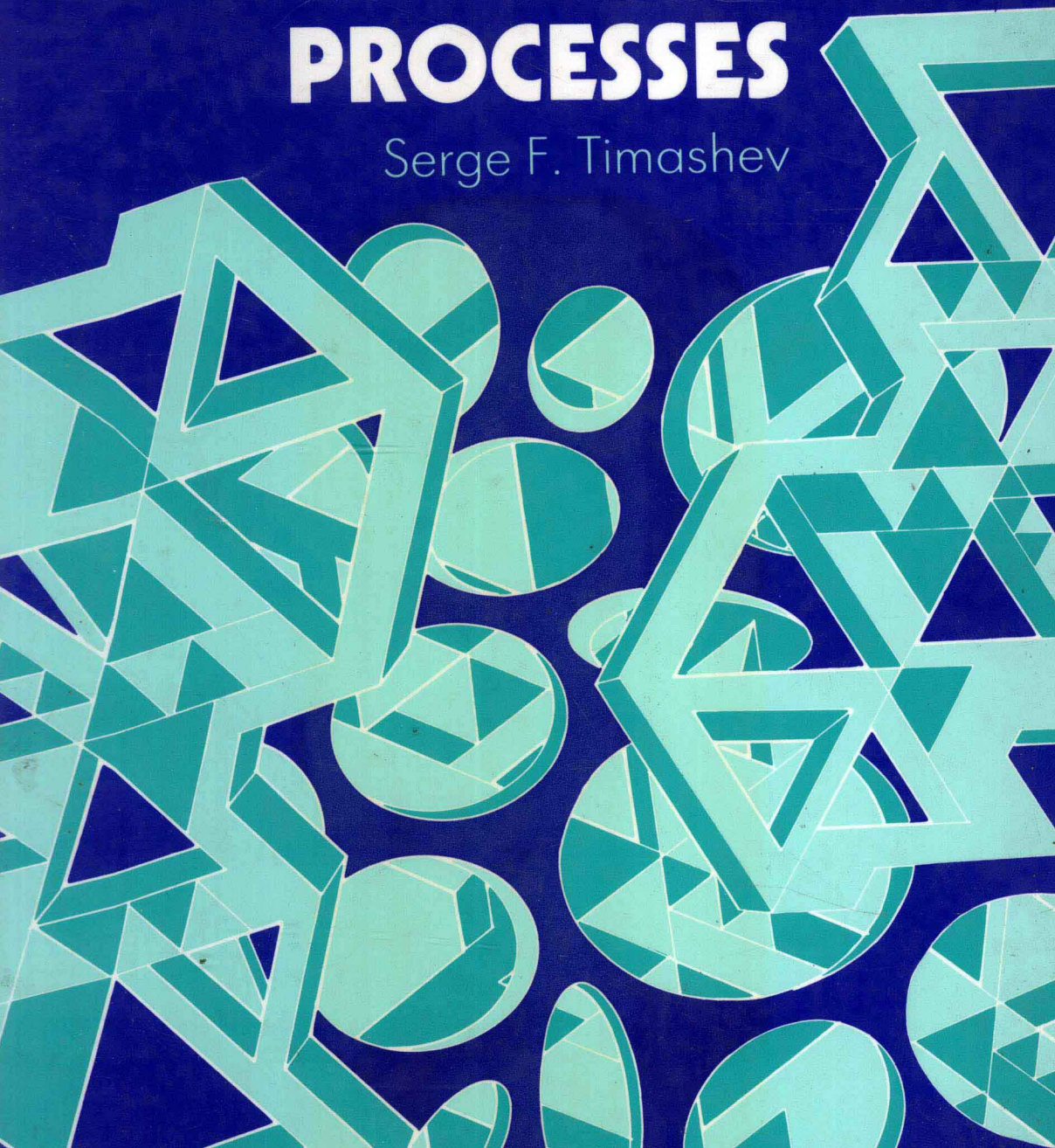


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PHYSICAL CHEMISTRY OF MEMBRANE PROCESSES

Serge F. Timashev



**PHYSICAL CHEMISTRY
OF MEMBRANE PROCESSES**

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PHYSICAL CHEMISTRY OF MEMBRANE PROCESSES

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Preface

The application of membrane processes for solving scientific and technical problems has shown them to be economical and ecologically clean. However, what we are witnessing are only the first, sometimes rather confident, steps in the membrane technology and membrane processes of the first and second generations. Enhancement of membrane processes accompanied by an increase in the selectivity, chemical stability, and durability of the membranes will greatly multiply the applications of this highly effective technology.

