Original Communication

Arrhenius' theory of partial dissociation and hydration completely replace existing ideas of activity and complete dissociation of electrolytes in solutions

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ABSTRACT

The author points out that Arrhenius's theory of partial electrolytic dissociation was immaturely displaced about eight decades ago by the empirical concept of ionic activities and the assumption of complete dissociation of electrolytes at all concentrations. The latter gradually amounted to converting the theory of electrolytes into a highly complicated set of parametrically extended Debye-Huckel equations without any physical significance. Therefore, the author abandoned the existing theory and undertook a systematic investigation of the available experimental data. Over the recent decades, the author could completely quantitatively restore the original theory of partial dissociation for all concentrations. Now solution properties can be easily explained through simple mathematical equations with absolute concentrations and volumes of ions and ion pairs and surface and bulk hydration numbers.

KEYWORDS: aqueous electrolytes, solution chemistry, electrolyte theory, thermodynamics of solutions, surface and bulk hydration

1. INTRODUCTION

Common table salt, also called the Divine substance [1], has been an indispensable ingredient in our daily lives for many centuries. However, a proper insight into its properties in aqueous solutions has intrigued the minds of many. It is only at the end of the nineteenth century that Arrhenius [2-5] made a big leap forward when he suggested that ".. *electrolytes, when dissolved in water, become to varying degrees split or dissociated into electrically opposite positive and negative ions. The degree to which this dissociation occurred depended above all on the nature of the substance and its concentration in the solution*" [3a].

Several biographies of Arrhenius can be found in [3, 5-7]. To quote from a recent tribute to Arrhenius [7], "Svante Arrhenius was an extremely talented man with an expansive range of interests, both inside and outside the academic domain. His early work with the dissociation of ionic substances, which was presented in his doctoral thesis (1884), earned him the Nobel Prize in Chemistry in 1903, twenty years after his first ideas in this area had been presented orally to a very sceptical and even scornful academic supervisor". Arrrhenius was awarded the Nobel Prize [3b] "*in recognition of the extraordinary services he has rendered to the advancement of chemistry by his electrolytic theory of dissociation*". For a preliminary version of this paper, see [8].

Arrhenius' theory of partial dissociation helped to explain the properties of dilute electrolyte solutions based on his idea that the conductivity ratio (which is ratio of the conductivity at a given

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Dedicated to Svante Arrhenius on the occasion of IYC 2011

concentration to that at infinite dilution) could be used as a measure of the degree of dissociation. Solution theory began to flourish and was developing well on this basis in the earlier decades of twentieth century. While researches were continuing to find ways of extending the theory to concentrated solutions, the seeming failure of the conductivity ratio in explaining the law of mass action or the Guldberg and Waage's law [9], gave rise to an 'interim' thermodynamics based on the empirical concepts of activities, activity and osmotic coefficients [10]. Since this was seemingly supported by the theory of interionic interaction between free ions [11] for dilute solutions with nearly completely dissociated electrolyte, the latter was (erroneously) assumed to be valid for all concentrations and the idea of partial electrolytic dissociation was soon dropped, despite many protests [12].

However, over the next few decades, explanation of the properties of solutions based on the empirical concepts of activity and osmotic coefficients and the idea of complete dissociation at all concentrations, amounted to converting painstaking data into more and more elaborate parametric equations to fit the data for higher and higher concentrations with less and less physical significance as noted by many [13-15]. Moreover, there was no unified explanation of the cause of non-ideality of solution properties for the whole range of concentrations.

On realizing that this clearly pointed to some conceptual errors in the development of solution chemistry, the present author systematically started re-investigating the available experimental data. It became evident gradually [16-33] that it was actually an unfortunate turn in solution chemistry to have prematurely abandoned the theory of partial electrolytic dissociation founded by Arrhenius.

This article shows briefly how partial dissociation and hydration are the two main causes of the non-ideal physicochemical properties of strong electrolyte solutions over the entire concentration range from zero to saturation. The series of papers in the last few decades leading to the above conclusion can be found in [16-33]. The full text of the plenary talk [34] contains the relevant

tables of data for many strong electrolytes, figures and a complete list of the main references. Additional tables of supporting data can be found in [35]. This article brings all the important main results together in favor of partial dissociation and hydration of electrolytes.

2. Brief account of arrhenius' theory of partial electrolytic dissociation (1883-)

Arrhenius [2a, b] put forth the pioneering idea that "all electrolytes in an extremely dilute state are completely active" (by active, he meant ionic due to dissociation). Taking for example the neutralization reaction of HCl with NaOH to form NaCl and water, he suggested [2b] the following equations,

$$(H^+ + Cl^-) + (Na^+ + O\,H^-) = Na^+ + C\,l^- + HOH \quad (1)$$

$$H^+ + OH^- = HOH \qquad\qquad\qquad (2)$$
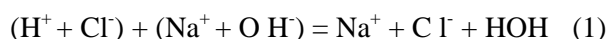
He thus explained the heat of neutralization, which is independent of the nature of the acid and base, as due to the formation of water from the ions, H^+ and OH^-.

