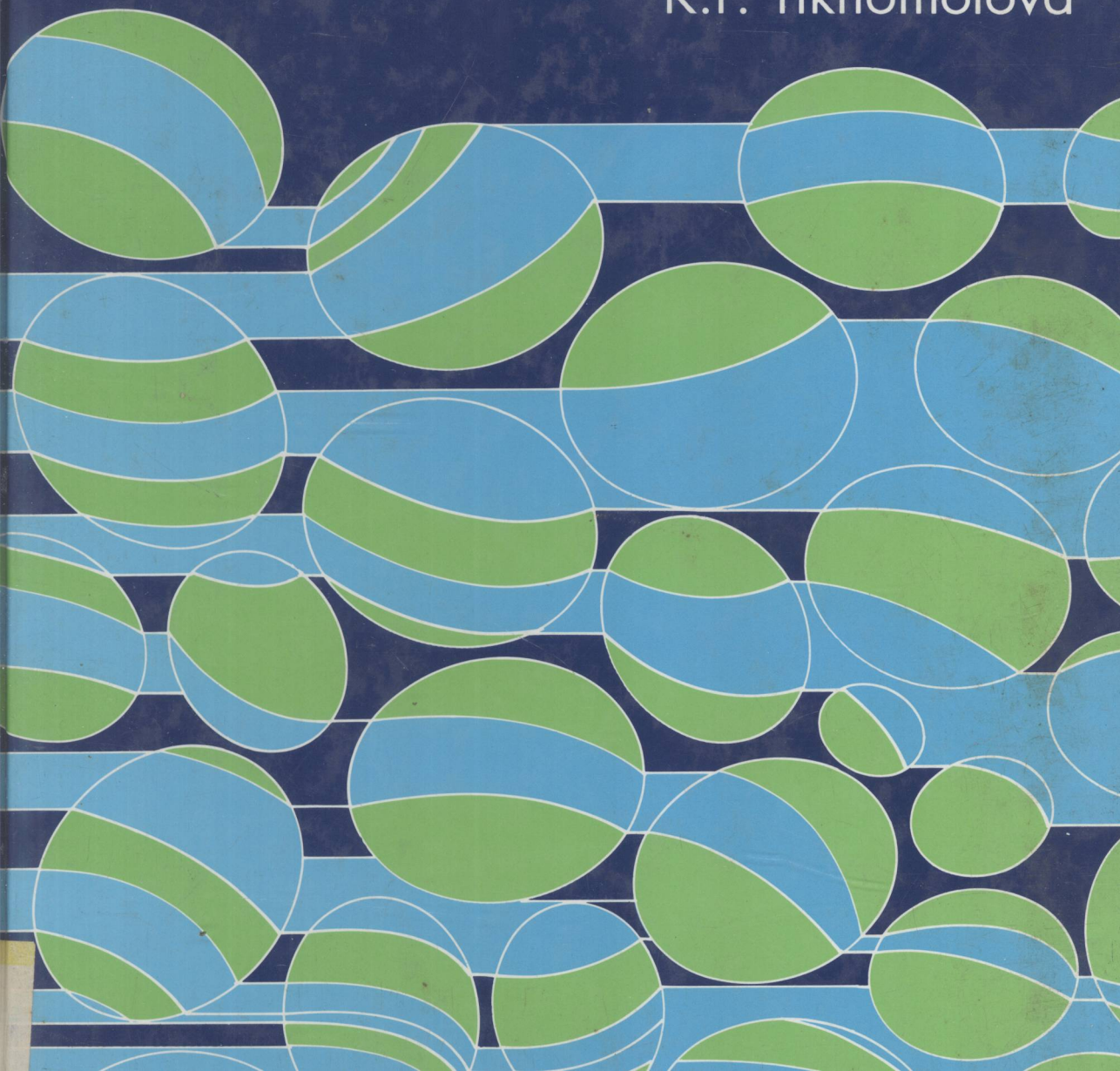


ELLIS HORWOOD SERIES IN PHYSICAL CHEMISTRY

ELECTRO-OSMOSIS

K.P. Tikhomolova



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ELECTRO-OSMOSIS



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E9462636



ELLIS HORWOOD

NEW YORK LONDON TORONTO SYDNEY TOKYO SINGAPORE

This English edition first published in 1993 by
ELLIS HORWOOD LIMITED
Market Cross House, Cooper Street,
Chichester, West Sussex, PO19 1EB, England



A division of
Simon & Schuster International Group
A Paramount Communications Company

The original Russian edition, *Electro-osmos*, was published in 1989 by Khimiya Publishers, the copyright holders.

