Solution Chemistry Simplified Based on Arrhenius' Theory of Electrolytic Dissociation and Hydration For all Concentrations

- Collected research work, dedicated to Svante August Arrhenius (1859 – 1927).

Raji Heyrovska

Private Research Scientist, Praha, Czech Republic. Email: rheyrovs@hotmail.com

Abstract: Arrhenius theory of partial dissociation of electrolytes rose to its heights and fame when he was awarded the Nobel Prize (1903). While the theory was still being developed to account for the non-ideal properties of electrolytes at higher concentrations, it was unfortunately replaced by Lewis’ empirical concepts of activity and activity coefficients. With the near success of the Debye-Huckel theory of inter-ionic interactions for very dilutions, the latter was erroneously extended over the next few decades by extended parametrical equations to higher concentrations assuming complete dissociation at all concentrations. This eventually turned solution theory into a mere catalogue of parameters. Therefore, the present author abandoned it all and started systematically analyzing the available experimental data as such. She found that with the degrees of dissociation and ‘surface’ and ‘bulk’ hydration numbers obtained from vapour pressure data, properties of electrolytes could be explained quantitatively over the whole concentration range, using simple mathematical equations.

Keywords. Arrhenius; Partial dissociation; Hydration; Surface and bulk hydration numbers; Strong electrolytes; Solution thermodynamics.

$^5$Academy of Sciences of the Czech Republic (former)
1. Introduction.

Over a century ago, Svante Arrhenius laid the foundations for the theory of electrolytic dissociation [1]. Initially it met with mistrust [2], but the theory soon gained confirmation and confidence and he was awarded the Nobel Prize in 1903. According to his original theory [1], a fraction \((\alpha)\) mole of an electrolyte like NaCl dissociates in water into \(2\alpha\) moles of ions, the rest \((1-\alpha)\) being in the undissociated form:

\[
\text{NaCl } (1-\alpha) \leftrightarrow \text{Na}^+ (\alpha) + \text{Cl}^- (\alpha) \quad (1)
\]

Thus every mole of salt, on dissolving in water, increased to \((1-\alpha) + 2\alpha = (1+\alpha) = i\) (> 1), where \(i\) is the van't Hoff factor. The Arrhenius conductivity ratio, taken as the ratio of the equivalent conductivity at any concentration \(\Lambda\) to that at infinite dilution \(\Lambda_0\) as a measure of the degree of dissociation \(\alpha\), explained the van't Hoff factor as the increase in osmotic pressure. This theory was greatly successful in explaining many other properties of dilute electrolyte solutions. Arrhenius and his supporters, van’t Hoff and Ostwald became known as the ‘Ionists’ [2,3].

While modifications of the conductivity ratio were being tried to extend the theory to concentrated solutions, and allowance for hydration and the idea of ‘free water’ were being developed [4], Lewis and Randall [5] replaced the use of ‘true ionic concentrations’ in solution thermodynamics by their empirical concepts of activity and activity coefficient correction factors. This was protested by many including by Bancroft, the then Editor of the Journal of Physical Chemistry [3].

Since the Debye-Huckel [6] theory of interionic interaction for complete dissociation of electrolytes, as shown,
\[
\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \tag{2}
\]

was able to nearly explain the concentration dependence of activity coefficients for very dilute solutions, the latter equations based on complete dissociation were gradually extended to higher concentrations until they resulted in extremely elaborate equations with many unknown parameters (see e.g., [7,8]) without any physical significance. Moreover, there was no unified explanation of non-ideality over the whole concentration range. This clearly indicated [9,10] that there was some basic flaw in the underlying theory of electrolytes.

2. Present solution theory based on partial dissociation and hydration [12-73]

The author became aware of the complexity of the theory of solutions of simple alkali halides like NaCl (aq) during her doctoral work [11] on aqueous solutions of strong electrolytes. In the following post-doctoral years, she abandoned the existing theory and started reinvestigating the available experimental data on the properties of electrolytes [12,13]. Gradually it became clear that, with the degrees of dissociation (\(\alpha\)) and the hydration numbers evaluated from the vapour pressure (or osmotic coefficient) data (instead of from the conductivity ratio), the original idea of partial dissociation due to Arrhenius, as per equation (1), and of 'free water' [4], could explain quantitatively the non-ideal properties of electrolytes over a large range of concentrations [12-40].

