Russian Chemical Reviews **63** (12) 1047 – 1062 (1994)
©1994 Russian Academy of Sciences and Turpion Ltd

UDC 62 – 278: 66.063.2

Membrane distillation

M T Bryk, R R Nigmatullin

Contents

I.	Introduction	1047
II.	Types of membrane distillation	1048
III.	Membranes for membrane distillation	1048
IV.	Mass and heat transfer in membrane distillation	1050
V.	Experimental studies on membrane distillation	1053
VI.	Modules and apparatus for membrane distillation	1056
VII.	Applications of membrane distillation	1058
VIII.	Conclusion	1060

Abstract. Studies in the field of membrane distillation are analysed. A critical analysis of the theoretical and experimental investigations of membrane distillation is presented. Attention is concentrated on the mechanism of mass transfer and the influence of various external factors on the process characteristics. Questions concerning the creation of modules and apparatus for membrane distillation and aspects of the practical employment of such distillation in order to obtain pure water, for the purification of waste water, and for the concentration of technological solutions in various branches of industry are considered quite fully. The advantages and disadvantages of membrane distillation compared with other membrane methods are analysed. The bibliography includes 97 references.

I. Introduction

The first mentions of membrane distillation (MD) as a separate membrane process date back to the beginning of the 1980s,[1–4] although at the end of the 1960s studies[5–8] were published of the membrane desalination of water, which is in essence membrane distillation. Since 1985, papers and conference proceedings devoted to the experimental and theoretical study of this process have been published systematically.[9–15] A special issue of the *Journal of Membrane Science* has been devoted to membrane distillation.[12] Each year the number of publications on membrane distillation increases and at the present time approximately 100 are already known.

Membrane distillation has aroused interest primarily as a method for the purification and desalination of water and also for the concentration of technological solutions. Compared with baromembrane methods (reverse osmosis, ultrafiltration, and microfiltration), membrane distillation has advantages which reside in the possibility of concentrating solutions of many involatile organic and inorganic substances up to conditions close to their solubility limit. The productivity in terms of the permeated material remains satisfactory under these conditions [5–10 litre(m^2 h)$^{-1}$]. The driving force of the membrane distillation process is the difference between the vapour pressures of the solvent on either side of the membrane, which is established as a result of the difference between the temperatures of the initial solution [the output side of the membrane] and of the permeated materials (or cooling agent) on its input (receiving) side. The temperature of the solution being concentrated is usually 50–80 °C, and that of the distillate is 20–25 °C. Consequently, high-energy heat can be used for membrane distillation. Furthermore, membrane distillation, not being a baromembrane process, does not require an excess pressure as in the case of microfiltration, ultrafiltration, and especially reverse osmosis.

Membrane distillation is a process in which the membrane itself does not affect the vapour–liquid equilibrium in the separation of solutions and liquids.[16] The term 'membrane distillation' is applied to processes which have the following characteristics: (1) the membrane must be porous; (2) it must not be wetted during the separation of the liquids; (3) there must be no capillary condensation within the membrane pores; (4) only vapour should be transferred through the membrane pores; (5) the membrane must not alter the vapour–liquid equilibrium during the separation of the components; (6) at least one side of the membrane must be in direct contact with the liquid; (7) for each component, the driving force of the mass transfer is the partial pressure gradient in the vapour phase.

Such an expanded definition of membrane distillation is necessary in connection with the fact that different investigators frequently name this process in different ways or employ for it the names of similar processes (transmembrane distillation, transvaporisation and thermotransvaporisation, membrane evaporation), which leads to confusion and errors. It must be emphasised that there is a fundamental difference between membrane distillation and transvaporisation, because the latter process is effected through nonporous membranes as a result of the dissolution and molecular diffusion of the solution components being separated.

Analysis of the existing publications indicates that membrane distillation is a promising membrane separation method as regards its applied aspect, which can be used with great effectiveness in processes such as the preparation of pure and highly pure water from waters with different salinities (including sea water),

M T Bryk, R R Nigmatullin Department of the Physical Chemistry of Membranes, Institute of Colloid Chemistry and the Chemistry of Water, National Academy of Sciences of Ukraine, prosp. Vernadskogo 42, 252680 Kiev, Ukraine. Fax (7-044) 452 02 76

Received 7 July 1994
Uspekhi Khimii **63** (12) 1114 – 1129 (1994); translated by A K Grzybowski

the purification of waste water containing inorganic electrolytes and involatile organic compounds (with the exception of surfactants), the concentration of salts from the wash waters in electroplating and dyeing industries, the concentration of thermolabile biologically active substances (vitamins, enzymes, etc.), the concentration of sugar and glucose-fructose syrups, and the concentration of solutions of dilute involatile inorganic acids, alkalis, and other substances.

