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Concentration Polarisation in the Electrodialysis Process and the Polarisation Characteristics of Ion-selective Membranes

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Complications in the electrodialysis process, due to the occurrence of concentration polarisation, are analysed. It is shown that most present-day methods for measuring the electrochemical characteristics of ion-selective membranes are not suitable for monitoring the behaviour of these membranes over a wide range of polarising current densities. An analysis of the polarisation characteristics of electromembrane systems shows the advantages of a system with a rotating membrane disc. It is shown that in the polarisation process there is a significant deterioration of the electrochemical properties of heterogeneous membranes whereas the properties of homogeneous perfluorinated sulpho-cation-exchange membranes remain almost unchanged.
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I. INTRODUCTION

The intensive growth of industry and power engineering, the utilisation of natural resources and the development of agriculture in new areas with limited supplies of fresh water, and the growth of population are creating a shortage of fresh water all over the world. At the same time the increasing volume of sewage is having a deleterious effect on the environment and the condition of the water basins. One of the key questions in the solution of problems of environmental conservation is the development of efficient methods for separating mixtures into their components.

Membrane methods of purifying and concentrating solutions are favoured because of their low energy consumption and material content, simplicity of maintenance, and economy. Of the various membrane technologies electrodialysis has a special place in that it provides unique possibilities for carrying out deionisation and concentration of electrolyte solutions and also synthesis and chemical reactions of various substances. A very widespread application of electrodialysis, both in the USSR and abroad, is the desalination of water. Questions of the theory and practice of electrodialysis are discussed most fully in Wilson's monograph,[1] which retains its value to the present day, and also elsewhere.[2-5] Electrodialysis (ED) is the process of directional transport of ions through an electromembrane system (EMS), which consists of one or several membranes, particularly ion-selective membranes, placed in the electrolyte solution. The driving force of the ED process is the electric potential gradient. In Fig.1 is shown a typical ED scheme employing ion-selective membranes which is used to deionise and concentrate electrolyte solutions. If (as in Fig.1) a stack of alternating cation-selective and anion-selective membranes is placed between a pair of electrodes, then the ions will migrate in equivalent quantities from the solution in the deionisation chambers (*I*), which have anion-selective membranes on the anode side and cation-selective membranes on the cathode side, to the adjacent concentrating chambers (*II*), which have cation-selective membranes on the anode side and anion-selective membranes on the cathode side, and will be removed from the concentrating chambers with the enriched solution (the concentrate).

The rate of transport of the ions through the EMS is determined by the current density and is directly dependent on it. However, the current density is restricted to a limiting value corresponding to the reduction of the ion concentration at the surface of the membrane on the desalination chamber side to zero. The limiting current density depends on the physicochemical properties of the solution undergoing treatment and the membranes and also on the hydrodynamic conditions in the chambers of the electrodialysis equipment, which are dependent on the constructional performance of the chambers and the rate of flow of the solution.

The concentration polarisation of the EMS which occurs as a result of the diffusion constraints leads to high energy consumption and also favours the deposition of precipitates of sparingly soluble salts and hydroxides on the membrane surfaces, so reducing the efficiency of the ED process.

II. BASIC PRINCIPLES OF THE ELECTRODIALYSIS PROCESS

The requirements imposed on electrodialysis apparatuses and on the organisation of the electrolyte deionisation process in them are determined by the interrelation between technological parameters that are governed by the state of the EMS.

The concentrations of the solutions remain constant in the central part of the flow and vary only within the so-called diffusion layers, which are adjacent to the surfaces of the ion-selective membranes. The thickness of a diffusion layer is an arbitrary concept and is defined by the coordinate (on an axis perpendicular to the membrane surface) at which the concentration of the solution differs from the concentration in the central part of the flow by 1%. The variation in the concentration in the diffusion layer is caused by the difference in the transport numbers of the ions in the solution and membrane phases. When the density of the current passing through the electromembrane system is increased the concentration of the diluate at the surface of the membrane falls. The limiting current density is the density at which this concentration approaches zero.

