SciencePG
Science Publishing Group

Gravity and Surface Tension as Driving Forces of Electroosmosis

Yuri Pivovarenko

Research and Training Centre "Physical and Chemical Materials Science", Kyiv Taras Shevchenko University/ The National Academy of Sciences of Ukraine, Kiev, Ukraine

Email address:

y.pivovarenko@gmail.com

Abstract: It is generally believed that electroosmosis is comprehensively described by the corresponding Helmholtz-Smoluchowski equation. Consequently, this belief has contributed to the fact that electroosmosis is still viewed as occurring in a time-invariant aqueous medium characterized by constant viscosity and dielectric permeability. Considering the inevitable chemical and physical changes of electrolytes through which electric currents flow, the correctness of such an acceptation is questionable. In particular, it is unlikely that the viscosity and dielectric permeability of electrolytes, which are part of the Helmholtz-Smoluchowski equation for electroosmosis, do not change under the influence of electric currents. This, accordingly, raises the question: exactly what valuesof these parameters should be inserted into the given equation? So, even the specified variability of electrolytes under the action of electric currents immediately calls into question the feasibility of applying of the Helmholtz-Smoluchowski equation for electroosmosis. Unfortunately, the formal perfection of this very equation supports belief in its correctness, which masks its unacceptability, first of all – for practitioners. Furthermore, this very belief has contributed to the fact that electroosmosis is still perceived as an exclusively electrokinetic phenomenon and, therefore, does not even allow suspecting the involvement of non-electrical forces in it, which is false. In any case, both calculations and experimental results presented here show that the main driving force of typical electroosmosis is gravity. Moreover, the obtained experimental results allow assuming the participation of other non-electrical forcesin electroosmosis. Thus, it is shown here that the main driving forces of electroosmosis are forces of a non-electric nature, and therefore – that electroosmosis should not be perceived as a purely electrokinetic phenomenon. At the same time, attention is paid here both to the granular structure of anolytes and to the filamentary structure of catholytes; accordingly, it is proposed to consider this difference in structures as one of the factors determining the predominant direction of typical electroosmosis. Eventually, the multilayered structure of aqueous salt solutions is demonstrated here. Accordingly, it is proposed to take into account this feature when explaining the movement of water and aqueous solutions, including electroosmotic ones. After all, here it is proposed to agree that the Helmholtz-Smoluchowski equation for electroosmosis contributes to the spread of distorted views of this phenomenon.

Keywords: Electroosmosis, Water, Internal Structure, Surface Tension, Laminarity, Flotation, Double Electric Layer

1. Introduction

Electroosmosis, which was first described by Reis in 1809 [1], traditionally means the penetration of aqueous phase through a layer of sand or clay from the anode compartment of a functioning electrolyzer into its cathode compartment (Figure 1) [1-3]. It is currently believed that the most important regularities of such penetration are fully reflected in the Helmholtz-Smoluchowski equation for electroosmosis:

$$v = \zeta \varepsilon \varepsilon 0 E / \eta \qquad (1)$$

where: v – aqueous phase velocity;

ζ – electro-kinetic (or zeta-) potential of the pores through which the aqueous phase moves;

ε – dielectric constant of the aqueous phase;

ε^0 – universal dielectric constant;

E – external electric field strength;

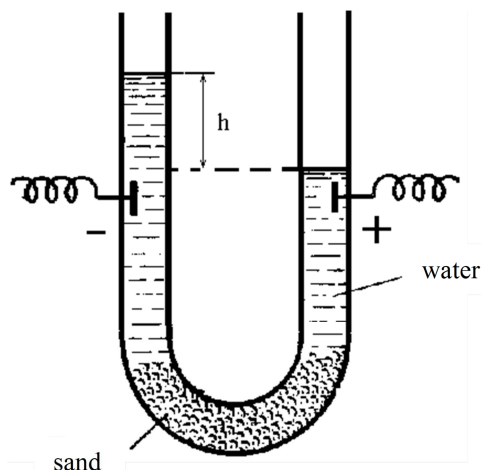η – aqueous phase viscosity [2, 3].

Figure 1. This is a diagram illustrating the phenomenon of electroosmosis, that is, the movement of water or an aqueous solution from the anode compartment of a functioning electrolyzer through the capillaries to its cathode compartment.