From his experiments on electrical conductivity [2a, b], supported by Ostwald's [36] theory of dilute solutions and van't Hoff's [37] results on the osmotic pressures of electrolyte solutions, he concluded that in dilute solutions of concentration M (moles per liter of solution), there exists the equilibrium, (using NaCl, as a typical example of a strong electrolyte),

$$NaCl <==> Na^+ + Cl^- \qquad\qquad (3)$$

$$(1-\alpha)M <==> \alpha M + \alpha M \qquad\qquad (4)$$

where, α, the degree of dissociation is the fraction of one mole of NaCl which dissociates into α mole each of Na^+ and Cl^- ions and $(1-\alpha)$ is the fraction that is left undissociated (stays in inactive electrically neutral state). The total molar concentration of the solute is the sum, $(1-\alpha)\,M + 2\alpha M = (1+\alpha)\,M = iM$, where $i = (1+\alpha)$, the factor found by van't Hoff in the equation for osmotic pressure (π_{os}),

$$\pi_{os} = iMRT \qquad\qquad\qquad (5)$$

at concentration M and temperature T in Kelvins, and R is the molar gas constant.

The dissociation constant, as per the Guldberg and Waage's law [9] (or the law of mass action for a reversible reaction in equilibrium) is given by

$$K_c = [Na^+][Cl^-]/[NaCl] = (\alpha M)^2/(1-\alpha)M = \alpha^2 M/(1-\alpha) \quad (6)$$

On using for α the conductivity ratio (Λ/Λ_0) suggested by Arrhenius, where Λ is the equivalent conductivity of the solution at concentration M, and Λ_0 is that at infinite dilution, Eq. 6 was found satisfactory for dilute electrolyte solutions. As this theory could explain satisfactorily many colligative properties of dilute electrolyte solutions, Arrhenius' theory of electrolytic dissociation gained wide acceptance, and Ostwald's laboratory became a learning center for scientists from far and wide [12].

Nernst [38] found that the e.m.f. of a concentration cell (ΔE), e.g., for a dilute 1:1 electrolyte like NaCl (aq), obeyed the equation,

$$\Delta E = (2RT/F) \ln (\alpha M) \quad (7)$$

where αM is the ionic concentration. Heydweiller [39] showed that the changes in volumes/densities of solutions were directly proportional to α.

As the conductivity ratio could not explain the properties of solutions at higher concentrations, there were many attempts to obtain the correct degree of dissociation. Suggestions were made by Arrhenius [4] and by Bousfield [40] that in addition to partial dissociation, hydration must be taken into account as in the case of the modifications for non-ideality of the Raoult's law [41] for non electrolytes like sucrose. The latter law is an ideal law [42] for the vapor pressures of dilute solutions,

$$(p_A/p_A{}^0) = N_A = n_A/(n_A + n_B) \quad (8)$$

where $(p_A/p_A{}^0)$ is the ratio of the vapor pressure (p_A) of the solvent (subscript A) over a solution to that $(p_A{}^0)$ of the pure solvent, n_A and n_B are the number of moles of solvent and solute (subscript B) in the solution and N_A is the mole fraction of the solvent. For a non-electrolyte like sucrose, the deviations from Raoult's law were attributed to hydration [43] and consequent reduction in the number of 'free' (subscript f) water molecules (as kinetic entities) from n_A to $n_{Af} = (n_A - n_B n_h)$,

where n_h is the number of water molecules held as hydration by one mole of the solute [19, 43].

For an electrolyte like NaCl(aq), the number of moles of solute changes due to dissociation from $n_B = m$ to $n_B = im$, where i is the vant Hoff factor given by Eq. 5 and m is the molality (m moles in one kg of water) of the solute. Thus Bousfield's [40] suggestion amounted to an equation of the form,

$$(p_A/p_A{}^0) = N_{Af} = n_{Af}/(n_{Af} + n_B) \quad (9)$$

where N_{Af} is the mole fraction of free water, $n_{Af} = 55.51 - mn_h$ is the number of moles of free water, 55.51 is the number of moles of water in one kg of pure water. The degrees of dissociation estimated from freezing point depressions by Bousfield [40] and the number of free water molecules which he used were still not satisfactory to explain quantitatively the experimental results.

3. The existing concepts of activities and complete dissociation (1921-)

Lewis and Randall [10] pointed out that the use of the conductivity ratio (Λ/Λ_0) for the degree of dissociation (α) did not give a constant value (as for weak electrolytes) for the dissociation constant of strong electrolytes. The latter phenomenon came to be known as the anomaly of strong electrolytes [12]. Circumventing the question of finding the correct degrees of dissociation, they [10] proposed the 'interim' empirical concepts of activities, activity coefficients and a (pseudo) dissociation constant (K_d) as,

$$K_d = a_+ a_-/a_B = 1 \quad (10)$$

where, the activity of the 'undissociated' solute (a_B) is equal to the product of the ionic activities, $a_+ a_- = a_B$. (Note the basic flaw in Eq. 10: Guldberg and Waage's law for a reversible reaction in equilibrium does not require that $K_d = 1$). In the absence of the knowledge of the ionic activities, they defined a mean ionic activity (for a 1:1 electrolyte) as, $a_\pm = (a_+ a_-)^{1/2} = m\gamma_\pm = a_B{}^{1/2}$ and termed $\gamma_\pm$ as the mean ionic activity coefficient [10, 42, 44]. (Note: why should electrolytes obey this equality?) Moreover, as pointed out in [45], the single ionic activities are still 'elusive' quantities.