The state of the EMS can be regarded as defined if we know how the electric potential is distributed in it and also the concentrations and rates of flow of the working solutions. A theoretical analysis of the mass exchange in the ED process reduces to the solution of

equations for electrodiffusion and convective diffusion. These equations, together with the equation of motion, the conditions of continuity and electroneutrality of the solution, and also the equation for the current density at the solution–membrane interfaces, form a closed system of equations.

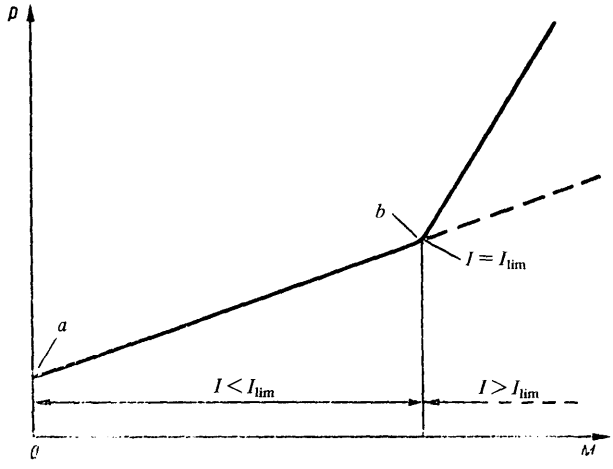


Figure 2. Relationship between the energy consumption P (calculated per unit mass) and the specific mass-transport M in the electrodialysis process.[4]

The relationship between the energy consumed in the electrodialysis and the amount of material transported across the effective area of the membrane in unit time is shown in Fig.2. Point *a* corresponds to the minimum energy consumption (P_{min}) required to achieve a given degree of deionisation in the absence of concentration polarisation and ohmic resistance of the solution and the membranes, and with a number of ther assumptions:[1]

$$P_{min} = 2RT\left(\frac{\ln(c_i/c_0)}{1-c_i/c_0} - \frac{\ln(c_i/c_c)}{1-c_i/c_c}\right)$$

where P_{min} is the minimum specific (i.e. per unit mass transferred) energy consumption, c_i and c_0 are the initial and final concentrations of the diluate, and c_c is the concentration of the mother liquor.

Point *b* corresponds to the limiting current density; on the section *ab* there is a proportionate increase in the specific energy consumption as the mass transport through the EMS increases. However, at current densities above the limiting value (the section to the right of point *b*) the slope of the curve changes, indicating unproductive energy consumption. To achieve a given degree of deionisation of the solution being treated it is possible, having increased the specific mass transport, to reduce the effective area of the ion-selective membranes correspondingly, e.g. by reducing the number of working chambers in the electrodialysis apparatus.

To intensify the ED process the working current density in the electrodialysis apparatus should be increased to its limiting value. To increase the limiting current density, i.e. to remove the diffusion constraints, the construction of the electrodialysis apparatus must be further perfected and the electrochemical properties of the ion-selective membranes improved.

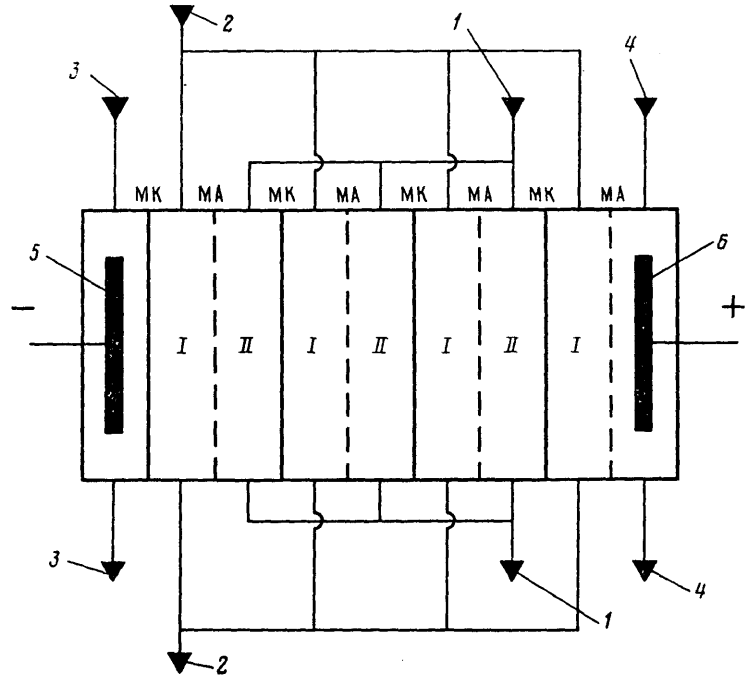


Figure 1. Diagram of an electrodialysis process using ion-selective membranes: MK) cation-selective membrane; MA) anion-selective membrane; *1*) deionisation channel; *2*) concentrating channel; *3*, *4*) channels for flushing electrode chambers; *5*) cathode; *6*) anode.[4]