However, there is a certain inconsistency: this belief has not yet stopped the study of electroosmosis [4-8]. Accordingly, these same ongoing studies suggest that the Helmholtz-Smoluchowski equation for electroosmosis (1) does not fully satisfy electroosmosis researchers. This, in turn, raises doubts about the ability of this very equation to comprehensively characterize electroosmosis. Let's make sure that such doubts are not unfounded.

First of all, it should be noted that the Helmholtz-Smoluchowski equation for electroosmosis (1) does not reflect the differences in viscosity and dielectric permeability of anolytes and catholytes, which necessarily increase due to the increasing changes in their composition during electrolysis. This, in turn, raises the question: what exactly is viscosity and dielectric permeability referred to in the discussed equation? (It is clear that such uncertainty suggests that this very equation corresponds to the start of electroosmosis, at best.).

In particular, the discussed equation neglects the appearance of hydrogen peroxide in the composition of anolytes ($2OH^- - 2e \rightarrow 2OH^* \rightarrow 2H_2O_2$ [9]). By the same token, the replacement of anolyte water with a much denser substance, which is hydrogen peroxide (~1.44 g/ml at 25°C [9], is also left out of consideration. Thus, the discussed equation does not foresee the possibility of the anolyte to prevail over the catholyte and, ultimately, to change the ratio of their levels in the U-tube (Figure 1).

However, quite understandable calculations show that a~7-centimeter "column" of pure hydrogen peroxide balances a 10-centimeter "column" of pure water, forming a ~30%-difference in levels in identical tubes. So, these same calculations show that this difference is 3 cm in tubes with a cross-sectional area of 1 cm^2 (r = ~0,57 cm) and ~1 cm in tubes with an inner radius of 1 cm.

Similarly, one can make sure that 10 ml of water balances 8,9 ml of perhydrol (1,13 g/ml at 20°C), which is a 30%-solution of hydrogen peroxide in water. Accordingly, this means that the difference in their levels is 1,1 cm in tubes

with a cross-sectional area of 1 cm^2 and ~0,3 cm in tubes with an inner radius of 1 cm.

Thus, all these calculations show that gravity can cause those changes in the ratio of electrolyte levels that are characterized as typical electroosmosis (Figure 1).

The possible transformation of chlorides, the solution of which are often used, into hypochlorites near the anodes [9] should be considered in the same aspect. Since 1M Cl$^-$ weighs ~ 35.5 g, and 1M ClO$^-$ weighs ~51.5 g [9], this transformation means a noticeable increase in the density of the corresponding anolytes. Thus, this very transformation provides an additional opportunity for gravity to be involved in electroosmosis (Figure 1).

Apparently, it is appropriate to note here that all of the above is well consistent with the fact that sediment flotation occurs exclusively in the anode compartments of the operating electrolyzers. Thus, each flotation can be explained by the action of the Archimedes force, which increases with an increase in the density of the anolyte in a functioning electrolyzer. This simple explanation of flotation, which was also first described by Reis [1], can be useful, given that this phenomenon has not yet received an acceptable, in my opinion, explanation [2, 3, 10, 11].

When discussing the root causes of flotation, one cannot overlook the fact that the surface tension of water with a positive electrical potential is much greater than the surface tension of water with a negative electrical potential, as well as the fact that the greater surface tension of positively charged water determines its ability to hold small objects on its surface [12, 13], which certainly contributes to the flotation of these objects.

However, it is worth remembering that the surface tension of hydrogen peroxide (~80,4·10^{-3}N·m^{-1} at 20°C [14]) is greater than the surface tension of water (~72,7·10^{-3}N·m^{-1} at 20°C [14]); this, accordingly, suggest that the holding abilities of anolytes increase in accordance with the increasing content of hydrogen peroxide in their compositions, which certainly contributes to the flotation of small objects in anolytes.

Continuing the discussion of the real causes of electroosmosis, it is worth paying attention to the fact that potassium salts dissolve noticeable better in hydrogen peroxide than in water, while sodium salts, on the contrary, dissolve much better in water than in hydrogen peroxide [9]. In particular, this difference in solubilities allows expecting that the electrolysis of aqueous solutions of KCl will be accompanied by its accumulation near the anode, which will contribute to the typical direction of electroosmosis (Figure 1). However, it can be expected that the electrolysis of aqueous solutions of NaCl will be accompanied by its accumulation near the cathode, which will contribute to the electroosmosis of an atypical direction, which is sometimes observed (Figure 2). Be that as it may, omnipresent gravity again intervenes in electroosmosis.