Further advance was made in 1995 [41-44] by the author, when she found that the hydration numbers and hence the molalities of free water in the "surface and bulk of solution" are different. This made it possible to extend the theory of
electrolytes based on the idea of partial dissociation and free water to the whole range of concentrations from "zero to saturation". The full paper was accepted (after refusal by a few other journals) with praise twenty years ago in JES [44]). Many thermodynamic properties of solutions could thus be explained quantitatively in terms of simple mathematical relations involving the degrees of dissociation, hydration numbers and volumes of ions and ion pairs. For review papers on the subject, see [49,50], [64], [67], [71] and [72]. A summarizing Table of simple equations describing the thermodynamic properties of aqueous electrolytes can be found in [72]

This work was appreciated by the award of the Invitation Plenary Lecturership to the author for the "Svante Arrhenius Symposium" in Sweden in 2003 commemorating the centenary of the award of the Nobel Prize to Arrhenius in 1903. See for the full text of the talk, [64] and [67], where Tables of data for many electrolytes can be found.

Refs. [1- 10] in Part I pertain to the Introduction and [11-39] in Part II & [40-73] in Part III pertain to the author’s work on electrolytes in aqueous solutions from 0 to ~3m and “from 0 to saturation” respectively. In [36], the anomalous Stokes ionic radii are explained. In [48,53,55], Bjerrum’s theory of ionic association was used in reverse to calculate the mean distance of approach of ions. Simple “equation-of-state” for all concentrations was established for gases [63] and for solutions [66].

Acknowledgement: This work was presented as lectures and posters in various international conferences and academic Institutions and she is grateful to her family and many scientists in Europe, USA and Asia for their moral support.
REFERENCES:

Part I:


Part II:

(Note: This work drew the author's attention to the complicated state of the theory of electrolytes!)

155th Meeting of Electrochemical Society, USA, Boston, Vol. 79-1 (1979)
abstract no. 354. (Extended abstract)
(Note: This work gave the author the clue to the fact that the underlying thermodynamics of solutions is common to both polarizers and non-polarizers at the electrode)

13. Heyrovksa, R. Dependence of van't Hoff factor, partition function, Yesin-Markov and transfer coefficients on the partial molar volume.
157th Meeting of Electrochemical Society, USA, St. Louis, Vol. 80-1 (1980)
abstract no. 526. (Extended abstract)
(Note: This work showed for the first time that the abandoned idea of van't Hoff factor for association/ dissociation of electrolytes is in fact valid for electrolyte solutions. The author then started gradually exploring the significance of the van't Hoff factor and the papers below followed).

14. Heyrovksa, R. The role of actual partial molecular volume, \( v \), in chemistry, parts A-E.
61-4. (Extended abstracts) (5 posters)

15. Heyrovksa, R. van't Hoff's factor for non-ideality of gases and aqueous solutions; hydration numbers from osmotic coefficients; Langmuir's formula extended for space coverage.
Heyrovksa, R. General equations for the chemical potential and its isobaric, isentropic and isothermal changes; variation of gas constant and its thermodynamic implications.

(Note: In this work, the van't Hoff factor was treated as a correction factor for the gas constant in the equation-of-state).

Heyrovksa, R. Simple inter-relations describing the concentration dependences of osmotic pressure, degree of dissociation and equivalent conductivity of electrolyte solutions.

(Note: In this work, the van't Hoff factor was related to the degree of dissociation, as suggested earlier by Arrhenius).

Heyrovksa, R. A simple equation connecting diffusion coefficient, coefficient of viscosity, concentration and osmotic pressure of electrolyte solutions; dynamics of Brownian motion.

Heyrovksa, R. A unified representation of properties of dilute and concentrated solutions without activity coefficient, further support: the linear dependence of E.M.F. on \( \ln \pi_{os} \).
20. Heyrovská, R. Concise equations of state for gases and solutions: \( PV_f = i*R_0 T \) and \( \pi_{os} V_A^B = i*R_0 T \)

21. Heyrovská, R. Thermodynamic interpretation of the \( E, \ln \pi_{os} \) linear dependence of E.M.F. of concentration cells, without activity coefficient.