III. POLARISATION CHARACTERISTICS OF ION-SELECTIVE MEMBRANES

In spite of the progress achieved in investigating the mechanism of electro-mass-transport in an EMS (which is substantially different at current densities below and above the limiting diffusion value[6-11]), most current methods of measuring the electrochemical properties of membranes (see, for example, a previous review[12]) do not make it possible to assess the behaviour of the membrane under investigation over a wide range of variation of the polarising current. This relates primarily to the monitoring of the selectivity of membranes through the transport numbers of the ions,[1,3,12] which remain constant only for small variations in the concentrations of the ions in the membrane phase.[13] The most promising methods for estimating the electrical conductivity of membranes are, in our opinion, those which enable the resistance of the EMS to be measured during the process of their polarisation.[14,15]

A study of the volt-ampere curves of the EMS enables the mechanism of electro-mass-transport in these systems under different polarisation conditions to be judged.[16-23] In most of this work the EMS's are investigated with a flowing solution although, owing to the difference in accessibility of the membrane surfaces as regards diffusion, a detailed study of the ion-transport mechanism in this type of system is difficult in principle. In other work[24-28] EMS's with free convection are examined because in the systems, in contrast to the flow type, identical thicknesses of the diffusion layers can be obtained.

In classical electrochemistry there is a system with forced convection, which is unique in its way and which ensures equal accessibility of the electrode surface as regards diffusion; this is the rotating disc electrode (RDE).[29,30] The theory of such a system has also been developed.[31] The first attempts to apply the RDE method to electro-membrane systems were reported in Ref.32 and later in Ref.33. They have, however, remained virtually undeveloped owing to the technical complexity of the experiment. The main defect in the apparatus that was proposed[32] is caused by mounting the membrane under investigation on a spindle with the aid of a nut; this disturbs the equal accessibility of the surface and the hydrodynamics of the system. A common defect of the apparatuses developed in Refs.32 and 33 is that the desalination and concentrating chambers adjacent to the membrane are not equivalent and this fundamentally limits the range of possible investigations.

An apparatus with a vertically aligned rotating membrane, which separates symmetrical immovable half-cells with polarising and measuring electrodes filled with solution, has been described.[34] We presume that precisely this type of EMS is suitable for use in studying the polarisation characteristics of membranes because, under conditions of equal accessibility of the membrane surfaces in respect of diffusion and with the possibility of accurate calculation of the thickness of the diffusion layer, the polarisation characteristics of the system can be analysed and the extra-diffusion stage of the electro-mass-transport isolated.

A disadvantage of voltammetry with linear scanning of the flow, as applied to an EMS, especially when dilute solutions are used, is the large drop in voltage in the regions between the membrane and the measuring electrodes, as a result of which there is a reduction in the accuracy of recording the overvoltages associated with the limiting stages of the electro-mass-transport. To eliminate the ohmic drop in voltage in the solution, which is not connected with the concentration polarisation processes, compensating measuring circuits are devised. A circuit similar to that proposed in Refs.35 and 36 is shown in Fig.3. The membrane being examined (*1*) is in a cell which contains, in addition to the polarising (*2*, *3*) and measuring (*4*, *5*) electrodes, a further electrode (*6*). First, in the absence of concentration polarisation on input of an alternating current pulse to the polarising electrodes, the amplification factor of the second differential amplifier DU2 is chosen so that the difference in the voltage drops between the probes *4* and *5* on the one hand, and *5* and *6* on the other, which is registered by the recording graph plotter, is equal to zero. Then, on input of a linearly increasing current from the