Translated from the Russian by Garson Leib

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Printed and bound in Great Britain
by Hartnolls, Bodmin

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0-13-249806-5

Library of Congress Cataloging-in-Publication Data

Available from the publisher

ELECTRO-OSMOSIS



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To my late mother—Tatyana I. Temnikova

Introduction

When a constant electric field is applied to a heterogeneous system consisting of a solid body (an insulator) contacting an electrolyte solution, a flow of the liquid known as *electro-osmosis* may develop. The solid is most frequently a capillary porous body, while the electrolyte is dissolved in water. The present monograph is mainly devoted to these systems.

The phenomenon of the appearance of a liquid flow in a capillary porous system under the influence of a constant external electric field (EEF) attracted the attention of scientists long ago. The first description appeared at the beginning of the 19th century. However, notwithstanding the unusual nature of this phenomenon, until the middle of the 19th century electro-osmosis remained only an interesting scientific curiosity. Scientific works raising the question of the causes of this phenomenon appeared only in the 1860s–1870s. The first qualitative views on the mechanism of electro-osmosis were advanced by Quincke (1861). His idea was adopted by Helmholtz, who gave the first quantitative interpretation. In deriving the relevant expression, he assumed a pore to be a uniform capillary (1879). Perrin introduced (1904) permittivity into Helmholtz's formula, while Smoluchowski expanded the theory and gave the profile of the velocity distribution over the cross section of a capillary (a flow diagram) and applied Helmholtz's expression to a cross section of arbitrary shape (1903, 1921).

The general views of these authors on the main forces underlying electro-osmotic flow, at least qualitatively, remained the cornerstone of all subsequent theories based on classical mechanics. At the same time, they consider a variant of electro-osmotic flow in the simplest of possible systems.

In view of the above, it is appropriate to describe their concept of the mechanism of electro-osmosis as the first qualitatively reasonable and also simplest one. It can be presented to the reader by a quite visualizable picture reflecting the most important features of a diagram of an electro-osmotic flow in its development and final form. Fig. I.1 illustrates an electro-osmotic flow from that corresponding to the instant of field superposition to that corresponding to a steady state.

The essence of the basic concept of Quincke and Helmholtz on the mechanism of electro-osmotic flow is as follows. The pore space of a solid is saturated with a liquid. Its

viscosity and permittivity are constant throughout its volume including the regions adjoining the neighbouring (solid) phase. In Helmholtz's time, ions were not singled out as separate particles having a volume. A salt introduced into water was considered to spread throughout its volume (to be present at every point of the solution). In other words, the liquid was considered as a single continuous fluid.

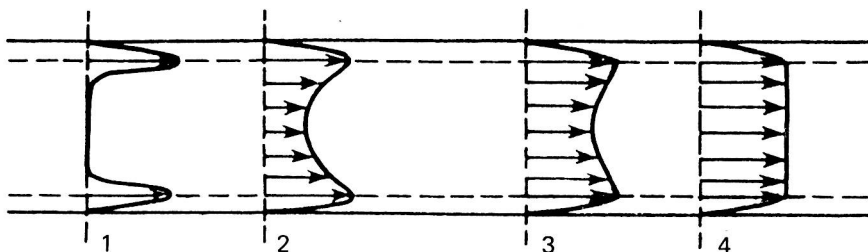


Fig. I.1. Development of electro-osmotic flow in a capillary; arrows represent flow velocities: 1—switching on of field; 2, 3—different stages of development of electro-osmotic flow; 4—diagram of steady-state flow. Dashed lines are outer boundary of charged liquid layer.

Quincke & Helmholtz postulated that there is a layer of charged liquid molecules at a certain distance from the surface of a pore wall and parallel to it. When an EEF with force lines tangential to the liquid–capillary surface interface is superimposed, the liquid layer begins to move toward a definite pole of the current source. Since the liquid is viscous, the motion of its charged layer is transmitted because of viscous friction to the adjoining layers of the uncharged liquid; the latter carry along the next liquid layers, etc., until a surface retarding the motion is encountered. Hence, the lines of liquid flow coincide with the lines of force.

We shall stress that the electrical forces and forces of viscous friction coming from this interpretation act at every point of the continuous fluid. Since the liquid in a pore is confined at all sides by the surface of the solid (except for the end sections of the capillary), and the volume of the liquid in the central (axial) part of a pore is surrounded by a layer of charged molecules, the entire 'central' liquid is equally involved in the electro-osmotic motion.

