain by any criterion. This shows that the intermediate position of Keia in the plot of Fig. 2 is not associated with a value of the ionic strength around the mean. Accordingly, Keia can be considered a low minerality, high purity mineral water.

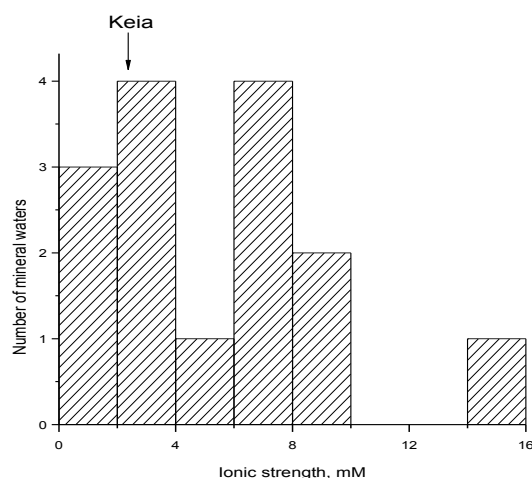


Figure 2. Ionic strength histogram of the investigated 15 mineral waters. Keia is located in the 2–4 mM interval.

The histogram of the conductivity for the 15 investigated mineral waters is much more compact (Fig. 3). It shows that the Keia mineral water is located in the 200–300 μS interval. In contrast to the one of ionic strength, it supports a fit with a Gaussian centered at 383 μS and with a halfwidth of $\pm 236 \mu\text{S}$. The weight center is at around 437 μS , in a position roughly symmetrical to the conductivity of the Keia mineral water at 242 μS with respect to the center of the Gaussian. Also, Keia is placed within the (mean \pm SD) domain of the Gaussian, where it is probable to find around 67 % of the data; in fact between ~ 150 and $\sim 600 \mu\text{S}$ one finds 10 of the measured conductivities (thus 10/15 is 66.7 %). The results suggest that, according to the conductivity, the A+B class of mineral waters where Keia belongs, is representative for a majority of the investigated mineral waters.

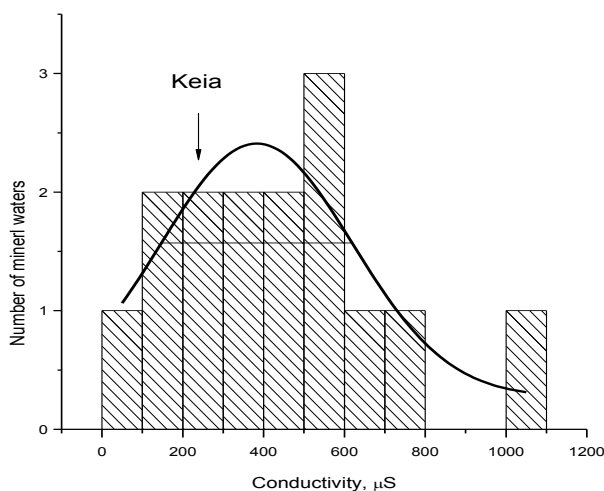


Figure 3. Conductivity histogram of the investigated 15 mineral waters. Keia is located in the 200–300 μS interval, relatively close to the center of the Gaussian fit curve of the histogram.

The histogram of Debye radius or length as calculated with eq. (10) for the investigated 15 mineral waters is shown in Figure 4. Our attempts to fit the histogram with a Gaussian or other peak function failed. The Debye radius of the Keia water is placed in the 6–7 nm interval of the histogram, which is close to the mean value of this parameter ($5.3 \pm 2.4 \text{ nm}$). This implies an intermediate value for the total volume of the Debye spheres outside of which ionic charges are electrically screened and where the water molecules interact mainly by hydrogen bonds.

As a final characteristic parameter of Keia, we note the concentration of kosmotropic ions, $[\text{Ca}^{2+}] +$

$[\text{Mg}^{2+}] = 1.134 \text{ mM}$, which is due mainly to the Ca^{2+} ion as the major electric charge carrier in this mineral water (Table 1). In the Hofmeister series²³, kosmotropes favor interactions between water molecules^{24,25} and stabilize intramolecular interactions in proteins²⁶.

The Hofmeister series correlates to the free energy of hydrogen bonding in solutions of electrolytes, and quantifies the extent of hydrogen bonding in water^{24,25}. At least alkaline ions have been classified according to their tendency to order or to disperse water in their vicinity and to their hydration entropies (which evaluate structure-ordering and structure-disordering effects). The Ca^{2+} and Mg^{2+} ions are among the strongest kosmotropic ions in the Hofmeister series, and their total concentration in Keia (1.134 mM) is more close to the values domain of this parameter typical for class A mineral waters (1.6–3.6 mM) than to the range of values in class B mineral waters (0.25–0.60 mM) [2].