At the same time, the membrane process has still not been investigated sufficiently fully experimentally and theoretically. There is as yet no complete analysis of the available studies on membrane distillation, although the need for this has become evident. A paper[18] in which this problem has been examined partially can be regarded as an exception. The aim of the present review is an attempt to fill this gap, which in our view will promote a clearer understanding of the subject of further research in the field of membrane distillation.

II. Types of membrane distillation

Membrane distillation can be carried out in different technological versions, and it is therefore important to distinguish several of its modifications.[17,18]

Contact membrane distillation (CMD) is a process in which a liquid is in direct contact with both sides of the membrane. The liquid in contact with the receiving side of the membrane is a medium for the condensation of the vapour being transported (Fig. 1*a*).

Membrane distillation through a gas (vapour) layer—a process in which the vapour beyond the receiving side of the membrane is condensed on a cooled surface at a specified distance from the membrane and the condensed liquid is not in contact with the membrane (Fig. 1*b*).

Membrane distillation at a reduced pressure (vacuum membrane distillation)—a process in which the rarefaction (vacuum) is created in the space between the receiving side of the membrane and the shell of the membrane element. The permeated material is condensed beyond the limits of the membrane module.[15,17]

Membrane distillation in a gas stream (membrane distillation with passage of a gas)—a process in which a gas stream (as a rule nitrogen) is supplied at a specified rate along the receiving side of the membrane. The vapour of the permeated material carried away by the gas stream is condensed beyond the limits of the membrane module.[17,19,20]

Osmotic membrane distillation is carried out with solutions having a high salt content in the receiving component. The permeated material in the form of vapour passes through a microporous hydrophobic membrane from solutions with a low osmotic pressure into a stream of solution with a high osmotic pressure of the solvent (Fig. 1*c*).[21,22]

III. Membranes for membrane distillation

There have been only a few publications devoted to questions of the preparation of membranes specially designed for membrane distillation (see, for example, Refs 23–26). As a rule, the existing hydrophobic microfiltration membranes are used for these purposes in the form of films, tubes, or fibres.[10,16,19,20]

In the case of contact membrane distillation, the transfer of permeated material through the membrane pores is effected in the form of vapour from the surface of the liquid meniscus at the inlets to the pores on the output side of the membrane to the surface of the liquid meniscus at the entrance to the pores on the input (receiving) size of the membrane (Fig. 2). The membrane pores contain a vapour–air mixture, i.e. the membrane should not be wetted by the solution being separated, so that the main requirement which must be met by membranes for membrane distillation is their hydrophobicity. The hydrophobicity makes it possible to maintain a liquid–vapour interface at one or both membrane surfaces and ensures the separation of the evaporation and condensation surfaces. Furthermore, the polymeric materials