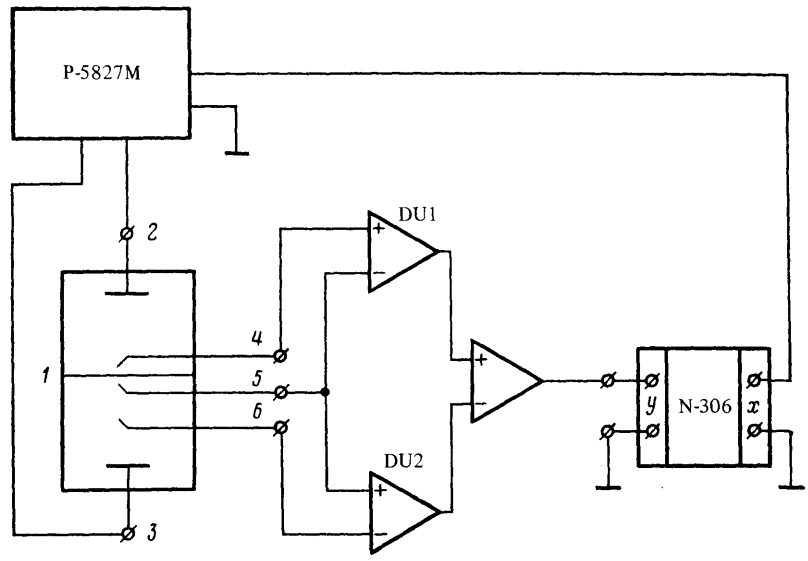


Figure 3. Block diagram of the apparatus for obtaining the volt-ampere characteristics of an EMS: P-5827M) potentiostat; N-306) graph plotter; DU1, DU2) differential amplifiers.

potentiostat, the volt-ampere curves registered by the recorder reflect the change in the voltage drop in the EMS due to concentration polarisation.

Specimens of well known commercial brands of membrane have been examined. The heterogeneous membranes MK-40, MA-40, and MA-41,[37] used in electrodialysis processes, are hydrophilic and possess a "porous" structure containing unexchangeable absorbed solution. The homogeneous perfluorinated sulpho-cation-exchange membranes (PSM), which have their main use in chlorine electrolysis processes,[38] are hydrophobic and in dilute solutions have properties close to the ideal selective membrane.

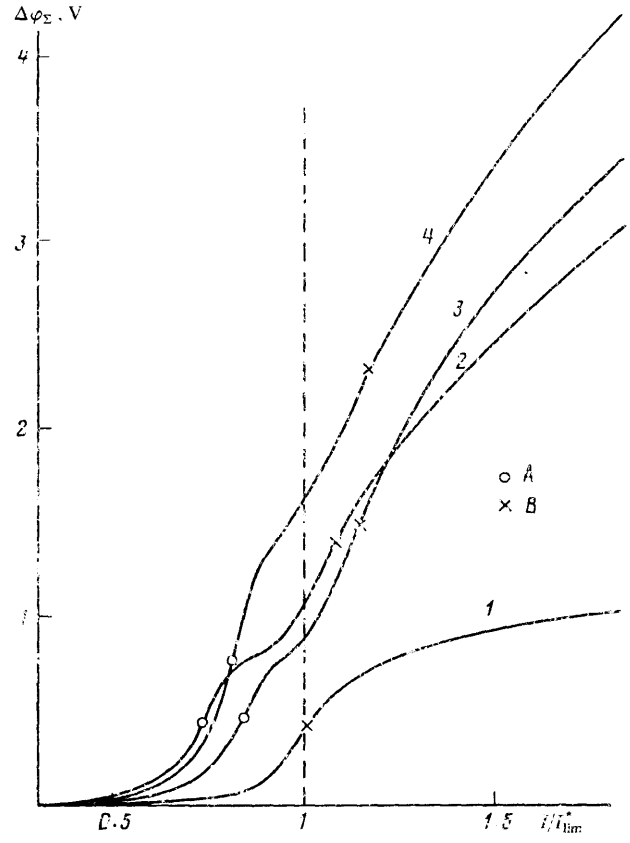


Figure 4. Volt-ampere curves for EMS's with the membranes: *1*) PSM; *2*) MA-41; *3*) MK-40; *4*) MA-40.