These developments already vividly illuminate the extremely specific nature of electro-osmotic flow. For example, the dependence of the flow velocity on the distance to the surface of the solid was found to be very typical—it reaches identical and maximum values at distances coinciding with the position of the charged layer, that is, as postulated by the authors, in direct proximity to the surface of the solid. As a result, the average velocity of electro-osmotic flow at pore radii not below sufficiently small values (in comparison with the distance from the surface to the charged layer) is virtually independent of the size of the pore (capillary). (Note that the average flow velocity in filtration rapidly drops with decreasing pore size).

The classical theories developed further in the direction of taking into account new concepts on the structure of liquid solutions. The 'charged layer of liquid molecules' became a layer of ions, that is, independent charge carriers with a non-zero volume. As a

result, the nature of the charge distribution near the surface changed somewhat, in a layer with a thickness of several or scores of nanometres. As previously, however, attention was given to only the simplest systems: the relevant expressions were derived on the assumption that (a) the surface is homogeneous throughout the entire pore volume, (b) the systems are so long that their ends do not affect the laws of motion (that is, are infinitely long), (c) the systems are not changed by current flow, and (d) the strength of the EEF is the same on all sections.

In the mathematical derivation, the initial equations are also based on the concept of a solution as a homogeneous continuum. The formulae obtained for the linear flow velocity differ from those of Helmholtz–Smoluchowski only in that part relating to the region of the charged layer. The values of the maximal velocities, on the other hand, are the same. For systems with a pore size even slightly exceeding the thickness of the charged layer, the average velocities also coincide; the rates of flow of the liquids are practically identical even with a smaller size.

Hence, for capillary bodies with sufficiently large pores, the formulae do not differ. The conclusions mentioned above on the specific nature of the relations between the electrical and geometric parameters also held in the new approach to the structure of the solution. In the classical formula of electro-osmosis (Helmholtz–Smoluchowski) obtained in these stages, the basic features of electro-osmotic flow are clearly reflected. This opened up definite prospects for their use for both scientific and practical purposes.

The emerging possibilities of applying the phenomenon, both scientifically for examining the surface properties of a variety of objects and for the direct practical use of the motion of liquids in capillary porous bodies, necessitated the definition of the laws operating in real dispersed systems. Numerous publications appeared whose results showed that the basic laws of the classical theory hold only over the relatively narrow limits of the conditions implied by Helmholtz and Smoluchowski. Many experimentalists arrived at the conclusion that the flow is too ‘capricious and uncontrollable’ because of (i) the intricacy of the problem, (ii) its apparently extreme sensitivity to the smallest changes in experimental conditions, and (iii) the difficulties appearing when interpreting the results obtained in practice. This is apparently why very few relevant publications appeared in the 1930s–1950s. We shall show this pessimism proved to be unfounded.

In engineering, however, electro-osmosis already began to be widely introduced from the late 1930s. Its application to systems of complicated composition and structure was dictated by the needs of the time. At present, there is no doubt that electro-osmosis is a phenomenon of great theoretical significance, and the prospects of its practical application are very broad and diversified. The laws governing the motion of liquids in porous bodies due to the effect of an electric field are very specific and have no analogues among the laws of motion due to other causes[†].

[†]In engineering, the theory of electro-osmotic filtration is used. It formally reduces electro-osmosis to an analogue of motion under the effect of pressure, that is, to filtration. The corresponding mathematical expression for filtration is the Darcy law, that is, the mean velocity $= k_{\Phi} \text{ grad } p$; in systems with a complicated pore space k_{Φ} is a constant determined only empirically. The expression for electro-osmotic flow is similar: the mean velocity $= k_e \text{ grad } \Phi$ (where Φ is the voltage drop of the electric field over the entire system); here k_e is also a constant determined only empirically.

The basic shortcoming of the theory is that although the typical dependences of the flows on the system parameters are concealed in the coefficients, even the goal of revealing these relations is not stated. Since the theory lacks rigorous experimental testing, formal analogy, and the theory of dimensions, it is obviously not strict, and fails to elucidate the specific nature of electro-osmotic motion. It is therefore weak as regards its theoretical aspects and we do not propose to deal with it in greater detail here.

