I. A. KABLUKOV'S AND D. P. KONOVALOV'S RESEARCHES ON THE ELECTROCHEMISTRY OF NONAQUEOUS SOLUTIONS

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The present article sets forth several comments on the significance of the researches of I. A. Kablukov [2,3] and of D. P. Konovalov [5-8] on electrically conducting nonaqueous solutions. Notwithstanding the rather wide knowledge of these researches, insufficient light has been shed upon their importance. We shall endeavor to do so in connection with the Nernst-Thomson rule.

As we know, that rule was set forth almost simultaneously by Thomson [28] and Nernst [24,25]. The substance of the rule is that the attractive force between the ions of the dissolved substance varies inversely with the dielectric constant of the solvent. This gave rise to the concept of the dissociating power of a solvent. Nernst indicated the parallelism between the dielectric constant and the conductance of a solution. Subsequently, Walden [30,31] derived the expression $\varepsilon_1 \sqrt[3]{v_1} = \varepsilon_2 \sqrt{v_2} = \text{const.}$ (ε = dielectric constant, and v = dilution), for tetraethylammonium iodide in a large number of solvents, the expression being valid for equal degrees of dissociation.

The Nernst-Thomson rule and the cited researches of Walden were criticized by various authors, principally V. A. Plotnikov [10-14] and M. I. Usanovich [18-20]. Plotnikov [13] asserted that Walden's expression was highly approximate for a large number of cases: in the given solvent pair $N(C_2H_5)_4I$ may have identical degrees of dissociation at equal dilutions, but the ratio of the values of ε does not equal unity for these solvents, lying rather between 1.2 and 1.5; the same salt may exhibit degrees of dissociation that differ by a factor of 1.5 in two solutions with approximately equal values of ε at equal dilutions.

In stating his rule, Thomson cited no concrete examples, while Nernst illustrated the rule with a table on p. 49.

In support of the rule, Nernst cited the results previously obtained by Kablukov [3] in his researches on solutions of hydrogen chloride in various organic solvents, noting the parallelism between conductance and dielectric constant, the conductance being extremely low in benzene, xylene, and hexane (ε = 2.2 - 2.4), appreciably higher in ether (ε = 4.4), and much higher in various alcohols, being highest in methanol (ε = 33.7) and dropping progressively in ethyl, propyl, and isobutyl alcohols, the ε being 25, 22, and 19, respectively. At the time the ε of isoamyl alcohol was unknown, so that Nernst made no mention of Kablukov's findings on the solution of HCl in that substance. The ε of isoamyl alcohol is 15,

Medium	Dielectric Constant	Electrolytic dissociation
Gas space	1.0	Not measurable at ordinary temperatures
Benzene	2.3	Extremely small, but definitely established conductivity, indicating traces of dissociation
Ethyl alcohol	25	Clearly perceptible
Water	80	Very strong

i.e., the lowest in this series, which agrees with the minimum conductance of HCl observed by Kablukov. In addition to Kablukov's researches, Nernst also mentions the later paper by Wakeman [29] who reported that the dissociation of acids dissolved in water decreased as alcohol was added, adding that this fact was a result of the decrease in the ε of the medium. As we see, Kablukov's findings were, at bottom, the main foundation for the rule in question. No mention has been made of this up to the present time. Plotnikov, for example, cites [13] some excerpts from Nernst's paper [25] without saying a word about Kablukov's findings in this connection. In his discussion of the Nernst-Thomson rule, Usanovich [18-20] likewise fails to indicate the significance of Kablukov's researches in this connection. In Walden's comprehensive work on the electrochemistry of nonaqueous solutions [30], the author often refers to this research of Kablukov's on various occasions, but does not mention the part played by the latter in the establishment of the rule.

Plotnikov found various instances of rather high conductance in solvents with very low dielectric constants [10-13] [solutions in bromine ($\varepsilon = 3.18$), benzene ($\varepsilon = 2.3$), ether ($\varepsilon = 4.4$), and chloroform ($\varepsilon = 5.0$)]. This was of fundamental importance in establishing the limits within which the Nernst-Thomson rule was applicable. Some authors (Plotnikov, Usanovich, and Fredenhagen) reject this rule entirely because of these and similar facts [10-14, 18-20, 22, 27].

With the passage of time, Walden's opinions of the role of the dielectric constant in conducting solutions changed considerably, influenced by the researches of the authors cited [10-14, 18-20, 22, 27] as well as by his own experiments [32,33] that postdated his initial researches [30,31]. His lecture at the Mendeleev Jubilee Congress in 1934 [1], where he acknowledged the ability of media with extremely small values of ε to dissociate dissolved substances into ions completely, is highly characteristic in this connection. Plotnikov made special mention of this point [14], asserting that "..... when Walden began his research, he spoke of nothing but the dissociating power; but now he has reached the conclusion that many substances become electrolytes when interacted with suitable solvents. I have always regarded electrochemical conformity as the most important factor in conductance phenomena."

Nernst, in his repeatedly republished Theoretical Chemistry, comments on the Nernst-Thomson rule without saying a word about the fact of appreciable conductance in media with low values of ε.