Keeping in mind the doubts about the validity of the Helmholtz-Smoluchowski equation for electroosmosis (1), it is appropriate to consider some experimental results.

2. Materials and Methods

Given the lack of alternating current (voltage) sources in the time of Helmholtz and Smoluchowski, whose equation is analyzed here, only direct current sources, including homemade ones, were used in this work.

All salts used here to create the corresponding solutions were purchased from «Ukrreachim» (Ukraine).

3. Results

3.1. Diluted Blood Electrolysis

Since it has already been mentioned, the result obtained by electrolysis of substantially diluted blood (~ 1/100) in a U-shaped tube without a membrane (Figure 2) should be considered first.

Figure 2. *This is the result of electrolysis of blood diluted with 0.1 M NaCl solution (1/100) in an electrolyzer without a membrane.*

The accelerating effect of blood catalases and dehydrogenases on the water electrolysis, which occurs both at the anode and at the cathode, was used.
The contents of the electrolyzer shifted towards the anode located on the left.
A potential difference of 10 V was maintained between the anode (left) and cathode (right) compartments for ~ 1 hour.

In fact, the abilities of blood catalases and dehydrogenases to significantly accelerate the formation of gaseous hydrogen and oxygen were productively used in this experiment. So, as you can see (Figure 2), the combination of both of these accelerating abilities makes it possible to implement electroosmosis even in U-tubes devoid of membranes. However, this result calls into question the need for an electro-kinetic (or zeta-) potential ζ, which, according to the Helmholtz-Smoluchowski equation for electroosmosis (1), characterizes the pores through which the aqueous phase moves.

At the same time, it should be noted that the noticeable difference in the levels of catholyte and anolyte (Figure 2)

undoubtedly reflects the difference in their densities, which appeared due to the better solubility of sodium chloride in the catholyte than in the anolyte enriched with hydrogen peroxide, which is certainly formed near the anode. Thus, this result conclusively proves the determining value of gravity to electroosmosis in U-shaped tubes.

3.2. The Difference in the Surface Tensions of Anolyte and Catholyte

It has been established that the shape of the crystals formed after drying (salt solutions) of anolytes and catholytes is different (Figures 3, 4).

Figure 3. *Such crystals were formed after drying of solutions from the anode (left) and cathodic (right) compartments of the operating electrolyzer, initially filled with a $CuSO_4$ solution.*

Figure 4. *Such crystals were formed after drying of solutions from the anode (left) and cathodic (right) compartments of the operating electrolyzer, initially filled with a K_2CO_3 solution.*

Thus, it was found that the crystals formed after the drying of the anolytes have more compact shapes (Figures 3 and 4, left) than the crystals formed after the drying of the catholytes (Figures 3 and 4, right). Based on the previously established dependence [12, 13], this difference allows concluding that the surface tension of anolytes is noticeably higher than the surface tension of catholytes. In fact, this very difference means that a higher surface tension of anolytes forms salt crystals with a smaller specific surface area, while a lower surface tension of catholytes allows the formation of salt crystals with a larger specific surface area.

The fact of the formation of small bubbles of hydrogen gas released at the cathode (Figure 5, left), and large bubbles of oxygen gas released at the anode (Figure 5, right) can also be interpreted in a similar way. So, the smaller bubbles of

hydrogen gas released at the cathode (Figure 5, left) and the larger bubbles of gaseous oxygen released at the anode (Figure 5, right) suggest that the surface tension of the anolyte significantly exceeds the surface tension of the catholyte, actually – that the high surface tension of anolyte allows the formation of large bubbles (Figure 5, right), and the low surface tension of catholyte – no (Figure 5, left).
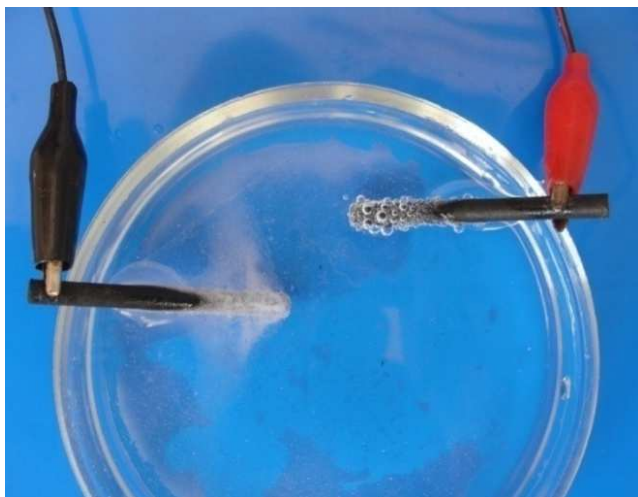

Figure 5. This is the electrolysis of an aqueous solution of sodium chloride (0.1 M). Small hydrogen gas bubbles form at the cathode (left), and large oxygen gas bubbles form at the anode (right).