The vapor pressure ratio of Eq. 9 was termed [10] solvent activity, a_A, and was related to the osmotic pressure [10, 42] by the equations,

$$(p_A/p_A{}^0) = a_A \qquad (11)$$

$$\Delta G_A = \pi_{os}V_A = \nu RTm\phi_{os}/55.51 = -RTlna_A \qquad (12)$$

where ΔG_A is the solvent free energy, V_A is the partial molal volume of the solvent and ϕ_{os} is the non-ideality correction factor called osmotic coefficient [10, 42].

The 'ionic concentration' term, αM, in the Nernst Eq. 7 for a 1:1 electrolyte, was then replaced [7] by the 'mean molal ionic activity', $a_{\pm} = m\gamma_{\pm}$, (replacing α by $\gamma_{\pm}$)

$$\Delta E = (2RT/F)ln\,(\gamma_{\pm}m) = -\Delta G_B/F \qquad (13)$$

where ΔG_B is the free energy of the solute and $\gamma_{\pm}$ is the mean molal activity coefficient [10, 42, 44].

The introduction of the above empiricisms into solution chemistry met with strong opposition by many eminent proponents of Arrhenius' theory of partial dissociation [12]. The concentration/activity crisis split the scientists of that period into two groups. Bancroft, the then editor of the *Journal of Physical Chemistry*, had to defend even the existence of the Journal from near extinction [12, 32] for opposing the empirical activity concepts.

Around that period, the theory of inter-ionic interaction between free ions in 'very dilute solutions' of completely dissociated electrolytes, e.g., NaCl(aq),

$$NaCl ---- > Na^+ + Cl^- \qquad (14)$$

by Debye and Huckel [11, 42, 44], was found to be a good approximation for the observed dependence of ΔE and other properties (like equivalent conductivity, molal volumes, etc.) on the square root of M. This was taken (erroneously) to imply support for the empirical activity coefficients and complete dissociation of electrolytes at all concentrations [42, 44]. (Note: In the latter case, the

activity of the undissociated electrolyte $a_B = 0$ and the equilibrium constant given by Eq. 10 loses significance).

Note that in Eq. 12, $\phi_{os} = -(55.51/\nu m)lna_A$, the factor by which the free energy ΔG_A exceeds the expected value, ΔG_A (ideal) $= \nu RTm/55.51$, for complete dissociation. Thus the experimental data on the vapor pressure ratio, a_A, were used for evaluating the correction factor for non-ideality, ϕ_{os} and have been tabulated. Conversely, the vapour pressure ratios, termed activity of the solvent[10], a_A, are stored as extensive tables of data [42, 44, 46] on ϕ_{os}.

Note from Eq. 13 that $\gamma_{\pm}$, a correction factor for non-ideality, is evaluated from the 'excess', ΔE - $(2RT/F)ln$ (m) $= (2RT/F)ln$ ($\gamma_{\pm}$), where ΔE is the measured e.m.f. and ΔE (ideal) $= (2RT/F)ln$ (m) is the expected value for complete dissociation. Conversely, the e.m.f. data on concentration cells, are stored as tables of data [42, 44, 46] on $\gamma_{\pm}$.

Subsequently both ϕ_{os} and $\gamma_{\pm}$ were evaluated using Eqs. 12 and 13 and tabulated assuming completing dissociation of electrolytes at all concentrations, and they became known as the 'thermodynamic' non-ideality correction factors. Thus Lewis and Randall [10] advocated the above empirical concepts avoiding the question of the state of the electrolytes as 'partially' or 'completely' dissociated.

However, since increasing evidence showed that there is ion association in multivalent electrolytes, Bjerrum [42, 47] derived an expression for their degrees of association at various concentrations. He also thought that for 1:1 strong electrolytes ionic association was unlikely since the critical distance for ion pair formation was too large.

The Debye-Huckel equations were then gradually tailored and extended with more and more empirical parameters to fit the data for higher and higher concentrations up to saturation [42, 44, 45-51] for all electrolytes. To give some examples, say from [48], the concentration dependence of $\gamma_{\pm}$ is expressed by,

$$ln(\gamma_{\pm}) = - z_M z_X A_\phi[(I^{1/2}/(1+bI^{1/2})+(2/b)ln(1+bI^{1/2})] + m(2\nu_M\nu_X/\nu\{2\beta_{MX}{}^{(o)}$$
$$+(2\beta_{MX}{}^{(1)}/\alpha^2 I)[1- (1 + \alpha I^{1/2}- \alpha^2 I/2)\,exp(-\,\alpha I^{1/2})]\} +\ m^2(2\nu_M{}^2\nu_X z_M/\nu)(3C_{MX}) \qquad (15)$$

where α is a parameter and not the degree of dissociation. See [48] for the explanation of various parameters. Note that Eq. 15 brings no simple explanation for non-ideality!

A similar elaborate equation [48] holds for the osmotic coefficient, ϕ_{os},

$$\phi_{os} = 1 - z_M z_X A_\phi I^{1/2}/(1+bI^{1/2}) + m(2\nu_M\nu_X/\nu)(\beta_{MX}^{(o)} + \beta_{MX}^{(1)}\exp(-\alpha I^{1/2}) + m^2(4\nu_M^2\nu_X z_M/\nu)C_{MX}$$
(16)

Eq. 16 does not explain non-ideality either like Eq. 15.