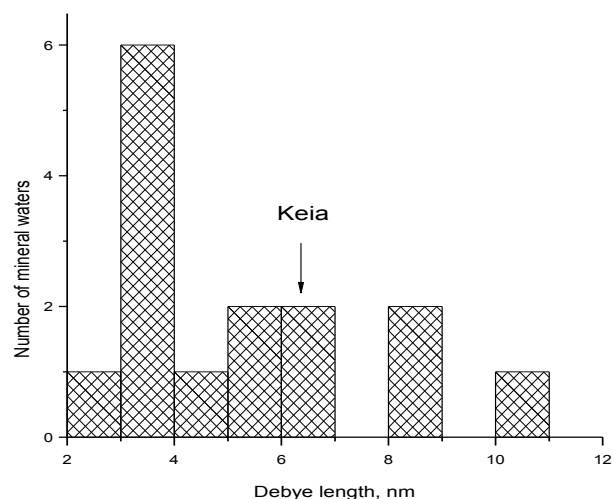


Figure 4. Debye length histogram of the investigated 15 mineral waters. Keia is located in the 6–7 nm interval, relatively close to the mean value of the Debye length represented in the histogram.

Therefore Keia, as a mineral water representative to the A+B class, can be expected to have a relatively high ordering of the water molecules between ions, including in clusters formed by hydrogen bonding. Such clusters²⁷⁻³¹ have been shown to possess strong dipole moments oscillating in the THz domain²⁷ by coherent vibrations and supposed to play important biological roles in regulating the cell functions³²⁻³⁷ and in homeopathy³⁸.

Due to the partial covalency of water's hydrogen bonding⁵, electrons are not held by individual molecules but are easily distributed amongst water clusters giving rise to coherent regions³²⁻³⁷. They are associated with the controversial issue of "memory of water" supposed to be involved in homeopathy, but they are supported by substantial, although indirect so far, physical evidence²⁸⁻³⁸. Recently, Nobel prize-winning Luc Montagnier has declared that quite dilute solutions of DNA show entirely different properties from the less diluted solutions that the authors propose depend on interactions with the ambient electromagnetic field³⁹⁻⁴⁰. The extraordinary results given in this paper have yet to be independently confirmed. Samal and Geckeler have published an interesting, if controversial, paper⁴¹ concerning the effect of dilution on some molecules. They found that some molecules form larger clusters on dilution rather than the smaller clusters which are thermodynamically expected. The presence of one such large, μm -sized cluster in the diluted solution could give rise to the noticed biological action. This paper is criticized by other authors⁴² but the new work by Luc Montagnier³⁹⁻⁴⁰ reinforces the unexpected dilution aspect of this work. A related phenomenon may be the occurrence of conductivity oscillations (~ 0.5 Hz) at similar concentrations of salts at the low concentration limit of obedience to Kohlrausch's law (Onsager's formula)⁴³. In brief, search of more direct physical evidence of water clusters has to be continued, because "[water] solutions are more complex than expected"³⁸.

CONCLUSIONS

Keia is a high purity mineral water, weakly mineralized, with the highest concentration shown by Ca^{2+} among the dissolved electrolytes followed by Mg^{2+} and Na^+ , and with very low HCO_3^- concentration. It does not contain neither the NO_3^- ion nor dispersed SiO_2 particles, but it contains traces of Fe and Mn ions, which may be used as cofactors in the active centers of some metabolically important enzymes. Very low traces of Pb, ~ 30 times below the maximum allowed concentration in drinking water, do not represent any biological risk. Its pH is slightly more alkaline than the blood plasma, and its alkaline nature together with the other compositional characteristics is probably of clinical relevance. Because Ca^{2+} is the dissolved ion with the highest concentration, it

is probably the most important charge carrier. The formation of ionic associations between this and other divalent cations on one side and divalent anions (of the type $\text{Ca}^{2+}\text{SO}_4^{2-}$, $\text{Mg}^{2+}\text{SO}_4^{2-}$, ...) could result in departures of conductivity from the theoretical predictions. A comparison of Keia with other 14 mineral waters in the Davies plot (an extension derived from Debye-Hückel theory), based on the measured conductivity and ionic strength data shows that the investigated mineral waters classify in two groups, and that Keia is located at the intersection of these groups. This suggests that Keia has intermediate properties, a good reason for deserving a particular attention. Noteworthy, in spite of the possible associations between divalent ions, Keia is well located on the Davies plot according to conductivity and ionic strength. A histogram of the ionic strength values of the 15 investigated mineral waters is irregular, and Keia is located in the lower values domain. This appears to be in accordance with the comparatively low minerality of Keia, and points to the large limits of the intermediate properties domain evidenced by the Davies equation plot.