Of course, the earlier separation of hydrogen gas bubbles from the cathode, as well as their smaller volume, can be explained by their lower weight and, therefore, their greater sensitivity to the action of the Archimedes's force. Here it is worth nothing that this very explanation again involves gravity in electroosmosis, albeit indirect.

Nevertheless, all these results (Figures 3–5) suggest that the difference in surface tension of anolytes and catholytes is capable creates a corresponding difference in their internal pressures and accordingly, the additional driving force of electroosmosis. At the same time, both the granular structure of anolytes and the filamentary structure of catholytes, which are obviously reflected by the forms of the corresponding dried salts (Figures 3, 4), suggest that this structural difference also determines the usual direction of electroosmotic movement throughout the capillary system, namely, from the anode to the cathode (Figure 1).

3.3. Flows of Catholytes Along Cathodes as Additional Driving Forces of Electroosmosis

It would be possible to limit this explanation, but one electro-kinetic phenomenon in the cathode compartment of electrolyzer, which may be important for explaining the nature of electroosmosis, was found. It is worth noting that this very phenomenon was found when the cathodes were in a horizontal position, which is quite unusual. Moreover, when using cathodes of various shapes, it was also found that the strongest flows joined with bubbles of gaseous hydrogen are formed along the curved cathodes (Figure 6); in our

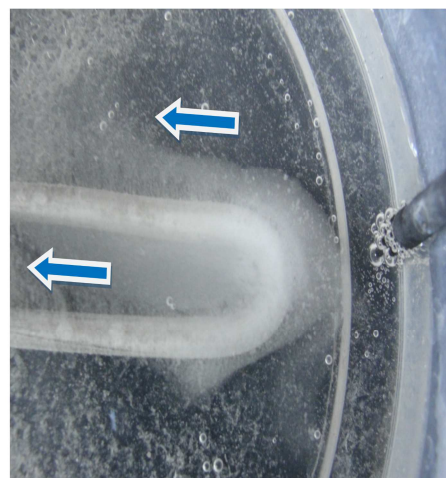experiments, this flow rate varied from 1 to 10 cm per second.

Figure 6. This is the electrolysis of an aqueous solution of sodium chloride (0.1 M). Blue arrows indicate that the water streams, saturated with bubbles of hydrogen gas, are directed along the curved aluminium cathode (white), which is located horizontally.

On the right is the graphite anode (black).
A potential difference of 6 V was maintained between the electrodes.

It was also found that the intensity and direction of these flows do not depend on the position and shape of the anodes, but depend on both the concentration (and type) of the electrolyte and the potential difference between the electrodes.

(Apparently, it should be noted that such flows do not occur at the horizontal anode.) Both the result presented here (Figure 6) and other results made it possible to make sure that the directions of these flows are very dependent on the shape of the cathode, which was previously not taken into account by anyone, including Helmholtz and Smoluchowski.

Accordingly, it can be expected that these cathodic flows create impulses that are undirected by the vertical location of the cathode. Be that as it may, the results obtained suggest the existence of other reasons for the rise of aqueous solutions in the cathode compartment of a typical electrolyzer (Figure 1).

3.4. Multilayer Structure of Still Water

As it follows from it, the Helmholtz-Smoluchowski equation for electroosmosis (1) is based on the idea of the existence of a single electric double layer on surfaces in contact with the aqueous phase, which has a single zeta potential value [2, 3]. Apparently, this idea does not completely correspond to reality, since immobile and inactive aqueous solutions can form multiple layers, at least in contact with the surfaces of glass and some metals (Figure 7). Moreover, the analysis of these very formations (Figure 7), on the basis of the previously revealed dependence [12, 13] suggests that they are alternating double electrical layers.