Another complex equation holds for the partial molal volume of solutions [51-52],

$$V_{\phi,MX} = (V_m - V_A^o)/m = V_{MX}^o + A_o + A_1\beta_{MX}^{(o)V} + A_2\beta_{MX}^{(1)V} + A_3\beta_{MX}^{(2)V} + A_4 C_{MX}^V$$
(17)

Eq. 17 conveys nothing about the volumes of the ions in the solutions.

Thus the theory of electrolytes was translated into many parametric equations and empirical concepts which gave no insight into the molecular phenomena responsible for the experimental data. Similarly, for the complicated equations for the concentration dependence of diffusion coefficient and equivalent conductivity, see [42]. Moreover, these gave no uniform concept of non-ideality for the thermodynamic properties of solutions over the whole concentration range. See [13-15] for some more criticisms.

4. Successful replacement of activities and complete dissociation by partial dissociation and hydration (1979-)

The present author, while analyzing the dependence on concentration of the polarographic half wave potentials due to adsorption found its similarity to the Yesin-Markov shifts of the potentials of zero charge [16]. This indicated that the underlying solution thermodynamics was common to both and pointed to the correctness of the long abandoned van Hoff factor [17]. This made the author analyze afresh the existing experimental data on the physico-chemical properties of electrolytes, and to eventually arrive at the conclusion that the earlier theory of partial dissociation due to Arrhenius is, in fact, correct [16-33]. On using the

degrees of dissociation evaluated from the vapor pressure data, instead of from the conductivity ratio [2] or the freezing point depression [40], the author found that thermodynamic properties could be explained quantitatively gradually from zero all the way up to saturation [24], based on the only two causes of non-ideality, 'partial dissociation and hydration (note: surface and bulk hydration numbers differ)' as suggested originally by Arrhenius [4] and Bousfield [40]. The details can be found in [24]. The author also obtained experimental support for the first time for the presence of electrostatic ion pairs in the work on X-ray diffraction studies of saturated alkali halide solutions, by Ohtaki and Fukushima [53-54].

Given below are some of the simple equations found valid for the solution properties of the common salt based on partial dissociation and hydration at all concentrations. See [16-35] for all the details.

1) Interpretation of vapor pressure and osmotic pressure in terms of partial dissociation and 'surface' and 'bulk' hydration numbers [24]:

$$(p_A/p_A^0) = n_{Afs}/(n_{Afs} + im) = N_{Afs} [= a_A] \qquad (18)$$

$$\pi_{os} = iRT/V_{Afb} [= -RT\ln a_A/V_A] \qquad (19)$$

$$-a_A\ln a_A/(1- a_A) = (n_{Afs}/n_{Afb}) \qquad (20)$$

$$-\ln a_A = (\pi_{os}V_A/RT) = 2m\phi_{os}/55.51$$
$$= (N_B/N_{Afs})(n_{Afs}/n_{Afb}) = im/n_{Afb} \qquad (21)$$

$$\phi_{os} = 55.51(i/2n_{Afb}) \qquad (22)$$

where $n_{Afs} = (55.51 - mn_s)$, $n_{Afb} = (55.51 - mn_b)$ are the molalities of free water at the 'surface' and 'bulk' (subscripts s and b), which concern respectively, the vapor pressure (surface property) and osmotic pressure (a bulk property), n_s and n_b are 'surface' and 'bulk' hydration numbers and $V_{Afb} = n_{Afb}v_A^o$, is the volume of free water in the bulk and v_A^o is the volume of one mole of water. The values of n_s, n_b and α can be obtained by using the available data on a_A (or ϕ_{os}) as described in [24]. (Note that osmotic coefficient simply stands for the ratio given by Eq. 22 unlike in Eq. 16.) The degree of dissociation α decreases with increasing m from a value of unity at infinite dilution to a minimum at about 1.5m and then increases to a limiting value at saturation, see [24]. The actual

ionic molalities, αm and the molality of the ion pairs, $(1- \alpha)m$ could thus be obtained for many strong electrolytes [24-26].

Figure 1 shows an example of the difference between the mean ionic activity ($\gamma_\pm m$) and the actual ionic molality (αm) from 'zero to saturation' for NaCl at 25°C. The osmotic coefficient data in[46] were used for the evaluation [24] of the degree of dissociation (α).

The 'surface' and 'bulk' hydration numbers for forty two 1:1 strong electrolytes were found to be related by the linear equation, see the Table and graph in [26],

$$n_s = 1.007 n_b + 0.88 \qquad (23)$$

where 0.88 is a constant independent of the type of the electrolyte. The excess surface hydration $n_s > n_s$ could perhaps be related to the hydrogen bonding at the vapor/liquid interface [55].

2) Interpretation of the e.m.f. of concentration cells and the mean ionic activity ($\gamma_\pm m$) from ~ 0.001m to saturation in terms of partial dissociation and hydration [24]:

$$\Delta E = -(2RT/F)\ln(\gamma_\pm m) = - \delta_A(2RT/F) \ln[(\alpha m/n_{Afs})/r_s^o] \qquad (24)$$

$$\ln(\gamma_\pm m) = -F\Delta E/2RT = \delta_A \ln[(\alpha m/n_{Afs})/r_s^o] \qquad (25)$$

where $n_{Afs} = (55.51 - mn_s)$, $(\alpha m/n_{Afs}) = r_s$ is the ratio which gives the number of moles of ions per mole of free water, and δ_A is a solvent-solute polarization factor [56] obtained as the slope of ΔE vs $\ln r_s$ straight line, $r_s^o = (\alpha m/n_{Afs})^o$ for $\Delta E = 0$ and $\Delta E^o = \delta_A(2RT/F) \ln r_s^o$.