22. Heyrovská, R. Dependence of the specific and equivalent conductivities and transport numbers on the degree of dissociation of electrolytes.


26. Heyrovská, R. Hydration numbers and degrees of dissociation of some strong acids, bases and salts in aqueous solutions at 25°C.


28. Heyrovská, R. Dependence of e.m.f. of concentration cells on actual concentrations of ions, and `true pH'.


31. Heyrovská, R. Quantitative interpretation of properties of aqueous solutions in terms of hydration and `true ionic concentrations'.

International Symposium on Molecular and Dynamic Approaches to Electrolyte Solutions, Tokyo (1988), abstract p. 44. (Extended abstract)
32. Heyrovска, R. Interpretation of properties of aqueous electrolyte solutions in terms of hydration and incomplete dissociation. 
Collection of Czechoslovak Chemical Communications, 53 (1988) 686. (Full paper in English)

33. Heyrovска, R. A re-appraisal of Arrhenius' theory of partial dissociation of electrolytes. 

34. Heyrovска, R. A re-appraisal of Arrhenius' theory of partial dissociation of electrolytes. 

35. Heyrovска, R. Degrees of dissociation and hydration numbers of six tetra alkyl ammonium halides and nineteen 2:1 strong electrolytes in aqueous solutions at 25°C. 
Collection of Czechoslovak Chemical Communications, 54 (1989) 1227. (Full paper in English)

36. Heyrovска, R. Effective radii of alkali halide ions in aqueous solutions, crystals and in the gas phase, and the interpretation of Stokes ionic radii. 
Chemical Physics Letters, 163 (1989) 207. (Full paper) (In this article, the anomalous Stokes ionic radii are shown to be due to the use of bulk instead of local viscosity in the Stokes-Einstein equation)
37. Heyrovská, R. Interpretation of A) solution properties in terms of solvation and incomplete dissociation and B) Stokes ionic radii in terms of ion-solvent interactions.

38. Heyrovská, R. Ionic concentration outlives ionic strength.
Chemistry in Britain, 27 (1991) 1114. (Letter)

39. Heyrovská, R. Degrees of dissociation and hydration numbers of twenty six strong electrolytes in aqueous solutions at 25°C.
Collection of Czechoslovak Chemical Communications, 57 (1992) 2209. (Full paper in English) (Work done as a visiting scientist in Johns Hopkins University);

40. Heyrovská, R. A: Incomplete dissociation of NaCl and 99 other strong electrolytes in a 'sea' of water; B: "Ionic radii" and the mystery of "Stokes ionic radii".
"Futures in Marine Chemistry, XIIth International Symposium", May 1993, Brijuni, Croatia. (2 posters)

**Part III:**

41. Heyrovská, R. Physical electrochemistry of strong electrolyte solutions based on partial dissociation and hydration.
187th Mtg of the Electrochemical Society, USA, Reno, USA, Vol. 95-1 (1995) abstract no.662 (Extended abstract) (First break-through: unified interpretation of solution properties for all concentrations, with partial dissociation and hydration as the causes of non-ideality.)


44. Heyrovská, R. Physical electrochemistry of strong electrolytes based on partial dissociation and hydration: quantitative interpretation of the thermodynamic properties of NaCl(aq) from "zero to saturation". Journal of Electrochemical Society, 143 (1996) 1789. (Full "breakthrough" paper)


45. Heyrovská, R. Partial dissociation and hydration of strong acids and the significance of "pH". Abstract, p. 13, Moderni Elektroanalyticke Metody XVI, Harrachov, Czech Rep., May 14-16, 1996. (Short abstract in English)


47. Heyrovská, R. Equations for densities and dissociation constant of NaCl(aq) at 25°C from "zero to saturation" based on partial dissociation.
48. Heyrovcka, R. Bjerrum's theory for ionic association in NaCl(aq) at 25°C from "zero to saturation".


49. Heyrovcka, R. Physical electrochemistry of solutions of strong electrolytes (partial dissociation and hydration from "zero to saturation")

Chemicke Listy, 92 (1998) 157. (Full invited review with data on hydration numbers)

50. Heyrovcka, R. Notes on hydration theory


51. Heyrovcka, R. My contributions to physical chemistry (1969 - 89)

216th National Meeting of the American Chemical Society, Boston, Aug. 1998, short abstract no. 49. (Lecture and poster)

52. Heyrovcka, R. No kidding! Strong electrolytes are only partially dissociated in aqueous solutions at all concentrations as Arrhenius supposed!