The volt-ampere curves shown in Fig.4 were obtained for the commercial grade membranes in 0.01 M sodium chloride solution with the membrane disc rotated at 100 rev min^{-1}, corresponding to a diffusion layer thickness $\delta = 5.8 \times 10^{-3}$ cm.[31] The possibility that the theory developed in Ref.16 is applicable to the system being used is confirmed by the occurrence of a characteristic linear dependence of the limiting current density on the square root of the angular velocity of rotation of the disc; this dependence is satisfied in the range of speeds 100–600 rev min^{-1}. In Fig.4 the dimensionless current density quantity I/I^*_{lim} (where I^*_{lim} is the limiting electrodiffusion current density for an ideally selective membrane) is plotted along the abscissa axis. In a solution of a binary electrolyte the following relationships are satisfied:[29,39]

$$I^*_{lim} = \frac{z_1 F D^* c_0}{(1 - t_1)\,\delta} \tag{1}$$

and

$$\delta = 1.61\,(D^*)^{1/3} \nu^{1/6} \omega^{-1/2}$$

where c_0 is the initial concentration of the solution, δ is the thickness of the diffusion layer, F the faraday, D^* the diffusion coefficient of the electrolyte solution, z_1 the charge number of the counter ion, ν the kinematic viscosity, and ω the angular velocity of rotation of the disc.

The volt-ampere curve for a homogeneous PSM is characterised by a relatively small voltage drop in the polarisation process: at the inflection point corresponding to the limiting current density I_{lim} the drop is 440 ± 30 mV. This is close to the value (450 mV) calculated using an equation obtained from Ref.40 and subtracting the ohmic voltage drop in the solution, which is not connected with concentration polarisation processes:

$$\Delta\varphi_\Sigma = 2\Delta\varphi_M + \frac{RT}{z_1 F} \ln\left\{\frac{[1 + \exp(\Delta\psi_M)]^2}{4\exp(\Delta\psi_M)}\right\}$$
$$\Delta\psi_M = \Delta\varphi_M \frac{z_1 F}{RT} \tag{2}$$

The membrane potential $\Delta\phi_M$ is determined by the diffusion relaxation method developed in Refs.26 and 28. The value $\Delta\phi_\Sigma$ can be used to estimate the polarisability of the membrane and the quantity $I_{lim} \cdot \Delta\phi_\Sigma$ characterises the energy consumption on polarisation of the system in the limiting state.

If the surface of the homogeneous PSM on the desalination chamber side is rubbed with emery paper the limiting current density decreases and the voltage drop increases, indicating a partial extension of the diffusion constraints on the transport of ions into the membrane phase because of the increased roughness of its surface.

The inflection point on the volt-ampere curve for the PSM (Fig.4) is displaced slightly to the right with respect to the limiting current density for an ideally selective membrane, I^*_{lim}. This indicates that the selectivity of the membrane is non-ideal. To estimate the reduction in selectivity we introduce a dimensionless quantity representing the displacement of the limiting current density for this membrane relative to the ideally selective membrane:

$$s = \frac{I_{lim} - I^*_{lim}}{I^*_{lim}} \tag{3}$$

The relative displacement for the PSM is 0.02, showing that it has a high selectivity.

On the volt-ampere curves for the heterogeneous membranes (Fig.4) two inflection points, to the left and right of I^*_{lim}, can be found using the three tangent method. If the displacement of the first point (point *A* in Fig.4) is evaluated using expression (3) it will be negative and that of the second point (point *B* in Fig.4) will be positive. The heterogeneous membranes investigated contained from 11 to 20 vol.% of equilibrium solution.[41] It is therefore likely that concentration polarisation in EMS's containing heterogeneous membranes involves both a near-membrane region in the solution, defined by the size of the δ-layer, and a near-surface region in the membrane pores occupied by the unexchangeably absorbed electrolyte, which can be defined by an effective thickness $\bar{\delta}$. The current density values corresponding to the *A* points in Fig.4 are probably

the limiting current densities in the $(\delta + \bar{\delta})$-layers whereas the *B* points represent the onset of the limiting state in the δ-layers of the "free" solution.