We shall show that the facts set forth in the papers by D. P. Konovalov, which were published in 1892-1893 [5-8], should have been taken into account in the period that immediately followed the establishment of the Nernst-Thomson rule (1893). Konovalov investigated the conductance of binary systems consisting of aromatic amines and aliphatic acids, finding appreciable conductance existing in systems consisting of aniline as one component and acetic, propionic, or butyric acid as the other [5,8]. It should be noted that the dielectric

constants of these acids were unknown in 1893 [16], so that Nernst, in his commentaries on the rule he had propounded [24,25], made the (incorrect) assumption that these constants must lie between the values of the respective constants for the alcohols and water. Thus the absence of any mention of Konovalov's researches in the cited paper by Nernst was quite natural. The dielectric constants of acetic, propionic, and butyric acids were reported by Jahn and Moller [23] in 1894 (in a paper published in the same issue of the journal as that of Nernst [25]) to be 6.4 (at 20°), 3.14 (at 19°), and 2.9 (at 16°), respectively.

This made appropriate comment on the Nernst-Thomson inescapably necessary, inasmuch as the facts established by Konovalov were evidence of the existence of appreciable conductance in solutions possessing low dielectric constants, contrary to the rule. Although the literature on the rule eventually became rather extensive, no light has been shed on the significance of Konovalov's researches for the rule down to the present time. Plotnikov [13], in a special discussion of Konovalov's views regarding the cause of the conductance of solutions, makes no mention of the latter's researches dealing with the Nernst-Thomson rule. In Waldens's monograph on the electrochemistry of nonaqueous solutions [30], he refers repeatedly to Konovalov's researches, but not in connection with this rule.

Konovalov's investigations [5-8] have been checked experimentally and discussed repeatedly from various standpoints [4,9,13,17,21,26]. The conductance of the aniline-acetic acid system has recently been measured by Cherbov [21], Trifonov and Cherbov [17], Klochko and Chanukvadze [4], and Naumova [9], their findings being close to those secured by Konovalov. There is, therefore, no ground for doubting Konovalov's findings on the binary systems consisting of aniline and propionic or butyric acid. Let us say at once that the conductance of systems containing aniline decreases in the following order: acetic acid – propionic acid – butyric acid, i.e., parallel to the decrease in their dielectric constants. We reproduce some of Konovalov's data for a temperature of 21°, the aniline concentration being always given in per cent by weight (first figure) and in molar per cent (second figure) [5,8].

Aniline – acetic acid system: 4.00 (2.62)% $\underline{x} = 0.267 \cdot 10^{-4}$; 20.60 (14.95)% $\underline{x} = 2.705 \cdot 10^{-3}$; 35.01 (26.06)% $\underline{x} = 2.47 \cdot 10^{-3}$.

Aniline – propionic acid system: 14.32 (11.74)% $\underline{x} = 0.66 \cdot 10^{-4}$; 22.30 (18.59)% $\underline{x} = 0.36 \cdot 10^{-3}$.

Aniline – butyric acid system: 15.65 (14.95)% $\underline{x} = 0.6 \cdot 10^{-5}$; 27.10 (26.02)% $\underline{x} = 0.7 \cdot 10^{-4}$.

The minimum concentrations cited above for the systems containing propionic and butyric acids agree with the figures given by Konovalov.

The first paper by Plotnikov, whose findings he opposed to the Nernst-Thomson rule, goes back to 1902 [10,15] (solutions of $AlBr_3$ in C_2H_5Br). At 15 mol.% of $AlBr_3$ $\underline{x} = 0.85 \cdot 10^{-3}$, at 24.7 mol.% $\underline{x} = 2.09 \cdot 10^{-3}$. This paper was described by Patten [27] as a striking demonstration of the error of the Nernst-Thomson rule, since the ε of ethyl bromide is 8.9.

The Konovalov figures cited above indicate that they can be used even more successfully than the figures cited by Plotnikov in opposition to the Nernst-Thomson rule, since they were published at a much earlier date and refer to solvents with lower dielectric constants.

The fact that the concentration of aniline in the systems containing propionic and butyric acids is relatively high in no way diminishes the

merits of Konovalov's figures as evidence against the Nernst-Thomson rule, since the dielectric constant of aniline is low (7.12 at 16°), as Jahn and Moller established in the same paper in which they gave the values of ε for the acids mentioned above [23].

Subsequently Plotnikov found a number of other instances of high conductance in solvents possessing low dielectric constants. In most of these cases the values observed by Plotnikov were of the same order of magnitude as in the papers by Konovalov. For example, when the percentage of phospheric acid in ether ranged from 12.7 to 54.1% by weight, it had a $\underline{x}$ ranging from $0.736 \cdot 10^{-5}$ to $0.838 \cdot 10^{-3}$ [12]. Concentrations of $SbBr_3$ in bromine, ranging from 7.1 to 47.7% by weight, had values of $\underline{x}$ ranging from $0.14 \cdot 10^{-6}$ - $98 \cdot 10^{-6}$. Solutions of the coordination compound of dimethylpyrone with trichloroacetic acid, $C_7H_8O_2 \cdot 2CCl_3COOH$, in benzene, chloroform, and ethyl bromide exhibited conductance ranging from 10^{-4} to 10^{-3} (in C_2H_5Br $\varepsilon = 8.9$, i.e., the largest value in this series even to 10^{-2}) [11,13]. PBr_5 in bromine exhibited a value of α ranging from $0.87 \cdot 10^{-8}$ at 3.31% by weight to $5.34 \cdot 10^{-2}$ at 36.0% by weight [15]. These and similar findings enabled Plotnikov to take a stand in 1908 [13] against the Nernst-Thomson rule as not being in agreement with actuality.

To sum up, it may be asserted that the part played by I. A. Kablukov and D. P. Konovalov in the evolution of one of the major hypotheses of the electrochemistry of solutions has been considerably minimized.

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