The specific nature of a phenomenon by itself substantiates the theoretical importance of studying it, particularly when it has an impact in many areas of natural science. Many publications have been devoted to the problem of ion transport through biological membranes and how it is affected by a flow stimulated by an electric field (either superposed from without or generated within). The laws of electro-osmotic flow are also of interest to soil scientists and geologists (the migration of solution components and of solutions themselves, the distribution of fluids in natural collectors and strata), and also for specialists in many other branches of science and engineering.

The studying of this particular flow, apart from its practical aspects, is also of theoretical interest because it enables one to obtain correct values of certain important parameters of the theory of surface electrical properties (in the broad meaning of the term). This, in turn, adds to our understanding of the electric field of a surface and on how it affects other colloid-chemical phenomena and processes (for example the stability of dispersions and thin liquid films).

The parameters of electro-osmosis are exceedingly sensitive to the nature of the surface, and close examination of them yields 'fine' information on the chemical structure of the surface and the physicochemical processes and chemical reactions occurring near it and in the bulk of the contacting phases.

In the overwhelming majority of heterogeneous systems, there is a region representing a special energetic state, that is, very large and non-uniform force fields near the phase interfaces within molecular distances. Consequently, the course of chemical processes at a surface should be very far from standard. In view of the above, electro-osmosis can activate physicochemical processes and chemical reactions because of the delivery of the components directly into the zone of a process or reaction and the withdrawal therefrom of the products.

In addition to their obvious scientific interest, the specific nature of the laws of electro-osmotic flow enables one to solve many practical problems associated with the flow of liquids in porous bodies. Here methods differing fundamentally from the existing methods can be employed. Under definite conditions, they may be more rational and economically profitable. In particular, it follows from the exceedingly low sensitivity of the velocity of electro-osmosis to the pore size that an electric field should be used in preference to pressure to ensure an effective flow through materials with fine pores. Such materials, both natural and artificial, are quite abundant. They include soils, various colloid sediments, fibrous materials, and numerous biological and geological systems.

The independence of flow velocities of pore size in electro-osmosis makes it possible to actively incorporate binders into the pore space of finely porous bodies with the aid of an electric field. Problems of this kind include the fortification of quicksands and soil fastening in construction. The prospects of employing an electric field for incorporating components changing the properties of pore surfaces (for example hydrophobization of them) are associated with the feature of electro-osmosis of reaching maximum velocities in direct proximity to a surface.

Electro-osmosis is also very promising for solving problems connected with the motion of two immiscible liquids in capillary porous bodies. The general theoretical treatment of the problem and analysis of the experimental results point to the numerous qualitative features of the motion of liquids produced by an electric field in comparison

to the laws of filtration of two liquids. These features can in principle be used in chemical technology and at oil fields.

The bulk of this monograph is devoted to questions of theory and to the results of research performed by the author and her associates. The monograph also briefly describes developed technical solutions and directs attention to some directions of the probable practical embodiment of electro-osmosis for which technology is not yet available, but its development may yield positive results on the basis of conclusions following from the main material.

There are very many publications relevant to this monograph which it would be useful to cite. But to cite even a part of them would require shortening the main text. Thus I consider it fairest to refer to the fundamental publications and to give special preference to collected works and monographs containing large, general bibliographies. For the same reason, I refer only to those of my publications which contain vital information in supplementation of the main text.

Although the title page of the present monograph carries only my name, its content is the result of the work of many of my associates, both past and present.

At the outset of my scientific career, I met my teacher, Oleg N. Grigorov (1904–1986), who proposed that I work on the subject of this book and supervised me for a number of years. On giving me independence, he maintained constant and supportive interest in the progress of my career, in good times and bad, and I shall always be in his debt.

For a clearer understanding by an experimentalist of the processes and phenomena occurring in specific systems, and also for confidence in the validity of the formulae employed at various points, it will be very helpful to have a record of the sum of the initial equations of motion of ions and of a liquid as a whole. The record should retain, in an explicit and clear form, all the physical concepts of the causes of the phenomenon and make clear the limits of applicability of the equations and the specific formulae following therefrom. In working on the material presented in Chapter 1, I often consulted Professors S. V. Vallander and V. A. Tsibarov. I would like to express my profound gratitude to them for their crucial help in providing mathematically the general system of equations of electrokinetic phenomena. This had to be done in such a way as to reflect the mechanism of the phenomena to the greatest extent while retaining sufficient rigour of the system.

