

Ghosh's Law*

A Retrospection

Rajarshi Ghosh

The first organized theory of strong electrolytes was proposed by the Indian scientist Jnan Chandra Ghosh (J C Ghosh) in 1918. As soon as it appeared, it was highly appreciated throughout the globe. However, from 1919 several scientific papers appeared, which criticized this theory. The publication of Debye–Hückel limiting law in 1923 initially subsided Ghosh's theory. But interestingly, the theory started to regain its importance since the middle of the last century when some important results were published by scientists from India and abroad.

1. The Background

Electrolytes are generally of two categories—strong and weak. The Swedish scientist Svante Arrhenius (1859–1927) proposed in 1887 [1] that the ionized and unionized (or undissociated) components of a weak electrolyte remain in equilibrium. We can state the example of acetic acid in an aqueous solution where the neutral (or undissociated) acetic acid molecules remains in equilibrium with acetate anions and protons. This important proposition helped to solve numerous problems of weak electrolytes in physical chemistry. For this very fundamental contribution, Arrhenius was awarded the Nobel Prize in Chemistry in 1903. Ironically, there was no such theory for strong electrolytes for many years. Arrhenius believed that strong electrolytes also possess a similar type of equilibria as weak electrolytes. In 1916, Niels Bjerrum (1879–1958) from Denmark first established [2] that there is no such equilibrium in strong electrolytes, instead, all the molecules



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are completely dissociated there.

2. Ghosh's Law

After he retired from government service at Presidency College, Calcutta, Acharya Prafulla Chandra Rây (P C Rây) joined the newly founded Chemistry Department of Rajabazar Science College (Calcutta University) as the first Palit Professor (the post was constituted with the generous donation of Sir Tarak Nath Palit) in October 1916 [3]. Jnan Chandra Ghosh (J C Ghosh), who was a student of Acharya Rây at Presidency College, joined the department as the Assistant to Palit Professor after the completion of his postgraduation [4]. J C Ghosh was next appointed as a chemistry lecturer in the same university in 1917 [4]. Joining the Chemistry Department, J C Ghosh was involved in the problem of strong electrolytes, which was, in fact, a burning issue in those days. In 1918, he published four consecutive scientific papers of fundamental importance [5] regarding the abnormalities of strong electrolytes. He proposed that a certain fraction of the ions of strong electrolytes in solution move freely, whereas, another portion of ions are fixed at definite points in the same way as the ions in solid lattices remain. He also proposed that in binary and ternary (strong) electrolytes, the ions are arranged as simple cubic and flourspar (CaF_2) lattice, respectively. The free-moving ions are responsible for conductance in the solution. J C Ghosh deduced a cube-root equation using which the number of free ions (which conduct electricity in the solution) in a particular dilution can be calculated. Two separate equations were derived. One for binary and another for ternary electrolytes. For binary electrolyte, Ghosh deduced

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$$2RT \log_e \frac{\mu_\infty}{\mu_\nu} = \frac{NE^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}}. \quad (1)$$

For ternary electrolyte it is



$$2RT \log_e \frac{\mu_\infty}{\mu_v} = \frac{3NE^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \sqrt[3]{V}} \quad (2)$$

Here R = universal gas constant, T = temperature in absolute scale, μ_∞ = The number of free conducting ions at infinite dilution, μ_v = The number of free conducting ions at any dilution, N = Avogadro's number, E = charge on an ion (in esu unit), D = dielectric constant of the solvent, V = Volume in cubic centimeter containing one gram-molecule.

This is Ghosh's law or Ghosh's theory of electrolytic solutions, which was appreciated by almost all the then great scientific minds across globe. The number of free ions in a solution (μ_v) is directly proportional to the solution conductivity and can be estimated using conductivity data. These experimentally determined values are correlated theoretically by the equations deduced by Ghosh. The experimentally determined μ_v values were compared and were well-correlated with the proposed theory for different binary and ternary ionic salts. So how does the conductivities of strong electrolytes vary with dilution is the subject of Ghosh's law. Regarding this fundamental contribution of J C Ghosh, Acharya P C Rây recorded [6], "As I may compare great things with small, the formulation of "Ghosh's law" has a similar history behind it. Deprived of the use of apparatus he shut himself up in his room in the College of Science with volumes of *Zeitschrift für Physikalische Chemie* and other Journals of Physical Chemistry scattered about him, he tabulated the enormous data on "conductivity" accumulated in their pages and by a sort of happy sagacious intuition as it were arrived at the equations which at once excited the attention and admiration of the scientific world."