Figure 2 shows the linear dependence of $\ln (\gamma_\pm m)$ on $\ln (\alpha m/n_{Afs})$ as per Eq. 24, with slope = $\delta_A = 0.957$ and intercept, $\ln r_s^o = 3.592$ for NaCl(aq) at 25°C. The mean ionic activity coefficient data in [46] were used. Figure 2 not only shows that ΔE is directly proportional to $\ln (\alpha m/n_{Afs})$, but also that the empirical mean ionic activity ($\gamma_\pm m$) and complicated Eq. 15 for $\ln(\gamma_\pm)$ are not needed anymore. This linearity has been confirmed for many more electrolytes [25, 26, 33].

Note that in the case of hydrogen ion concentrations, $p[H] = -\ln [H] = -\ln (\alpha m/n_{Afs})$, whereas the existing definition [10], $p(a_{H+}) = -\ln (\gamma_\pm m) = F\Delta E/2RT$ is different [26].

3) Interpretation of the molal volumes, V_m in terms of partial dissociation [24]:

The molal volumes, V_m are given by [24, 26, 28, 34],

$$V_m - V_A^o = m[(1- \alpha)V_B^o + \alpha\phi_v^o)],$$
for $(m < m_{\alpha min})$ $\qquad (26a)$

$$V_m - V_A = \alpha m(\phi_v^o + \delta V_d) = \alpha m(V_B^o + \delta V_{el}),$$
for $(m > m_{\alpha min}$ up to saturation) $\qquad (26b)$

where V_A^o is the volume of 1kg of water in the pure state; V_B^o is the volume of one mole of the pure electrolyte, $\phi_v^o = (V_+ + V_- + \delta V_{el})$; $V_+ + V_-$ is the sum of the volumes per mole of the ions, δV_{el} is the electrostriction, $\delta V_d = V_B^o - (V_+ + V_-)$ and $V_A < V_A^o$. Thus, changes in the volumes of solution are due to αm, δV_d and δV_{el}. Note the complicated Eq. 17 based on complete dissociation in comparison with the simple meaningful Eqs. 26a,b based on partial dissociation.

Further work on the volumes of ions and ion pairs in aqueous solutions [57, 58] and on hydrogen bonding [59] have brought new insights.

4) Interpretation of the dissociation constant:

For the ionic dissociation equilibrium given by Eq. 3, the dissociation constant is given by [26, 34, 35, 60],

$$K_d = \{(\alpha m/V_i)^2/[(1 - \alpha)m/V_{ip}]\}_{soln} = K_{cr}$$
$$= [V_{cr}/(V_+ + V_-)^2]_{cr} = const \qquad (27)$$

where V_i and V_{ip} are volumes of solution occupied by the ions and ion pairs respectively, $(\alpha m/V_i)$ and $(1 - \alpha)m/V_{ip}$ are the concentrations of the ions and ion pairs and V_{cr} and $(V_+ + V_-)$ are the volumes per mole of the crystal and ions respectively. For NaCl(aq) at 25°C, $K_d = 0.080$ mol.cm^{-3} from "zero to saturation". Thus, NaCl and similar electroytes dissociate in solution such that $K_d = K_{cr} = $ constant, which demonstrates *the simple and beautiful workings of Nature.*

Note also that the pseudo Eq. 10 by [10] is replaced by the meaningful Eq. 27.

5) Bjerrum's theory of ionic association found applicable for 1:1 strong electrolytes:

Since now the degrees of dissociation are known [24-26, 34, 35], the author used Bjerrum's equation [42, 47],