My colleagues and pupils participated in my research in different ways. A substantial part of the experimental data set out in section 2.2.4 were obtained by L. A. Shishkanova, who also participated actively in developing the method of electro-osmosis in alternating fields. The application of this method by I. R. Zon when studying the dependence of the velocity of electro-osmosis on the pore radius of powder diaphragms under various conditions demonstrated the possibility of calculating the correct values of the electrokinetic potential from the results of measuring the flow velocity through electrochemically active diaphragms (section 2.3.4). N. G. Sharova was a constant colleague in studying the laws of electro-osmotic flow with the prolonged effect of an electric field on systems changing under current; S. A. Demin also participated actively in this work. An appreciable part of the experimental material set out in section 2.4 was obtained by L. K. Aleksandrova, on the basis of which we proposed a mechanism of specific adsorption on oxides of hydrolysing ions.

For many years, E. E. Voznaya has been studying the laws of electro-osmosis of two liquids, using the technique of experiments on regular capillaries which she had developed. The data obtained here revealed points relevant to the theory of surface properties of the interface of two liquid phases. The material set out in section 3.2.2 was largely due to E. D. Taevere.

Over a number of years, I. N. Fokina participated very actively in studying the laws of electro-osmotic displacement; she obtained most of the relevant experimental material detailed in the monograph.

Since almost all my scientific career has been centred on Leningrad State (now St. Petersburg) University, I have had the opportunity of constant interaction with my students, which has been a source of lasting pleasure. Not being able to list all their names here, I must indicate that they appear as co-authors of published papers.

I consider it my pleasant duty to thank Professor V. N. Izmailova of the Moscow State University and Professor S. V. Nerpin, associate member of the All-Union Lenin Agricultural Academy, for their helpful critical discussion of the material and their recommendations when reviewing the monograph.

I shall be grateful for all comments on the present monograph.

S. Petersburg

Kseniya P. Tikhomolova



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1

General theoretical concepts

This chapter gives an overview of the relation between an electric field and the motion of liquids in a capillary porous body, rather than solving specific problems. It sets out consecutively (i) the basic concepts of the mechanism of electro-osmosis (ii) the most general forms of expressing the equations of this highly specific flow, and (iii) analyses of the prerequisites underlying the formulations of these laws. The use of a specific mechanical model and the construction on its basis of a general closed system of differential equations that in principle characterizes the process being studied at any point of pore space at any instant, help one to understand the physical causes of the phenomenon.

Another object of this chapter is to help experimentalists to formulate a realistic model for each specific case and to appraise the validity of the existing or derived specific formulae.

1.1 MECHANISM OF ELECTRO-OSMOSIS

At the molecular level, the present view is based on the assumptions of (i) the directed motion of an ion when an external constant electric field (EEF) acts on an electrolyte solution, (ii) the carrying along, by the ion, of the surrounding medium, and (iii) the appearance of viscous frictional forces in the bulk of the medium. As a result, the macroflow of the solution as a whole is observed. A solution begins to flow when it contains different numbers of cations and anions. The presence of excess charges of one sign causes the resultant of the mechanical action of all the ions on the liquid to have a finite value. In principle, the electro-osmotic motion of a liquid can also appear when the numbers of ions of opposite signs are identical, but the distances from their centres of gravity to the interface are not. In the latter case, the variations in these distances will cause the frictional forces affecting the motion of the cations and anions to differ.

In heterogeneous systems consisting of an aqueous electrolyte solution and a contacting phase (solid, liquid, or gas), these conditions arise because of the presence of electrical double layers (EDL) at the phase interface. There must be a sufficient number of ions for the results to have a practical significance.

We have mentioned in the Introduction that in the simplest variant of electro-osmosis (classical electro-osmosis), an electrical and viscous frictional force couple must act. But in many real systems further forces act on the components of a solution, and this should affect the laws of electro-osmotic motion.

Theoretically interesting and practically important cases are sometimes encountered when the composition of the pore solution, the surface properties, and the geometry of the current-conducting channels change in a system experiencing the effect of an electric field. Such changes may be the result of the introduction into the pores from outside of a solution differing in composition, of redistribution of the pore solution components between the bulk solution[†] and the solution in the region of the phase interface, of the occurrence of physicochemical processes and chemical reactions, of mechanical effects on the mobile phase interface, etc. All this results in the electro-osmotic flow being unsteady for quite a considerable time. This fact is very important in many practical cases.

The number and nature of the charge carriers, how they are arranged in the pores, and the change in these parameters in time and space all affect the laws of flow of liquids in capillary porous bodies stimulated by the application of an external, constant electric field. As a result, the laws may be immeasurably more complicated than in the simplest model possible for electro-osmosis considered above (hereafter this model is called the classical variant of electro-osmosis).