The histogram of the measured conductivity for the 15 investigated mineral waters looks like a rough approximation of a single mode distribution and supports a Gaussian fit. Keia is placed within the ($\text{mean} \pm \text{SD}$) domain, where it is probable to find around 67 % of the data; in fact one finds 66.7 % of the measured conductivities (namely, a domain containing 10 of the 15 examined samples). Thus according to the conductivity, the class of mineral waters where Keia belongs is representative for a majority of the investigated mineral waters. For the Debye radius values of the 15 mineral waters under study, the histogram hardly shows any regular pattern, and fit attempts with a Gaussian or other peak function failed. The Debye radius of Keia is close to the mean value, suggesting an intermediate value for the total volume of the Debye spheres outside of which the water molecules interact mainly by hydrogen bonds. This last feature of Keia may be related to a presumptive high ordering of the water molecules by hydrogen bonding in the volume between ions. Possible ordering may take the form of water clusters. This hypothesis is in agreement with the total concentration of the kosmotropic ions $\text{Ca}^{2+} + \text{Mg}^{2+}$ and their water ordering influence. By this

parameter, Keia is located also in an intermediate domain, but more close to the class of mineral waters with higher conductivity. By these characteristics, Keia water might be used also in children and even in newborns.

Water clusters formed by hydrogen bonding could have strong dipole moments oscillating coherently and are supposed to play important biological roles in the cell. Although large support exists, further studies are required to provide more direct evidence for their involvement in homeopathy. To resume, conductometry together with compositional data led to a relevant picture and an open perspective of specific physical-chemical properties of mineral waters, well illustrated by our case study of Keia.