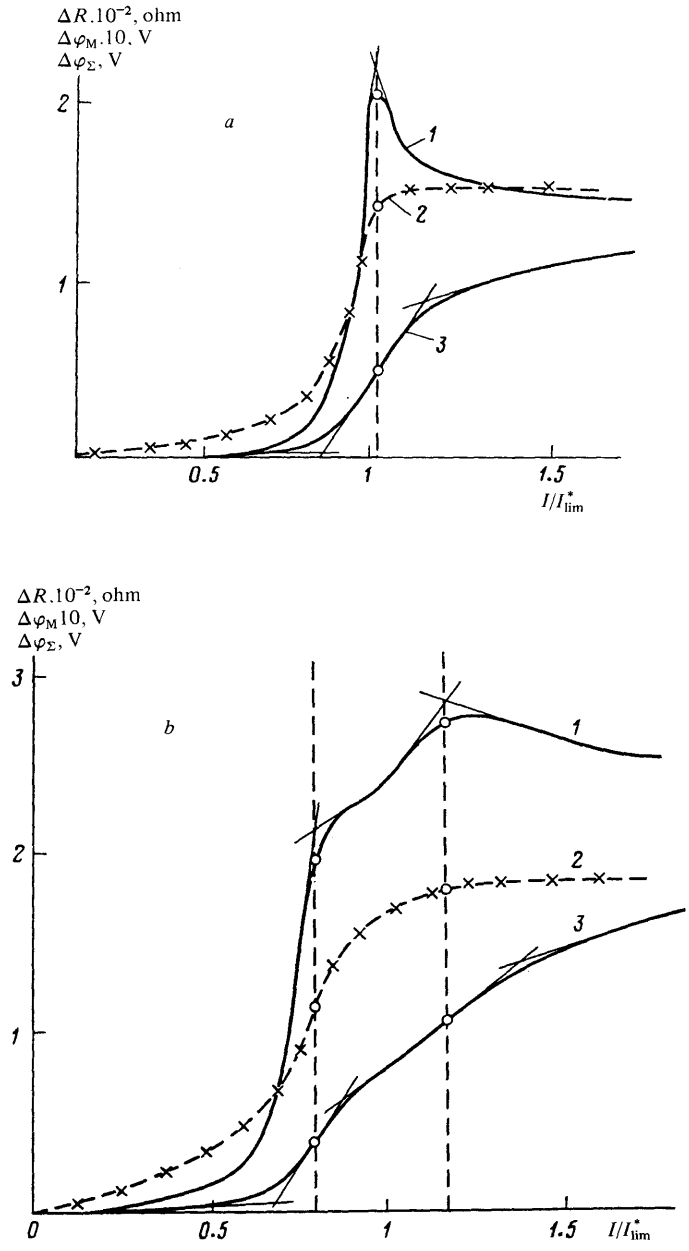


Figure 5. Plots of the change in resistance (*1*), membrane potential (*2*), and total voltage drop (*3*) against the dimensionless current density for EMS's with the membranes: *a*) PSM; *b*) MK-40. 0.01 M NaCl solution, rate of rotation of the membrane disc = 100 rev min^{-1}.

Thus the first inflection point on the volt-ampere curve is probably associated with the concentration polarisation which is due to the diffusion constraints on the transport of ions in the solution contained in the heterogeneous membrane phase. The value of the current density $\bar{I}_{lim}$ corresponding to this sudden change in the difference between the potentials can be termed the limiting current density for the equilibrium solution of the membrane. This is confirmed by the weak dependence of $\bar{I}_{lim}$ on the rate of rotation of the membrane.

To test the stated assumptions and to locate the inflection points on the volt-ampere curves more accurately by using the method described in detail in Refs.42 and 43, the ohmic resistance of the EMS in the polarisation process was determined. In Fig.5 the volt-ampere curves are compared with the variation of the resistance with current density for EMS's with PSM (Fig.5*a*) and MK-40 (Fig.5*b*) membranes, identical conditions being used. In the first case the inflection point on the volt-ampere curve coincides with the maximum on the curve for ΔR as a function of I/I^*_{lim} and corresponds to the limiting electrodiffusion current density in the solution. For the MK-40 membrane the $\Delta R(I)$ curve shows two local maxima which coincide with the inflection points on the volt-ampere curve corresponding to the negative and positive relative displacement of the limiting current density.

