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Daniel Berthelot. Part II. Contribution to electrolytic solutions

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ABSTRACT

Daniel Berthelot (1865-1927) used the electrical conductivity method to carry on fundamental research on the chemical equilibrium present in highly diluted electrolyte solutions, using the electrical conductivity method. In this way he was able to follow the kinetic details, particularly of the processes taking place in normal or pathological fluids of a living organism. He developed the so-called neutralization curve method, which allowed by simple inspection to judge the march of the reaction. The Académie des Sciences of France awarded him the Jecker Prize for his achievements on the subject.

KEYWORDS: electrical conductivity, neutralization curve method, salts, pathological fluids

Resumen

Daniel Berthelot (1865-1927) usó el método de la conductividad eléctrica para realizar estudios fundamentales sobre el equilibrio químico presente en soluciones electrolíticas altamente diluídas. De esta manera fue capaz de seguir los detalles cinéticos, especialmente de los procesos que tienen lugar en los fluidos normales o patológicos de un organismo vivo. Desarrolló el llamado método de la curva de neutralización que permite observar la marcha de una reacción por simple inspección visual. La Academia de Ciencias de Francia le otorgó el Premio Jecker por sus logros en este tema.

In a previous publication we gave some details about the life and career, and the contribution of Daniel Berthelot to the subject of thermodynamics (Wisniak, 2010). Here we describe his contributions to the study of electrolyte solutions, which should be judged against the state of the art at his time. The results of this work led Berthelot to receive the 1898 Jecker Prize of the Académie des Sciences for a total of ten thousand francs awarded for work destined to the progress of organic chemistry, jointly with Joseph Louis François Bertrand (1822-1900) (for his work on soluble ferments) and Alphonse Buisine (-1918) (for his work on the chemical composition of lamb grease).

According to Berthelot (Berthelot, 1917), the study of the constitution and equilibrium of chemical compounds in solution requires the use of methods based on the physical properties of the system such as thermal, optical, electrical, etc. The first methods employed by Marcelin Berthelot (1827-1907) were calorimetric and gave a direct evaluation of the energy changes involved in the phenomena. Afterwards came measuring the electrical resistance which allowed continuing the examination of chemical reactions up to highly diluted liquors, a clear advantage in the case of substances slightly soluble in water. For most of his experiments Berthelot employed solutions containing 1/100 or 1/200 equivalent/liter of the base, acid, or salt, and in some particular cases dilutions 100 times higher. In the beginning, Berthelot was intent in studying certain chemical equilibria similar to those taking place in the human body. He believed that the electrical method was particularly applicable to the examination of reactions that take place in liquids with low concentrations of salt. When examining in the normal or in the pathological state the principal liquids of the organism, such as urine, blood, gastric fluid, etc., and also the equilibrium of several organic salts such as sodium chloride, phosphates, sodium carbonate, and bicarbonate, etc., in the presence of the above liquids, it was observed that substances having simultaneously acid and basic properties, such as glycolamine, alanine, leucine, thyrosine, serine, albumin and its derivatives, etc., played a critical role in physiological reactions. The presence in a given compound of two antagonistic functions, such as the acid and basic ones, gave place to complex equilibria. It is this coexistence of two functions that allowed Emil Fischer (1852-1919) to combine these bodies and build complex structures of polypeptides and be the first to synthesize albuminoids. The phenomena that Berthelot studied became more complicated if the reactions took place in the presence of a membrane: certain compounds were dialyzed easily and the equilibrium altered. He believed that this sort of studies would help in the search for the explanation of certain paradoxical observations, such as blood becoming more alkaline, urine becoming more acid, etc. (Berthelot, 1917).

One of the first tasks was selection of the method for measuring the conductivity of a solution. Two procedures were available, one based on alternating currents, the other on the electrometer. The first method had the advantages of being relatively fast and allowed changing the concentration of the solution in a systematic manner, without the need of preparing separately solutions of different concentration; the same

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advantage was present when it was necessary to mix solutions in different ratios. The method suffered of the serious inconvenience of being subject to systematic and hard to evaluate errors. The experimental evidence indicated that two repeated measurements could yield results differing by 1/40, polarization was not eliminated, only restricted to an unknown level; for highly diluted solutions it gave unreliable results, and in addition, in many situations the platinum plates serving as electrodes became corroded. The second method was the electrometric one, proposed by Gabriel Lippmann (1845-1921, 1908 Nobel Prize for Physics), based on the simultaneous use of non-polarizable electrodes and the capillary electrometer (Lippmann, 1876); it was free of the limitations of the first method and was more sensitive and precise. Its only inconvenience was in being less expedient. Berthelot chose the Lippmann method with the arrangement described by Jules Jamin (1818-1886) and Bouty (Jamin and Bouty, 1888). The unit of conductivity selected was that of an aqueous solution of KCl, containing 0.01 equivalent/L at room temperature (about 17 °C). The reason for selecting this patron was that its conductivity changed very little with temperature.