$$(1- \alpha) = [2.755 f(a)]c \qquad (28)$$
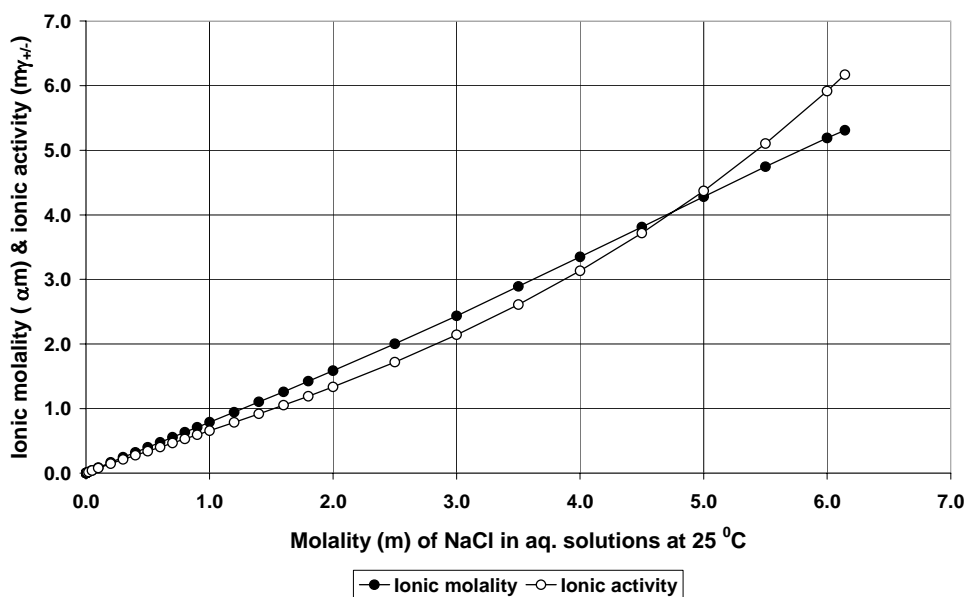
Figure 1. Comparison of ionic molality (αm) with ionic activity ($m\gamma_{+/-}$) at various molalities (m) of NaCl in aq. solutions at 25°C from zero to saturation (6.14m).
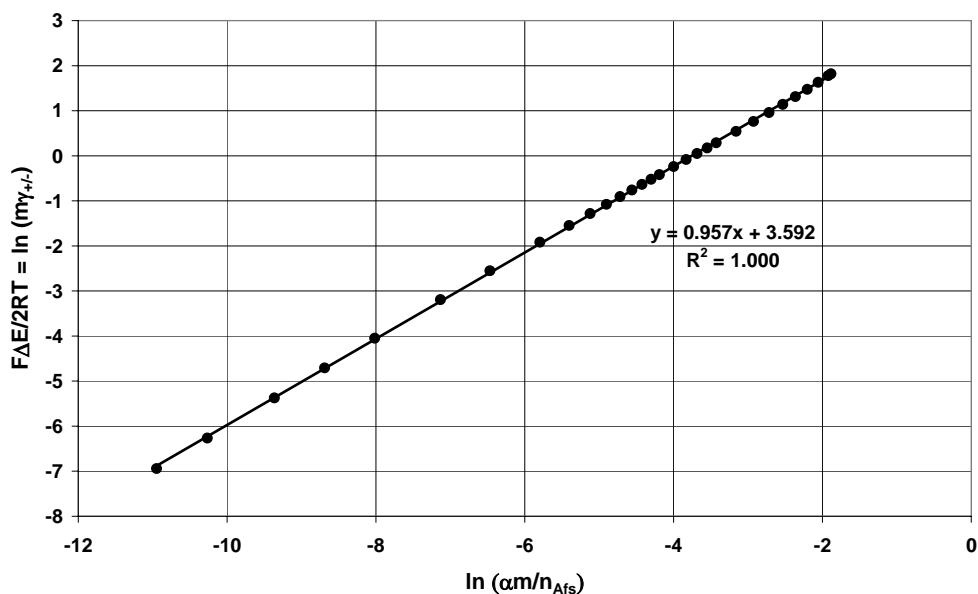
Figure 2. Linear dependence of ($F\Delta E/2RT$) on $\ln (\alpha m/n_{Afs})$ for aq. solutions of NaCl at 25°C from 0.001m to saturation (6.14m), (slope $= \delta_A$). This graph also shows the replacement of mean ionic activity, $a_{+/-}$ ($= m\gamma_{+/-}$) by ionic molality per mole of free water, ($\alpha m/n_{Afs}$).

where f(a) is a function of the mean distance of closest approach, a, of the oppositely charged ions, to calculate (for the first time) the distance, a, for NaCl(aq) from zero to saturation [30, 31]. The value of a was found to increase from 1.85Å at 0.1m to 3.53Å at saturation. The latter is close to the critical distance of approach [42], q = 3.57Å, predicted by Bjerrum for ion association. Thus Bjerrum's equation was shown to be useful for evaluating the mean distance of closest approach

of ions in solutions of 1:1 electrolytes. Note that Bjerrum thought on the contrary that since q = 3.57Å, it is too large for ion association in 1:1 strong electrolytes.

6) Equation of state for solutions incorporating thermodynamics:

A concise equation of state for aqueous electrolyte solutions [61], analogous to those for gases [62] incorporating thermodynamic properties like the heat capacities, was established.

$$\pi_{os}(V_A - V_h)/i = \pi_{os}V_{Af} = (C_{\pi f} - C_{Vf})T = RT \qquad (29)$$

where π_{os} and V_A are the osmotic pressure and total volume of water (A) respectively of a solution containing one mole of solute at temperature T, i $[= 1 + (\nu - 1)\ \alpha]$ is the van't Hoff factor (for non-electrolytes i = 1), V_h is the volume of water held a hydration, $V_{Af} = (V_A - V_h)/i$ is the free (subscript f) volume of solvent per mole of solute. The heat capacity at constant osmotic pressure $(C_{\pi f})$ and constant volume (C_{Vf}) respectively, are defined here on the free volume per mole basis. The ideal heat capacity difference is equal to the gas constant, R. Note that the ideal law and Eq. 29 here are of the same form but with V_{Af} in place of V (the volume of solution in the case of ideal law).

Since the molar entropy S = RlnW, where W is the maximum probablity of existence at the given π_{os}, V_{Af} and T, on combining this with Eq. 29, one obtains,

$$Q_s = TS = RTlnW = \pi_{os}V_{Af}lnW \qquad (30)$$

Thus, entropy, heat capacities and the thermodynamic laws are integral parts of the new equation of state, Eq. 29. For more details, see [61].

5. List of tables of data

Degrees of dissociation (α) of strong electrolytes at various molalities (m) in aqueous solutions at 25^oC and surface (n_s) and bulk (n_b) hydration numbers.