Fig.5 also shows the dependence of the membrane potential $\Delta\phi_M$ on the dimensionless current density, as obtained by the diffusion relaxation method.[28] For the homogeneous PSM $\Delta\phi_M$ reaches a maximum at I_{lim} and then shows hardly any change. For the MK-40 membrane the sharp jump in $\Delta\phi_M$ begins at the limiting current density in the equilibrium solution of the membrane $\bar{I}_{lim}$ but the membrane potential reaches saturation only at a current density equal to the limiting electrodiffusion current density in the free solution I_{lim}, which is determined from the second inflection point on the volt-ampere curve.

This is confirmed by an analysis of curves, obtained under similar conditions,[28,29] showing the decrease in the membrane potential with time for PSM and MK-40 membranes at different current densities (Fig.6). Fig.6 also shows curves calculated assuming purely extra-diffusion kinetics for the process. For the PSM the observed and calculated curves agree. The reason for the slightly larger experimental values of $\Delta\phi_M$ is probably that the value of the liquid diffusion potential was not taken into account in the calculation. In the case of the MK-40 membrane the drop in the membrane potential in the first 0.1 s is considerably more rapid than would be expected if purely extra-diffusion processes took place; the experimental curves lie considerably above the calculated curves. Similar results were obtained for the heterogeneous membranes MA-40, MA-41I, and also MK-44 and MK-41, indicating that they are strongly polarisable compared to homogeneous membranes.

Analysis of results obtained by independent methods suggests that concentration polarisation of an EMS is due to both intra- and extra-diffusion constraints on electro-mass-transport. With the heterogeneous membranes MK-40, MK-44, MK-41, MA-40, and MA-41 the diffusion constraints on the transport of ions in the membrane phase permit a limiting state to be reached at current densities I_{lim} smaller than the limiting current density for an ideally selective membrane I^*_{lim}. A further increase in the current leads to the establishment of a limiting state in the free solution at current densities $I_{lim} > I^*_{lim}$, indicating non-ideal selectivity of the heterogeneous membranes. The relative displacement of the limiting current density *s* gives a quantitative description of the selectivity of the membranes in the limiting state and the product $I_{lim}.\Delta\phi_\Sigma$ gives the energy consumption on polarisation of the membrane.