It has been said that future successful application of membrane processes is impossible without understanding the principles governing the functioning of biological membranes. However, at the present level of their development, physicochemical biology and membrane technology are virtually independent of one another. Expectations of the late 1970s concerning the biochemical synthesis of ionophores as ion carriers through lipophilic phases and their use for extracting target ions from technological solutions have remained unfulfilled in part, the more so in that the mechanisms based on the use of ionophores as carriers for ion transport in natural systems have proved to be secondary.

What are the prospects for the future interaction between physicochemical biology and membrane technology? What can we learn from nature? How can the study and understanding of the kinetics of processes in biological membranes help us to solve the practical problems of synthesis and modification of new membrane materials and to develop new effective membrane processes?

In this monograph I have tried to present an approach to the above problems based on the study of ionic and molecular transport in synthetic and natural membranes conducted at the Karpov Research Physico-Chemical Institute. The great variety of problems arising in the research determined the presentation of the material, namely the use of concepts of physical chemistry — a surprisingly broad field of human knowledge — concerning the general characteristics of elementary chemical (and biochemical) phenomena in condensed submicroheterogeneous systems on the basis of the principles and experimental methods of physics. Of course, this attempt (to my knowledge the first of its kind) to present extremely

heterogeneous material from a single standpoint and to come up with a general concept of the main principles of ionic and molecular transport in biological and synthetic membranes may be shrugged off as 'a caricature' (to use an expression of Ya.I. Frenkel) and too subjective. While I am aware of the inevitable shortcomings in this approach, I have, nevertheless, tried to infuse the book with my firm conviction that the physical chemistry of elementary processes in natural and synthetic membranes is one and indivisible, in spite of the fact that biological systems are extremely complex, and that the close interrelationship between the sciences dealing with transport processes *in vivo* and in synthetic membranes holds the promise of future success in understanding the principles governing the functioning of living systems and in making new practical advances in membrane technology.

I express my deep gratitude to the research workers of the laboratory of membrane processes at the Karpov Research Physico-Chemical Institute, in particular to V. I. Volkov, A. V. Vorob'ev, P. P. Zolotarev, Yu. E. Kirsch, O. V. Kozlova, S. G. Lakeev, A. V. Maksimych, Yu. M. Popkov, Yu. K. Tovbin, and F. Kh. Chibirova for their part in the discussion of many problems presented in the monograph and for invaluable help in the preparation of the manuscript. I thank also Professor N. P. Gnusin and participants in his annual Djubga seminars on membrane processes where I had numerous opportunities to discuss the most debatable problems raised in this book. I am thankful to E. M. Balavadze, I. N. Bekman, O. V. Bobreshova, Yu. K. Godovskii, S. G. Durgar'yan, V. G. Ivkov, L. N. Chekalov, and Yu. P. Yampolskii for interesting and instructive discussions of problems of membrane separation. I am grateful to reviewers Professor A. E. Chalykh and Professor Yu. A. Chizmadjev for their valuable advice and comments.

Introduction

Membrane technology is a technology of the future, being energy- and resources-saving and ecologically clean. Even today it is used for solving such challenging problems as desalination of brackish and sea water with a throughput of up to 10^4 – 10^5 cubic metres per day, preparation of alkali and chlorine, hydrogen recuperation (10^4 cubic metres per hour) in ammonia synthesis, and so on.

To attain current levels of membrane technology, however, many firms had to carry out extensive research into the corresponding processes over a long period.