216th National Meeting of the American Chemical Society, Boston, Aug. 1998, short abstract no. 82. (Poster),

http://hackberry.chem.trinity.edu/PHYS/fall1998.html

53. Heyrovcka, R. Mean distance of closest approach of ions in NaCl(aq.) at 25°C calculated from degrees of association using Bjerrum's theory.

Current Science 76 (1999) 179. (Full paper)

54. Heyrovcka, R. Volumes of ions, ionpairs and electrostriction of alkali halides in aqueous solutions at 25°C
217th National Meeting of the American Chemical Society, Anaheim, March 1999, short abstract no. 61. (Lecture)

Marine Chemistry, 70 (2000) 49, Dedicated to Frank J. Millero on the occasion of his 60th birthday. (Full paper)


56. Festina Lente (Hurry Slowly): The development of the theory of electrolytes. (Abstract of talk, 1.17.3 BBL)

Abstract of: R. Heyrovska's talk

Chem. Heritage Magazine, 11 March 1999

57. Heyrovksa, R. Degrees of dissociation and hydration numbers of M$_2$SO$_4$ (M = H, Li, Na, K, Rb, Cs and NH$_4$) in aqueous solutions at 25°C. 1999 Joint International Meeting (196th Meeting of The Electrochemical Society, USA, 1999 Fall Meeting of The Electrochemical Society of Japan with technical cosponsorship of The Japan Society of Applied Physics), Honolulu, Hawaii, October 1999, short abstract no. 2041. (Extended abstract);


Chemical Heritage 18 (2000) 29; (Short report by M. V. Orna)

59. Heyrovksa, R. Sorry Lewis, Bancroft was right: the concentration/activity controversy and the survival of the Journal of Physical Chemistry. 219th Meeting of The American Chemical Society, San Francisco, March 2000, Abstract no. 37. (Short abstract)
60. Heyrovská, R. J. Heyrovsky's data in 1923 on the deposition potentials of alkali metal cations interpreted here in terms of partial dissociation and hydration. J. Heyrovsky Memorial Symposium on Advances in Polarography and Related Methods, Prague, Czech Republic, August/September 2000. Extended abstract in Book of Abstracts, p. 36.


62. Heyrovská, R. E.m.f. of cells: simple dependence on hydration, partial dissociation and transfer coefficient (not on activity coefficients and extended Debye-Hückel equations!)
3rd Workshop of Physical Chemists and Electrochemists, Masaryk University, Brno, February 2002, Book of abstracts, page 24. (In English)
http://cheminfo.chemi.muni.cz/ktfch/PROGRAM_A4.doc

First International Conference on Quantum Limits to the Second Law, San Diego, California (USA), 29-31 July 2002. (Invited talk)

64. Heyrovská, R. "Yes Arrhenius, electrolytes are indeed partially dissociated in solutions at all concentrations"

Full text in: http://www.jh-inst.cas.cz/~rheyrovs/text-sa-.htm

65. Heyrovská, R. A new century begins in solution science with "Development of the theory of electrolytic dissociation - Nobel Lecture by Svante Arrhenius, December 11, 1903"


68. Heyrovská, R. Gender discrimination is a drawback for the progress of science.


ACS Spring Meeting March 2011, Anaheim, CA, USA. (Invited talk)


http://www.softconference.com/ACSchem/player.asp?PVQ=HGFE&fVQ=FIDDGM&hVQ (Full .ppt text with audio, includes work on electrolytes)
69. Heyrovská, R. Partial dissociation and hydration quantitatively explain the properties of aqueous electrolyte solutions and hence empirical activity concepts are unnecessary. (Dedicated to Svante Arrhenius on the occasion of IYC 2011) Nature Precedings http://precedings.nature.com/documents/6416/version/1
73. Heyrovská, R. Unified Thermodynamics for All Concentrations of Electrolytes Based on Hydration and Partial Dissociation (Without Activity Coefficients, 1995-)