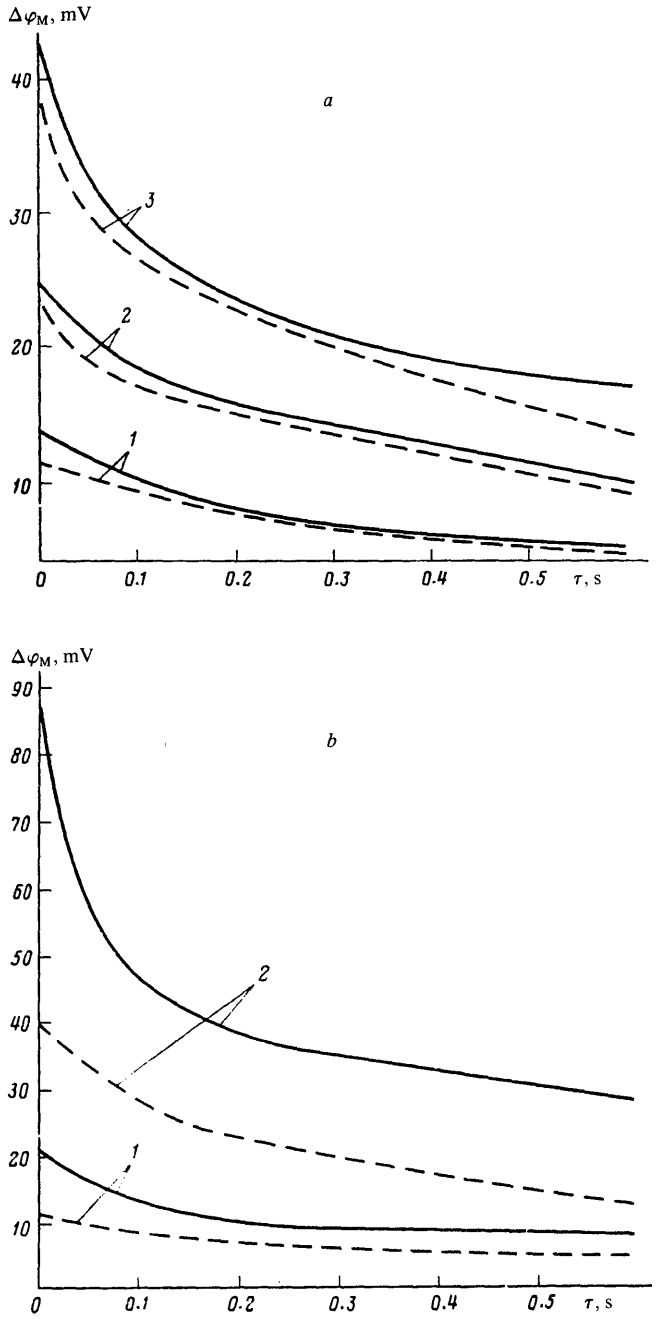


Figure 6. Experimental (full lines) and calculated (broken lines) curves showing the decrease in the membrane potential for a PSM (*a*) and an MK-40 membrane (*b*) with time after switching-off the polarising current. Polarising current density (mA cm^{-2}): *1*) 1; *2*) 2; *3*) 3; rate of rotatation of the membrane disc 100 rev min^{-1}, 0.01 M NaCl solution.

The values of the limiting electrodiffusion current densities, their displacements, and the voltage drops corresponding to $\bar{I}_{lim}$ and I_{lim} (see Table) can be used to judge the energy consumption on polarisation of the membranes and their selectivity; in our opinion this provides fairly full information on the electrochemical behaviour of membranes in the polarisation process.

Polarisation characteristics of EMS's containing different membranes.*

Membrane	10^3c, M	I^*_{lim}, mA cm^{-2}	$\bar{I}_{lim}$, mA cm^{-2}	$\bar{s}$	$\Delta\bar{\varphi}_\Sigma$, mV	I_{lim}, mA cm^{-2}	s	$\Delta\varphi_\Sigma$, mV
PSM	11.5	5.0	—	—	440	5.1	+0.02	440
MK-40	10.0	4.2	3.5	−0.17	450	5.1	+0.21	1750
MA-41I	10.0	6.75	4.6	−0.32	280	8.2	+0.21	1680
MA-40	10.0	6.75	5.2	−0.23	680	7.6	+0.13	2200

* The parameters $\bar{I}_{lim}$, $\bar{s}$, and $\Delta\bar{\phi}_\Sigma$ describe the membrane phase.

The data in the Table indicate that the heterogeneous membranes MK-40, MA-40, and MA-41 have a negative value of s as well as a positive value and this is explained by their polarisability owing to the presence of unexchangeably absorbed electrolyte in the membrane phase. The homogeneous PSM has only a positive displacement which is much smaller than the corresponding values for the heterogeneous membranes; this indicates that it has a high selectivity whereas the selectivities of the heterogeneous membranes in the polarisation process are reduced. The values of $\Delta\phi_\Sigma$ for the heterogeneous membranes, which are much larger (by a factor of 4—5) than the corresponding value for the PSM, typify a higher energy capacity of processes with heterogeneous membranes.

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Analysis of the polarisation characteristics of an EMS in a system with a rotating membrane disc thus indicates that the limiting stage of the mass transport through heterogeneous membranes is internal diffusion when the current density is below the limiting value for an ideally selective membrane but external diffusion at current densities above I^*_{lim}. Polarisation of the membrane entails a reduction in its selectivity and an increase in the electrical resistance of the system. When homogeneous PSM's are polarised the mass-transport process takes place under extra-diffusion control.

In other words, in the polarisation process heterogeneous membranes which contain a sufficient amount of the equilibrium solution display a considerable deterioration in their electrochemical properties. In this case increasing the intensity of the electrodialysis process only by removing the extra-diffusion constraints will be not be sufficiently effective. Consequently, in our opinion, special attention must be given to the production of new, desirably homogeneous types of membrane.

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