Membrane technology proved to have an extremely high 'science content'. The early steps of its development required a comprehensive analysis of all of its aspects: the transport of ions and molecules through membranes, interrelations between the separation parameters such as efficiency and selectivity and the structure of the membrane materials, the processing of polymers into membrane components and the optimum management of membrane processes.

The traditional approach to membrane separation of components of gaseous and liquid mixtures consists in the development of quasiequilibrium concepts of the transport of molecules and ions through polymeric materials ('the model of dissolution and migration–diffusional transport'). For a stationary flux of gaseous molecules of the type i , J_i , to pass through the membrane, the following expression is assumed to be valid

$$J_i = \pi_i \Delta p_i / d, \quad \pi_i = D_i \sigma_i, \quad (\text{I.1})$$

where π_i is the permeability constant of the material independent of the pressure, D_i and σ_i are the diffusion coefficient and the thermodynamic parameter of the solubility of component i in a given material (the Henry constant) respectively, Δp_i is the pressure drop of component i across the membrane, and d is the membrane thickness.

The analysis of ion transport through ion exchange membranes usually involves the use of the Nernst–Planck equation for the ion flux and the use of the Einstein relationship linking the diffusion coefficient of the ions to their electrical mobility.

From this standpoint an increase in the efficiency and selectivity of membrane devices for separating liquid and gaseous mixtures is achieved as a result of a decrease in the effective thickness d of the membrane (in particular, when passing to asymmetric membranes), an increase in the driving force of the process, i.e. the difference between the chemical or electrochemical potentials of the components on either side of the membrane, and a switch to new materials with a higher permeability coefficient and greater selectivity towards the target components.

In deriving equations of the type (1.1) for the flux passing through the membrane, we assume that the bulk of the membrane is a homogeneous and isotropic medium and the interfaces of polymeric membranes are characterized by a low 'surface resistance' to the molecules and ions being transferred. In other words, the processes associated with the transport of ions and molecules through the interfacial regions are taken into account under the assumption that the transport rate is high and there is an equilibrium at membrane-medium interfaces with respect to the species crossing the membrane.

Such a quasiequilibrium approach to the description of processes involving membrane separation of liquid and gaseous mixtures based on concepts of the linear thermodynamics of non-equilibrium processes is presented in a number of monographs [1–6].

In dealing with regimes involving high levels of mass transfer (fluxes), quasiequilibrium approximations become inadequate. Here new problems arise, namely:

- (1) the problem of making adequate allowance for kinetic effects in the formulation of the boundary conditions for problems of ionic and molecular transport through the membrane-medium interface (the dependence of the kinetics of this process on the partial flux densities of the components, on the character of the electrical potential or pressure drops in the interfacial region, and on the structure of the liquid phase layers adjacent to the membrane);
- (2) the determination of kinetic factors governing the effective solubility in the membrane of the ions and molecules being transferred (because of the structural inhomogeneity of the membranes, the fluxes of ions and molecules involved in extensive mass transfer are characterized by different local densities, so that we may refer to the formation of effective transfer pathways for each of the components passing through the membrane; in this case the traditional 'dissolution and diffusional-drift transport' models proved to be inadequate);
- (3) the analysis of phenomena in the regions of the medium adjacent to the membrane including, in particular, spontaneous convection effects in the electrolyte layers close to the membrane responsible for the increase in the 'over-limiting' current in electromembrane systems.

The possibility of non-equilibrium regimes in mass transfer through polymeric ion exchange membranes was demonstrated by Sata [7]: the surface modification of cation exchange membranes with surfactant molecules acquiring a positive charge in the electrolyte solution changes the charge selectivity of the membranes, e.g. the flux of Na^+ ions increases in comparison with that of Ca^{2+} ions under conditions of electrodialysis. A similar effect of a modified membrane surface on the permeability of siloxane-containing gas separation membranes was subsequently observed [8,9].

Under strongly non-equilibrium conditions when H^+ and OH^- ions are generated in the course of heterolytic dissociation of water molecules, bipolar ion exchange membranes are used [10]. The effects of 'separation into layers' of the components passing through the polymer matrix, typical of intense transport regimes, can be achieved in gas separation membranes under high pressures [11].