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3. Line of Criticism

Ghosh's law was first questioned by the British chemist J R Partington [7] in 1919. Before criticizing the law, Partington highly praised J C Ghosh by stating [8], "Whilst the present communication was in course of preparation, a series of very interesting pa-



pers on the dilution law appeared, in which the problem is treated from a novel standpoint.” Partington expressed the equation of Ghosh law as [9]:

$$2RT \log_e \frac{\Lambda_\infty}{\Lambda_\nu} = \frac{NE^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} \quad (3)$$

where Λ_∞ and Λ_ν are equivalent conductances of the solution at infinite dilution and at any dilution ν , respectively. As $\frac{\Lambda_\nu}{\Lambda_\infty}$, by definition, is equal to degree of dissociation (α) of the electrolyte, so the above equation takes the form

$$2RT \log_e \frac{1}{\alpha} = \frac{NE^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt[3]{V}} \quad (4)$$

If α is same for same electrolyte in different solvents at same temperature (as J C Ghosh considered) then the above equation reduces to:

$$D_1 \sqrt[3]{V_1} = D_2 \sqrt[3]{V_2} = \dots \quad (5)$$

Moreover, Partington pointed out the following shortcomings of Ghosh’s law (i) the chemical affinity between the ions in addition to the electrostatic forces should be considered, (ii) the range of dilutions used was too small, (iii) equation (5) is identical with that deduced by Walden, (iv) the assumption that some electrolytes, usually regarded as binary, are really ternary in non-aqueous solvents.

In the same year, Ghosh replied to some of the queries raised by Partington [10]. Those are (i) there were some arithmetic errors in Partington’s calculation, (ii) there was a confusion between molar and equivalent dilution. The calculation of α from Ghosh’s theory using molar dilution is compared with the α using corresponding equivalent dilution, (iii) Partington’s data for the conductance of HCl in EtOH agrees well with the calculation provided by Ghosh.

In a note added to this paper [11], Dr Partington wrote, ”My chief objection to Mr Ghosh’s treatment of the data for non-aqueous



solvents is the perfectly arbitrary way in which he assumes the electrolyte to be binary or ternary, as the case may be, in different solvents. He has not offered any explanation of this procedure.” In the following years, few more criticisms appeared against Ghosh’s law [12].

In 1923, Peter J Debye and E Hückel published their famous limiting law for dilute solutions of strong electrolyte [13]. Their proposed equation goes as

$$\log \gamma_{\pm} = -Az_+z_- \sqrt{I}. \quad (I = \text{ionic strength})$$

This theory diminished the value of Ghosh’s law for the time being. The above stated Debye–Hückel theory which is basically a square-root law also had limitation. This was applicable up to ~ 0.001 (N) concentration [14].

4. Present Status

In 1964, Desnoyers and Conway first supported the lattice model of Ghosh [15], and stated that the properties of strong electrolytes at higher concentration follows a cube-root law. L W Bahe similarly supported Ghosh’s theory in 1972 [16]. In the 1980s, Prof. Bhupendra Nath Ghosh (interestingly, he was the younger brother of Jnan Chandra Ghosh) of Calcutta University’s Chemistry Department published a series of papers [17] where he modified the Debye–Hückel law and suggested that at moderately higher concentration of strong electrolyte, the cube-root law is followed. His work was also supportive of the lattice model of J C Ghosh. More recently, this idea of lattice or pseudolattice model is found to be pertinent [18] for electrolytic solutions.

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5. Jnan Chandra Ghosh: A Brief Life-sketch

Jnan Chandra Ghosh was born on 4th September 1893, in Purulia of undivided Bengal (now West Bengal), though their native home was in Hooghly district [19]. After completion of his grad-

uation and postgraduation in chemistry from Presidency College, Kolkata, he joined the Chemistry Department of Calcutta University as a lecturer in 1917. In 1919, Jnan Chandra was awarded the Tarak Nath Palit scholarship and moved to the University College of London to work under Prof. F G Donnan, FRS [19]. Returning from abroad, Jnan Chandra joined the newly established Dacca University (presently University of Dhaka, Bangladesh) as the Professor and first Head of the Department of Chemistry in 1921. In 1939, he left Dacca to join the Indian Institute of Science (IISc), Bengaluru, as Director in succession to Sir C V Raman [19]. In 1950, he was nominated as the Director of the proposed Indian Institute of Technology (IIT), Kharagpur. He left IIT in 1954 to take up the vice-chancellorship of Calcutta University. In the year 1959, he passed away. Besides, his monumental work on strong electrolytes, he did a lot of significant work on photochemistry, catalysis, etc. Moreover, his magnificent role in formulating modern education policies in the post-independent country will be remembered with extreme gratitude forever.

6. Conclusion

Ghosh's cube-root law, particularly the lattice model of the strong electrolytes, has gained much credibility.

Ghosh's theory of strong electrolytes was supposed to lose its importance after the publication of Debye–Hückel limiting law in 1923. But since the middle of the last century, it has been revived after the publication of several important solution chemistry data by scientists from India and abroad. Ghosh's cube-root law, particularly the lattice model of the strong electrolytes, has gained much credibility. The theory which “once excited the attention and admiration of the scientific world” [6] is again approaching the centre of attraction of physical chemists across the globe, and being Indian, we could be proud of that.

Suggested Reading

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GENERAL ARTICLE

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