1.2 GENERAL SYSTEMS OF EQUATIONS DESCRIBING ELECTROKINETIC PHENOMENA. CONSTRUCTION OF A SYSTEM OF EQUATIONS BASED ON A MODEL OF A MULTIVELOCITY MEDIUM

Numerous publications contain systems of equations dealing either only with electro-osmosis or with all electrokinetic phenomena. They also contain formulae showing how the velocity of electro-osmosis depends on the parameters of the EEF, the electrolyte concentration, and the geometry of the pore space. These systems of equations and formulae are based on fundamentally different approaches to the problem: (i) from phenomenological standpoints relative to the general equations of flows, (ii) with use of the concepts of mechanics, (iii) by finding the relevant laws empirically, and (iv) by 'correcting' available classical formulae in accordance with experimental data. The first two approaches are based on constructing systems of differential equations using definite basic theses or general laws, while the other two are founded on novel solutions of previously proposed equations or on introducing 'corrected' values of some parameters of a system into existing solutions. In the present chapter, we shall consider material relating only to general approaches.

As indicated earlier, the mechanistic scheme of electro-osmosis is based on consideration of interactions at the molecular level. The macroscopic motion observed experimentally is the result of the motion of a very large number of ions separated by the solvent (water). The difficulties encountered in the quantitative solution of the problem of elec-

[†] The term *bulk solution* signifies the part of the liquid phase which is so far from the surface that the latter does not change its properties (in particular, there is no excess charge).

A solution in the region of the surface layer is the part whose properties are affected by the closeness of the interface of the given liquid and neighbouring phases.

tro-osmosis as a whole are associated primarily with the intricacy of the mathematical expression of a general system of equations that would, on the one hand, adequately reflect ion-solvent interaction and, on the other, would make it possible to use developed methods of mechanics and physics to solve specific variants of real systems with the acquiring of information on the results of all the processes occurring in systems under current flow. It is quite difficult to construct a system of equations in strict accordance with the qualitative picture presented, but it is still more complicated to solve the system. The latter is associated with the fact that it is impossible to give a mathematical description of the geometry of an entire surface between the components of a solution.

The inevitable simplifications in modelling, and also the need to introduce a number of restrictions and simplifications in the solutions, narrow the field of application of the theoretical developments and introduce elements of approximation. The objects to which the systems of equations may be applied vary, depending on the specific concepts they are based on. These concepts determine the degree of generality of the proposed systems.

It must be stressed that there are conditions limiting the generality that have been adopted in virtually all cases. The following conditions have been set for all the systems: (i) constancy of the temperature both over the entire capillary porous body and during the effect of an EEF (disregarding the Joule heat), (ii) disregard of the magnetic field (which in principle is related to the motion of the electric charges), (iii) the laminar nature of the flow; (iv) the restricted velocity of both the ions and the solution as a whole, and (v) the incompressibility of the liquid, which is also assumed to be Newtonian. Its viscosity and permittivity are generally considered to be constant up to the slip boundary. The electric field is always characterized in some way or other; generally, Poisson's equation is employed for this purpose.

With any approach to writing the general equations on a phenomenological basis, either proceeding from the laws of thermodynamics of irreversible processes or with the use of the laws of continuum mechanics, values averaged over a physically infinitely small volume of a solution are employed as the characteristic values of the parameters in these equations.

Let us now consider the basic systems of equations. They are presented in Table 1.1 for ease of comparison. Each law is written either in its author's version or with only algebraic transformations. The table also includes formulae that do not represent a definite law, but are directly related to it. Since the equations of the law of conservation of the momentum of a component and the thermodynamic equations of flow of the relevant component are readily transformed from one form to another by elementary algebraic transformations (they are founded on a single common physical law), they are written on the same line in the table.

In the overwhelming majority of publications proposing systems of equations of electrokinetic phenomena, the theorems typical of a phenomenological approach to writing the equation of flow are the fundamental ones. The equations used here are (i) those reflecting the law of mass conservation for the components separately and for the solution as a whole considered as a continuous fluid (or a homogeneous liquid)[†]; (ii) the

[†]In other words, a description of the molecular structure of electrolyte solutions when each molecule (or ion) occupying a finite volume is replaced with a description wherein any physical or physicochemical property of the sum of molecules in a physically infinitely small volume is considered as averaged over the entire volume.