Comprehensive physicochemical investigations of ion transport in perfluorinated ion exchange membranes, widely used for the electrolytic preparation of alkalis and chlorine, determination of the submicrostructure of these membranes, and elucidation of the relation between the structure and specific features of ion transport under intense conditions of 'chlorine' electrodialysis have also enabled the conclusion to be drawn that the generally accepted 'dissolution and diffusional-drift transport' models are inadequate in these cases and that the role of ion transport pathways ('ionic channels') in the perfluorinated matrix must be introduced [12,13].

Especially important is the study of the dimensions of membrane structure, namely from nanometres to micrometres, since with an increase of ionic or molecular fluxes passing through the membrane, inhomogeneities of smaller sizes appear (down to nanometres — a typical distance between the adjacent centres of localization in the membrane of the species being transferred).

Investigations of membrane structure involve extensive use of modern physicochemical methods, namely radiospectroscopy, X-ray scattering, IR spectroscopy, Mössbauer spectroscopy, etc. The results are given in Chapter 4.

Consideration of the above-mentioned and other transport phenomena in various synthetic membranes (ion exchange, gas separation, reverse osmosis and ultrafiltration membranes) shows (for details see chapters 2, 3, and 4) that, when passing to intense non-equilibrium regimes, molecular and ionic transport through synthetic membranes becomes similar to that through the most effective biological membranes with respect to the type of organization of the transport processes (through channels) and the kinetic trends (the determining role of the submicrostructure, effectiveness of surface modification, non-stationary character of the transfer, non-Arrhenius kinetics of the activation processes).

Thus, a closer study of transport systems in biological membranes with a view to practical application of the main principles of membrane systems functioning *in vivo* is of great current interest. One of the first attempts to systematize the characteristics of ionic and molecular transport in natural systems and to apply this knowledge to discovering new possibilities in membrane engineering and technology is described in chapter 1 (see also Ref. [14]). Although biological systems are extremely complex, and the creation of artificial devices closely modelling biological transport structures are virtually impossible, one should bear in mind that biological membranes are thermodynamically open systems characterized by an effective exchange of energy and mass with the environment. Artificial membranes generally function under much 'calmer' quasiequilibrium conditions. Therefore, trends in membrane technology require a change to high fluxes of transmembrane transport (enhanced current density and increased pressure) so that future membrane systems will to a greater extent resemble natural systems with respect to rates of energy and mass exchange with the environment. Hence, the problems of searching for effective external effects on selective and highly efficient transfer through synthetic membranes are very

acute. Here it is extremely useful to know the underlying principles governing the consumption of energy accumulated by the organism or photoexcitation energy for the energy-dependent transport processes in biological membranes (the relevant hypotheses are presented in Chapter 1). Of course, consideration of transport processes in biological membranes also gives rise to many problems associated not only with the detailed description of the processes (which is evident) but with the fundamental aspects as well.

Transport processes in ion exchange membranes are discussed in Chapter 4 and it is shown that transfer in artificial membranes can model separate aspects of transport in biological membranes. This opens up possibilities for a deeper understanding of the essence of complex biochemical phenomena with the help of suitable research objectives. Thus, we may hope that future studies of transport processes in biological and synthetic membranes not only will enrich one another with new ideas, by examination of particular problems, but will combine their efforts for solving general problems.

1

Transport of ions and molecules in biological membranes

Biological membranes have a great variety of functions in a living organism which comprise the reception and transfer of information, energy transformations, the maintenance of salt composition and acid–basic equilibrium, regulation of complex biochemical processes, and the removal of metabolic products from the cells [15]. These and many other processes are based on membrane transport. The transport systems in biological membranes generally comprise specialized proteins which form stable complexes with lipids of the cell membranes and are able to change their conformation reversibly.

Many versions of membrane transport of charged and neutral components are known. It is beyond the scope of this chapter to give a complete picture of the known concepts of the functioning of natural transport systems, which could have been the subject of a special monograph (see, for instance, Refs [16,17]), the more so as most of them are debatable. It is usual to divide all membrane transport processes into two large groups: active and passive. In active transport, the substance being transferred moves along the concentration gradient[†]: from a region with a lower concentration, or, in the general case, from a region with a smaller thermodynamic potential to a region with a greater thermodynamic potential. This requires energy consumption. In passive transport the substance moves against the concentration gradient.