Figure 7. This is a "copper" coin in a Petri dish with a dried aqueous solution of MgSO₄.

Accordingly, all this calls into question the possibility of characterizing electroosmosis with a single value of the ζ-potential.

Be that as it may, this very multi-layering (Figure 7) suggests that the laminar flow of water and aqueous solutions is essentially the simultaneous sliding of some water layers from others. Here it is worth noting that this interpretation of laminarity does not conflict with established views on it; the only disagreement with these views concerns the thicknesses of sliding water layers [15, 16]. At the same time, it is worth hoping that the given visualization (Figure 7) allows overcoming this disagreement.

4. Discussion

Before discussing the presented results, it is worth trying to save the Helmholtz-Smoluchowski equation for electroosmosis (1). So, taking into account that glass and sand, like any silicates, adsorb aqueous hydroxyl ions, OH⁻ [2, 9], it becomes clear that any aqueous environment acquires a positive charge upon contact with these materials. Thus, there are real reasons for the positive electrization of water and aqueous solutions in a typical electrolyzer. Accordingly, there are real causes for the movement of positively charged water and aqueous solutions along an electric field (Figure 1). Obviously, all this is in good agreement with the Helmholtz-Smoluchowski equation for electroosmosis (1) that presents electroosmosis as a kind of electrophoresis.

Since the mentioned positive electrization of water and aqueous solutions is fundamentally important for this very equation, it is worth supplementing the list of its causes. So, it is well known that negative charges, including electrons, are concentrated on the outer surface of a conductor with an electric current – this phenomenon is called the skin effect [17].

Considering that the voltage of the source that Reiss used to obtain electroosmosis was ~ 100 V [1–3], it can be assumed that the electric currents he received and, therefore, the skin effects were significant. Thus, already Reiss unknowingly used these same skin effects, which contribute to the sorption of aqueous hydroxyl ions by glass and sand. Accordingly, Reiss unconsciously achieved such a positive electrization of the used water and aqueous solutions, which later contributed to the appearance of the Helmholtz-Smoluchowski equation for electroosmosis (1).

Since the skin effect is important for electroosmosis, it is worth citing some little-known features of the flow of electric currents in aqueous solutions. So, despite the fact that in typical electrolyzers mainly constant voltage sources are used, the electric currents in them always pulsate. One of the causes of such pulsations is the gases that are released on both electrodes, changing their working surfaces; these changes in the working surfaces of the electrodes cause corresponding changes in the densities of electrode currents and, ultimately, pulsations of electric currents in electrolytes. (It was these pulsations or ripples that allowed Wehnelto propose the design of the first DC electrolytic breaker [18].)

Since this is directly related to electroosmosis, especially traditional, it is worth mentioning another reason for such pulsations, namely, steam bubbles that periodically form in the pores of the separating membranes of functioning electrolyzers and clog them; here it is also worth adding that it was precisely these pulsations that Simon was counting on when designing another DC electrolytic breaker (Figure 8) [19].
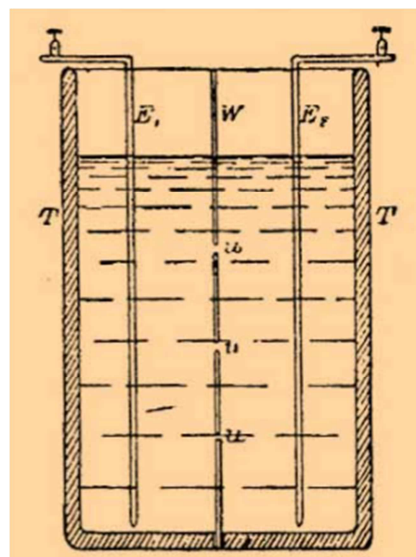

Figure 8. This is a Simon DC electrolytic breaker. T – lead cylinder, E1, E2 – lead electrodes, W – perforated glass partition [19].

Taken into account that alternating electric currents cause greater skin effects than constant ones [17], it can be assumed that these pulsations contribute to the skin effect in electrolytes and, because of this, to their positive electrization. In any case, the above analysis of the causes of these pulsations can contribute to the formation of a more complete view on electroosmosis.

Be that as it may, it is worth realizing the existence of real reasons for the positive electrization of electrolytes during electroosmosis. This positive electrization of electrolytes is very important, because it explains their movement exactly in the direction of the electric field vector E, according to the Helmholtz-Smoluchowski equation for electroosmosis (1). Therefore, it is precisely this electrization that allows presenting electroosmosis as a type of electrokinetic phenomena, as is usually done [2, 3].