1) Sodium chloride: see [24].
2) All alkali halides: see [25].
3) All halogen acids, perchloric acid, nitric acid; all alkali hydroxides, lithium perchlorate, sodium perchlorate; all alkali nitrates, sodium thiocyante,

potassium thiocyanate; all alkali acetates and ammonium chloride: see [26, 35].
4) All monovalent sulfates: see [33, 35].

6. Support for the author's work

The author's work has gained support in the form of an invitation to contribute to two books [27, 58], a review of a talk [63], award of 'invitation plenary lecturer' for the Arrhenius symposium [34] and from other researchers, e.g. [64-76].

REFERENCES

1. Kurlansky, M. 2002, Salt, A World History, Walker and company, New York.
2. Arrhenius, S. a) 1887, Z. phys. Chem., 1, 631, b) http://www.nobelprize.org/nobel_prizes/ chemistry/laureates/1903/arrhenius-lecture.pdf
3. The Nobel Prize in Chemistry 1903, Svante Arrhenius, a) Biography http://www.nobelprize.org/nobel_prizes/ chemistry/laureates/1903/arrhenius-bio.html; b) http://nobelprize.org/nobel_prizes/ chemistry/ laureates/1903/press.html
4. Arrhenius, S. 1912, J. Am. Chem. Soc., 34, 353.
5. Arrhenius, S. http://en.wikipedia.org/wiki/ Svante_Arrhenius
6. Crawford, E. T. 1996, Arrhenius: From Ionic Theory To The Greenhouse Effect, Canton, MA; Science History Publications, USA.
7. Arrhenius, G., Caldwell, K., and Wold, S. 2008, A Tribute to the Memory of Arrhenius (1859-1927), A Scientist Ahead of His Time, OH-Tryck, Stockholm, Sweden.
8. Heyrovska, R. 2011, Nature Precedings, http://precedings.nature.com/documents/641 6/version/2
9. Waage, P. and Guldberg, C. M. 1864, Studies concerning afinity. Forhandlinger: Videnskabs-Selskabet i Christiana, 35.
10. Lewis, G. N. and Randall, M. 1921, J. Amer. Chem. Soc., 43, 1112.

11. Debye, P. and Hückel, E. 1923, Physik. Zeit., 24, 185.
12. Servos, J. W. 1996, Physical Chemistry from Ostwald to Pauling, The making of a Science in America, Princeton Univ. Press, New Jersey, 2nd printing.
13. Darvell, B. W. and Leung, V. W. H. 1991, Chem. Brit., 27, 29.
14. Franks, F. 1991, Chem. Brit., 27, 315.
15. Heyrovska, R. 1991, Chem. Brit., 27, 1114.
16. Heyrovska, R. 1979, Extended Abstracts, 155th Meeting of Electrochemical Society, USA, Boston, 79-1, abstract no. 354.
17. Heyrovska, R. 1984, 166th Meeting of Electrochemical Society, USA, New Orleans, 84-2, abstract no. 652.
18. Heyrovska, R. 1987, 8th International Symposium on Solute-Solute-Solvent Interactions, Regensburg, Germany, abstract no. L.1.19.
19. Heyrovska, R. 1987, Faraday Symposium on 'The Physical Chemistry of Small Carbohydrates', Regensburg, Germany, abstract no. L.6.05.
20. Heyrovska, R. 1988, Collect. Czech. Chem. Commun., 53, 686.
21. Heyrovska, R. 1989, In Electrochemistry, Past and Present Ch. 6, Stock J. T. and Orna, M. V. (Eds.), ACS Symposium Series No. 390, Washington DC.
22. Heyrovska, R. 1995, 187th Mtg of the Electrochemical Society, Reno, USA, 95-1, abstract no. 662.
23. Heyrovska, R. 1995, The Autumn Meeting of The Royal Society of Chemistry, Faraday Symposium on "Ions in Solution", Sheffield, UK.
24. Heyrovska, R. 1996, J. Electrochem. Soc., 143, 1789; Erratum: 1996, J. Electrochem. Soc., 143, 3038.
25. Heyrovska, R. 1997, In: Special Issue in honor of Marco Branica: Croat. Chem. Acta, 70, 39.
26. Heyrovska, R. 1998. Chemicke Listy, 92, 157.
27. Heyrovska, R. 1998, Notes on Hydration Theory. In: Ionic Equilibrium Ch. 11, Butler, J. N. (Ed.), John Wiley and Sons, New York, 477.
28. Heyrovska, R. 1999, 217th National Meeting of the American Chemical Society, Anaheim, abstract no. 61.
29. Heyrovska, R. 2000, In: Special issue honoring Frank J. Millero. Marine Chemistry, 70(1-3), 49.
30. Heyrovska, R. 1999, J. Mol. Liq., 81, 83.
31. Heyrovska, R. 1999, Current Science, 76, 179.
32. Heyrovska, R. 2000, 219th Meeting of The American Chemical Society, San Francisco, March 2000, abstract no. 37.
33. Heyrovska, R. 1999, Joint International Meeting: 196th Meeting of The Electrochemical Society, USA, Fall Meeting of The Electrochemical Society of Japan with technical cosponsorship of The Japan Society of Applied Physics), Honolulu, Hawaii, short abstract no. 2041. Extended abstract, 99-2.
34. Heyrovska, R. Plenary talk in: Symposium Svante Arrhenius, commemorating the 100th Anniversary of the Award of the Nobel Prize to Arrhenius, Uppsala, November 2003: text in: http://www.jh-inst.cas.cz/~rheyrovs/text-sa-.htm
35. Heyrovska, R. 2006, Special issue in honor of Peter Zuman. Electroanalysis, 18, 351.
36. Ostwald, W. 1888, Z. Physik. Chem., 2, 270.
37. van't Hoff, J. H. 1887, Z. Phys. Chem., 1, 481.
38. Nernst, W. 1889, Z. Phys. Chem., 4(2), 129.
39. Heydweiller, A. 1910, Z. Physik. Chem., 70, 128.
40. Bousfield, W. R. 1917, Trans. Faraday Soc., 13, 141.
41. Raoult, F. M. 1888, Z. Physik. Chem., 2, 353.
42. Robinson, R. A. and Stokes, R. H. 1955 and 1970, Electrolyte Solutions, Butterworths, London.
43. Porter, A. W. 1917, Trans. Faraday Soc., 13, 123.
44. Harned, H. S. and Owen, B. B. 1958, The Physical Chemsitry of Eletrolytic Solutions, Rheinhold, New York.
45. Bates, R. G. 1989, Pursuit of the Elusive Single-Ion Activity. In Electrochemistry. Past and Present Ch. 10, Stock J. T. and Orna, M. V. (Eds.), ACS Symposium Series No. 390, Washington DC.
46. Hamer, W. J. and Wu, Y-C. 1972, J. Phys. Chem. Ref. Data, 1(4), 1047.
47. Bjerrum, N. 1926, Danske Vidensk. Selsk., 7, No. 9.