1.1 THE STRUCTURE OF BIOLOGICAL MEMBRANES

The cells of a living organism include a wide variety of membranes and membrane structures [15,17] — surface membranes (cellular or plasmatic) and a multiplicity of

[†] As pointed out in ref. [18], when describing transport in biological membranes, use is traditionally made of the terms ‘transfer along the concentration gradient’ and ‘transfer against the concentration gradient’, which do not correspond to the generally accepted definition of the gradient, and active transport is defined as ‘ion transport against the concentration gradient’. We shall use (in agreement with ref. [18]) the terminology corresponding to the generally accepted definition of gradient, i.e. a definition different from the traditional.

intracellular membranes. The surface membranes fulfil important barrier functions maintaining the internal autonomy of the cells and protecting them from the entry of foreign substances. Enzyme transport systems, using energy stored in the organism and ensuring the supply to the cell and the removal from the latter of different components which makes it possible to maintain the required concentrations of the necessary substances within the cell and in their organelles, function simultaneously in the surface membranes. The plasmatic membranes accomplish not only exchange of energy between the cells and the environment but also exchange of information which is achieved by the great variety of receptors and specific 'recognition sites' on the surface of the plasmatic membranes.

The functions of intracellular organelles with a membrane structure (mitochondria, lysosomes, peroxysomes) are diverse. They participate in processes utilizing the energy supplied to the organism in enzymatic transformations and in the complex processes of cellular metabolism and catabolism. The cellular organelles are retained at particular sites by a system of protein microthreads and microtubes constituting the cytoskeleton of the cell.

Biological membranes consist of proteins and lipids. Membrane lipids are a mixture of several hundred compounds. The most widespread membrane lipids (up to 90%) are bilayer-forming phospho- and glycolipids which manifest pronounced amphipathic properties, i.e. they can be divided in space into polar and non-polar parts (the latter consist of hydrocarbon chains). In a phospholipid molecule a hydrophilic 'head' is formed by a phosphate group bonded to the residue of choline, ethanolamine, and serine. Two hydrophobic 'tails', which are chains of fatty acids, emanate from the 'head'. The other lipids in the membrane cannot usually form stable bilayers (in aqueous media), although they have a small polar 'head' which ensures their orientation in a bilayer [19,20]. The hydrophilic parts of the lipid molecules in a bilayer face towards the aqueous phase whereas the hydrophobic parts (the residues of fatty acids) form the parallel lines of hydrocarbon chains associated via hydrophobic interactions.

The structure of the bilayers being formed depends on the balance between hydrophilic and hydrophobic interactions. Stabilization of the bilayer structure is favoured by hydrophobic interactions and by the formation of intermolecular salt bridges between the negatively charged oxygen atoms of the phosphate groups ($pK_a=2.1$) and trimethylammonium ($pK_a=13.9$) or amine ($pK_a=10.6$) groups (for details see Ref. [20]). The thickness of biomembranes varies from 5 to 10 nm.

Under physiological conditions the bilayers are in a mesomorphic state and any description of their molecular organization must therefore include the dynamic aspect apart from the structural (geometrical) aspect. The bilayer is illustrated schematically in Fig. 1.1 [2]. An important element of this model comprises regions a ('clusters') in which short-range order is retained, their characteristic transverse dimensions being 0.8 nm. They incorporate up to 40–60 hydrocarbon chains (20–30 phospholipid molecules). The molecular packing in the clusters is fairly close to crystal packing and is more compact than in the isotropic region i of the bilayer.

The clusters are dynamic formations with a lifetime of $\sim 10^{-7}$ s. They are continuously decomposed and re-formed, migrating along the bilayer. The movement of the chains in the cluster should then occur simultaneously, i.e. it should represent a cooperative process (according to Ref. [20], in the lethicin bilayer, the