At the same time, both the calculations and the experimental results given above destroy this usual presentation of electroosmosis. Accordingly, they both lead to the following conclusion.

5. Conclusion

Thus, electroosmosis should be perceived as a phenomenon resulting from the combined action of both electrical and non-electrical forces. The contribution of electrical forces to electroosmosis is sufficiently adequately reflected by the corresponding Helmholtz-Smoluchowski equation, and the contribution of non-electrical forces to electroosmosis is demonstrated (probably convincing enough) by the above calculations and experimental results.

At the same time, one gets the impression that the proposed perception of electroosmosis is capable of clarifying most of its features, including those that are currently perceived as paradoxical [20].

References

[1]   Reiss F. F. Memoires de la Societe Imperiale des Naturalistes de Moscou, 1809, Vol. 2, pp. 327-337.

[2]   Friedrichsberg D. A. Course of colloid chemistry. Leningrad: Chemistry, 1974. 352p. In Russian.

[3]   Mahmoud A., Olivier J., Vaxelaire J. at al. Electrical field: A historical review of its application and contributions in wastewater sludge dewatering. Water Research, 2010, Vol. 44, pp. 2381-2407.

[4]   Maduar S. R., Belyaev A. V., Lobaskin V., Vinogradova O. I. Electrohydrodynamics Near Hydrophobic Surfaces. Physical Review Letters, 2015, Vol. 114, № 11, pp. 118301-118305.

[5]   Raats M. H. M., van Diemen A. J. G., Laven J. at al. Full scale electrokinetic dewatering of waste sludge. Colloids and SurfacesA: Physicochemical and Engineering Aspects, 2002, Vol. 210, pp. 231-241.

[6]   Squires T. M., Bazant M. Z. Induced-charge electro-osmosis. Journal of Fluid Mechanics, 2004, Vol. 509, pp. 217-252.

[7]   Curvers D., Maes K. C., Saveyn H. at al. Modelling the electro-osmotically enhanced pressure dewatering of activated sludge. Chemical Engineering Science, 2007, Vol. 62, pp. 2267-2276.

[8]   Jiang H., Weng X., Li D. at al. Microfluidic whole-blood immunoassays. Microfluidics and Nanofluidics, 2011, Vol. 10, pp. 941-964.

[9]   Nekrasov B. V. Basics of general chemistry, Vol. 1. Moscow: Chemistry, 1974. 656p. In Russian.

[10] Laskowski J. S., Nyamekye G. A. Colloid chemistry of weak electrolyte collectors: the effect of conditioning on flotation with fatty acids. International Journal of Mineral Processing, 1994, Vol. 40, № 3-4, pp. 245-256.

[11] Wang L., Li C. A Brief Review of Pulp and Froth Rheology in Mineral Flotation. Journal of Chemistry, 2020, pp. 1-16.

[12] Pivovarenko Y. Potential-Dependent Changes of the Surface Tension of Water. Fluid Mechanics, 2017, Vol. 3, № 4, pp. 29-32.

[13] Pivovarenko Y. ±Water: Demonstration of water properties, depending on its electrical potential. World Journal of Applied Physics, 2018, Vol. 3, № 1, pp. 13-18.

[14] Kuchling H. Handbook for physic. Moscow: Mir, 1982. 520p. In Russian.

[15] Batchelor G. K. An Introduction to Fluid Dynamics. Cambridge: Cambridge University Press, 2002. 615p.

[16] Johnson R. W. Handbook of Fluid Dynamics. Florida (USA): CRC Press, 2016. 1580p.

[17] Fink D. G., Beaty H. W. Standard Handbook for Electrical Engineers (14th Ed.). NY: McGraw-Hill Companies, Inc., 2000. 656p.

[18] Wehnelt A. Unterbrecher mit regulierbarer Elektrode. Wiedemann's Annalen der Physik und Chemie, 1899, Vol. 68. p. 265.

[19] Simon H. Th. Wiedemann's Annalen der Physik und Chemie, 1899, Vol. 68. p. 273.

[20] Andreev V. P. (2013) Cytoplasmic electric fields and electroosmosis: possible solution for the paradoxes of the intracellular transport of biomolecules. PLOS ONE, 8 (4), 1-14.