48. Archer, D. G. 1991, J. Phys. Chem. Ref. Data, 20(3), 509.

49. Archer, D. G. 1992, J. Phys. Chem. Ref. Data, 21(1), 1.

50. Archer, D. G. 1999, J. Phys. Chem. Ref. Data, 28(1), 1.

51. Pitzer, K. S., Peiper, J. C. and Bussey, R. H. 1984, J. Phys. Chem. Ref. Data, 13(1), 1.

52. Krumgalz, B. S., Pogorelsky, R., and Pitzer, K. S. 1996, J. Phys. Chem. Ref. Data, 25(2), 663.

53. Ohtaki, H. and Fukushima, N. 1992, J. Solution Chem., 21(1), 23.

54. Ohtaki, H. 1993, Pure Appl. Chem., 65(2), 203.

55. Stiopkin, I. V., Weeraman, C., Pieniazek, P. A., Shalhout, F. Y., Skinner, J. L., and Benderskii, A. V. 2011, Nature, 474, 192.

56. Conway, B. E. and Marshall, S. 1983, Aust. J. Chem., 36, 2145.

57. Heyrovska, R. 2006, Chem. Phys. Lett., 429, 600.

58. Heyrovska, R. 2009, The Golden Ratio In The Creations Of Nature Arises In The Architecture of Atoms and Ions. In: Innovations in Chemical Biology, Ch. 12, Bilge Sener (Ed.), Springer.com.; Proceedings of the 9th EurasiaConference on Chemical Sciences, Antalya, Turkey, 2006.

59. Heyrovska, R. 2006, Chem. Phys. Lett., 432, 348.

60. Heyrovska, R. 1997, J. Electrochem. Soc., 144, 2380.

61. Heyrovska, R. 2004, Entropy, 6, 128.

62. Heyrovská, R. 2002, A new concise equation of state for gases incorporating thermodynamic laws, entropy and partition function. In: Quantum Limits to the Second Law, First International Conference, AIP Conference Proceedings No. 643, Sheehan, D. P. (ED.), San Diego, California, pp 157-162.

63. Orna, M. V. 2000, Chem. Heritage Mag., 18, 29.

64. Loehe, J. R. and Donohue, M. D. 1997, AIChE Journal, 43(1), 180; online: 17 June 2004.

65. Leung, V. W.-H. and Darvell, B. W. 1997, Journal of Dentistry, 25(6), 475.

66. Mammen, M., Carbeck, J. D., Simanek, E. E., and Whitesides, G. M. 1997, J. Am. Chem. Soc., 119(15), 3469.

67. Jungwirth, P. and Tobias, D. J. 2000, J. Phys. Chem. B, 104(32), 7702.

68. Shultz, M. J., Baldelli, S., Schnitzer, C., and Simonelli, D. 2002, J. Phys. Chem. B, 106(21), 5313.

69. de Berg, K. C. 2003, Science and Education, 12(4), 397.

70. de Berg, K. C. 2004, Austr. J. Educ. in Chem., 64, 16.

71. de Berg, K. C. 2008. The Arrhenius Story: More than a Legend from the Past. In: Proceedings of the Second International Conference on Story in Science Teaching. July, 2008, Munich, Germany:

72. Gopalakrishnan, S., Liu, D., Allen, H. C., Kuo, M., and Shultz, M. J. 2006, Chem. Rev., 106(4), 1155.

73. Minofar, B., Vacha, R., Wahab, A., Mahiuddin, S., Kunz, W., and Jungwirth, P. 2006, J. Phys. Chem. B, 110(32), 15939.

74. Kumar, S. K., Pennakalathil, J., Kim, K., Park, J. K., and Hong, J. D. 2009, Langmuir, 25(3), 1767.

75. Frosch, M., Bilde, M., and Nielsen, O. F. 2010, J. Phys. Chem. A, 114(44), 11933.

76. Marcus, Y. 2011, Chem. Rev., 111 (4), 2761.