Neutralization of an acid was followed by addition of increasing amounts of base, simultaneous measurement of the electrical conductivity of the solution, and plotting the conductivity against the concentration, a method that Berthelot named *neutralization curves*. The shape of the curve was found to be strongly influenced by the nature of the acid or base (strong or weak), and also that there exists a certain parallelism between the electrical conductivity and the chemical strength of acids and bases, which allowed dividing electrolytes into two groups. The first group comprises the strong acids and bases, as well as their neutral salts. They are good conductors, even in concentrated solutions, and their molecular conductivity changes little with concentration. The second group comprises the weak acids (almost all of the organic acids) and the weak bases. They are poor conductors in concentrated solutions, but their conductivity changes rapidly with dilution. Well diluted they are as good conductors as the compounds in the first category (Berthelot, 1891ab, 1917).

Consider now a mixture of two electrolytes having the same molar concentration. If they belong to the first group, the conductivity x of the mixture can be calculated as the ponderated weight of the conductivities of the pure components:

$$x = \frac{v_1 c_1 + v_2 c_2}{v_1 + v_2} = \frac{n_1 \mu_1 + n_2 \mu_2}{v_1 + v_2} \qquad (1)$$

where v_i, n_i, c_i, and μ_i are the volume (liter), the number of moles, the specific conductivity, and the molecular conductivity, respectively of components 1 and 2. Clearly the graphical representation of the phenomenon will be a straight line. This is not the situation when mixing one electrolyte from the first class with another of the second, or two of the second group. The conductivity of the mixture cannot be calculated as above. In order to calculate it, Berthelot indicated that it was necessary to consider the following facts (Berthelot, 1917): Experience showed that the electrical conductivity did not increase indefinitely with dilution, but tended to a limit μ_∞. The ratio μ/μ_∞ is what Edmond Bouty (1846-1922) called the number of electrolytic molecules and Svante Arrhenius (1859-1927; 1903 Nobel Prize for Chemistry) called the number of dissociated ions per unit volume. In order to apply a proportionality rule it was necessary that both solutions *A* and *B* contain the same number of electrolyte molecules per liter. This condition was fulfilled by assuming that one molecule of the water of the *B* solution is withdrawn and added to the *A* solution. In this manner solution *A* becomes more diluted and its conductivity increases; at the same time, *B* becomes more concentrated and its conductivity decreases. A graphical representation of the results obtained with electrolytes of the second group showed that now the phenomenon was represented by a curve (instead of a straight line), which characterized the relative force of acids and bases. In every case it was possible to calculate the theoretical value of the conductivity of a mixture, assuming that there was no chemical action. The actual conductivity was now measured; any difference between the two figures was indicative of a reaction.

Berthelot proceeded then to analyze and discuss the curves of neutralization for the following cases (Berthelot, 1889a): (a) Strong acid with a strong base. Here the curve of neutralization was composed of two straight lines meeting at an acute angle, so that acid liquors could be envisioned as a mixture of acid and neutral salt, and vice-versa, all alkaline liquors could be considered as a mixture of a neutral salt and a base, (b) weak acid (acetic acid) and strong base (KOH). The neutralization curve was now composed of two sections, a convex one corresponding to acid mixtures equivalent to a mixture (for example) of neutral acetate and acetic acid. The results showed that the neutral salt was stable in solution and addition of an excess of acid or alkali did not result in chemical action. The second section corresponded to alkaline liquors, representing the neutral salt and potassium hydroxide (two electrolytes of the first group). It was a straight line passing through the point corresponding to the conductivity of potassium hydroxide, and (c) weak acid (acetic acid) and weak base (ammonia). The neutral salt continued to be stable, even when diluted.

In all the above situations there was a steep change in slope at the point of neutralization. This was not the situation in the neutralization of ammonia (a poorly conducting base) by phenol (a non conducting body in solution), where the alcohol group is analogue to the acid function but weaker. The neutralization curve did not present an angular point; its two sections joined smoothly. In this situation the combination of phenol with alkali at equal number of equivalents yielded a compound mostly dissociated by the water, which tended to become complete by increasing additions of either phenol or ammonia. The same behaviour was observed when acetic acid (a weak acid and poor conductor) was neutralized with aniline (a very weak non-conducting base).