REFERENCES

- Ionescu-Tirgoviste C., Preoteasa E., Carniciu S., The electrical conductivity of various natural still waters. *Rom. J. Diab. Nutr. Metab. Diseases* **2009**, *16*(4), 1-5.
- Preoteasa E.A., Ionescu-Tirgoviste C., Ionic structure in mineral waters: A conductometry study. Proceedings of the Romanian Academy B, **2016**, in press.
- Debye P., Hückel E., Zur Theorie der Elektrolyte. I. Gefrierpunktniedrigung und verwandte Erscheinungen [The theory of electrolytes. I. Lowering of freezing point and related phenomena], *Physikalische Zeitschrift* **1923**, *24*, 185-206.
- Davies C.W., "Ion Association", Butterworths, London, 1962.
- Pauling L., "General Chemistry", Third edition, W.H. Freeman Co., San Francisco, 1970.
- Stumm W., Morgan J.J., "Water Chemistry", New York, Wiley, 1996.
- Wright M.R., "An Introduction to Aqueous Electrolyte Solutions", Wiley, 2007.
- Engel T., Reid P., "Physical Chemistry", Prentice Hall-Pearson, Upper Saddle River, NJ, 2006, p. 194.
- Skoog D.A., West D.M., Holler F.J., Crouch S.R., "Fundamentals of Analytical Chemistry", Brooks/Cole Pub. Co., Pacific Grove, CA, 2004.
- Antropov L., *Theoretical Electrochemistry*, Mir Publishers, Moscow, 1972.
- Gerasimov Ya. (ed.), "Physical Chemistry", Vol. 2, Mir Publishers, Moscow, 1985.
- Onsager L., Fuoss R.M., *Proc. Natl.Acad.Sci. (U.S.)* **1955**, *41*, 274.
- Onsager L., The motion of ions: principles and concepts, *Nobel lecture*, 1968.
- Russel W.B., Saville D.A., Schowalter W.R., "Colloidal Dispersions", Cambridge University Press, Cambridge, 1989.
- Keia mineral water – producer information, Mihail House of Wines, Cheia 107356, DN1A 331, Romania.
- Glasstone S., "An Introduction to Electrochemistry", Maurice Press, 2008, p. 101
- Bockris J. O'M., Reddy A.K.N., Gamboa-Aldeco M., "Modern Electrochemistry" (2nd. ed.). Springer, Heidelberg – New York (1998).
- Bešter-Rogač M., Habe D., Modern advances in electrical conductivity measurements of solutions, *Acta Chim. Slov.* **2006**, *53*, 391.
- Debye P., Falkenhagen H., *Physik. Z.* **1928**, *29*, 401.
- Falkenhagen H., *Rev. Mod. Phys.* **1931**, *3*, 412.
- Anderson J.E., The Debye-Falkenhagen effect: experimental fact or fiction?, *J. Non-Crystalline Solids.* **1994**, *172-174 (Part 2)*, 1190.
- Tiemann M. Lead in Drinking Water: Washington, DC, Issues and Broader Regulatory Implications. (Report **2005**). Congressional Research Service, The Library of Congress. RS21831. Retrieved June 22, 2011.
- Chaplin M., Kosmotropes and chaotropes, in „Water Structure and Science”, South Bank University, London, Retrieved 2014-May-09.
- Nucci N.V., Vanderkooi J.M., Effects of salts of the Hofmeister series on the hydrogen bond network of water, *J. Mol. Liquids* **143** (2008) 160-170.
- Marcus Y., Effect of ions on the structure of water: structure making and breaking, *Chem. Reviews* **2009**, *109*(3), 1346.
- Moelbert S., Normand B., De Los Rios P., Kosmotropes and chaotropes: modelling preferential exclusion, binding and aggregate stability, *Biophys. Chem.* **2004**, *112*(1), 45.
- Johnson K., Terahertz vibrational properties of water nanoclusters relevant to biology, *J. Biol. Phys.* **2012**, *38*, 85.
- Chaplin M.F., A proposal for the structuring of water, *Biophys. Chem.* **83** (2000).
- Chaplin M., Shelton D.P., Long-range orientation correlation in water, *J. Chem. Phys.* **141** (2014) 224506. 211-221.
- Müller A., Bögge H., Diemann E., Structure of a cavity-encapsulated nanodrop of water, *Inorg. Chem. Commun.* **2003**, *6*, 52-53; Corrigendum: Müller A., Bögge H., Diemann E., *Inorg. Chem. Commun.* **2003**, *6*, 329.
- Garcia-Ratés M., Miró P., Poblet J.M., Bo C., Avalo J.B., Dynamics of encapsulated water inside Mo₁₃₂ cavities, *J. Phys. Chem. B*, **115** (2011), 5980-5992.
- Preparata G., "QED Coherence in Matter", World Scientific, Singapore–New Jersey, 1995.
- Del Giudice E., Preparata G., Vitiello G., *Phys. Rev. Lett.* **1988**, *61*, 1085.
- Del Giudice E., Doglia S., Milani M., *Phys. Scripta* **1982**, *26*, 232.
- Del Giudice E., Doglia S., Milani M., Vitiello G., *Nuclear Phys. B* **1986**, *275*, 185.
- Preoteasa E.A., Negoita C., A semi-classical approach of the relationship between simple cells' size and their living temperature limits based on number fluctuations of water coherence domains. *J. Phys. Conf. Ser.* **2011**, *329*, 012002 1-18.
- Apostol M., Preoteasa E., Density oscillations in a model of water and other similar liquids. *Phys. Chem. Liquids* **2008**, *46*(6), 653.
- Chaplin M., Memory of Water, in "Water Structure and Science", South Bank University, London, Retrieved 2014-May-09.
- Montagnier L., Aïssa J., Ferris S., Montagnier J.-L., C. Lavallée, Electromagnetic signals are produced by aqueous nanostructures derived from bacterial DNA sequences, *Interdiscip. Sci. Comput. Life Sci.* **2009**, *1*, 81-90.

-
40. Montagnier L., Aissa J., Del Giudice E., Lavalley C., Tedeschi A., Vitiello G., DNA waves and water, *J. Phys.: Conf. Ser.* **2011**, *306*, 012007, arXiv:1012.5166v1 [q-bio.OT].
 41. Samal S., Geckeler K.E., Unexpected solute aggregation in water on dilution, *Chem. Commun.* **2001**, *21*, 2224-2225.
 42. Hallwass F., Engelsberg M., Simas A.M., Lack of evidence of dilution history-dependence upon solute aggregation in water. A nuclear magnetic resonance determination of self-diffusion coefficients, *Chem. Commun.* (2002) 2530-2531.
 43. Lo S-Y., Li W., Onsager's formula, conductivity, and possible new phase transition, *Modern Phys. Lett. B* **13** (1999) 885-893.