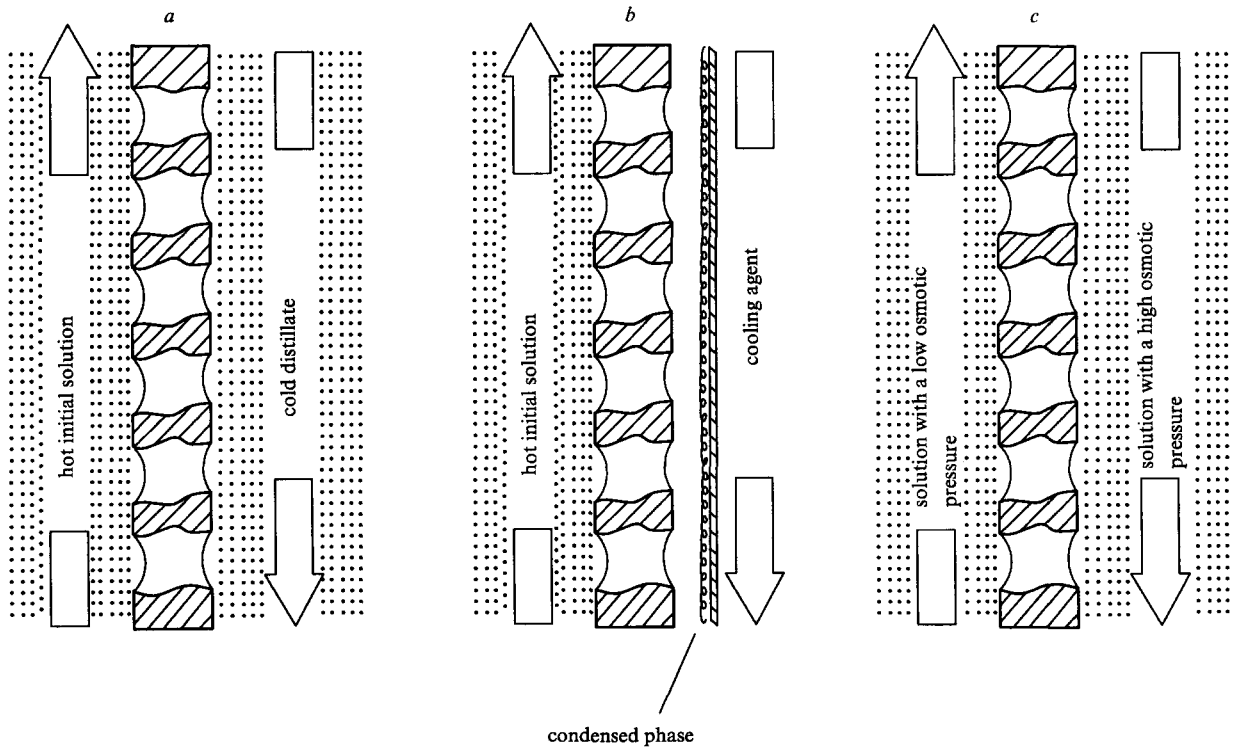


Figure 1. Different versions of the membrane distillation process; (*a*) contact membrane distillation;[17–19] (*b*) membrane distillation through a gas layer;[12,15,19] (*c*) osmotic distillation.[21,22]

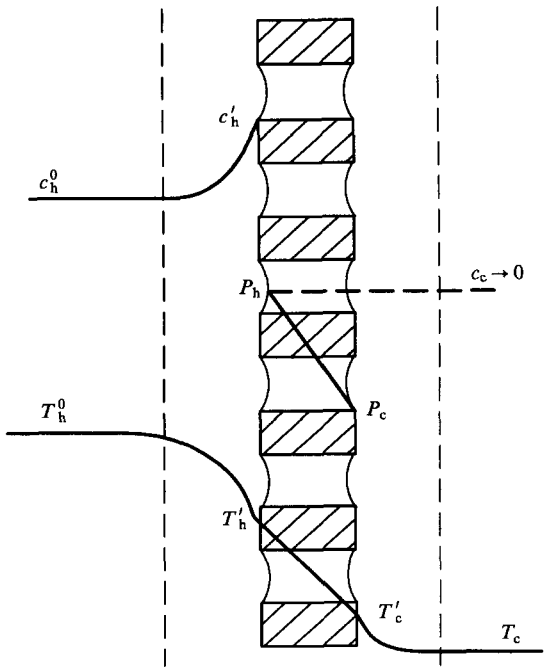


Figure 2. Schematic illustration of the membrane distillation process and the concentration and temperature profiles in membrane distillation.

used to prepare the membranes must possess a sufficiently high thermal stability and heat resistance in corrosive aqueous media.

Polypropylene,[10,20,21] polytetrafluoroethylene and other fluorine-containing polymers,[2,10,19-21] polyorganosiloxanes, poly(vinyl chloride),[27] etc. are mainly used as the polymeric materials satisfying the above conditions and possess in addition fibre- and film-forming capacities.

It is known[2,10,17,19] that, apart from the requirements stated above, the membranes used in membrane distillation must have a low thermal conductivity, a narrow size distribution of their pores, and an overall porosity of 30%–80%. A fairly important parameter for the productivity of the membrane in terms of the permeated material is the average pore diameter, which is believed to be optimum in the range 0.2–0.6 μm.[10,17,19] The membrane thickness must be as small as possible to ensure a high productivity of the membrane distillation process, but heat transfer must be minimised at the same time. The thickness of the membranes for membrane distillation is usually 100–300 μm.[17,19,24]

As already mentioned above, an important characteristic of the membrane is its hydrophobic properties. Therefore it is virtually impossible to employ membrane distillation for the separation of solutions and mixtures containing surfactants, which lower the surface tension and improve the wettability of the hydrophobic surface of the microporous membrane by water. Studies on the relation between the transport of water through polytetrafluoroethylene membranes and their wetting angle ($\alpha \approx 106°$) established[28] that there is a critical water pressure above which it permeates through the membrane as a convective stream. The absolute values of this pressure vary in the range 0.4–1.2 MPa and depend also on other parameters of the membrane (the pore size and the pore distribution) and on the surface tension of the medium being separated, which should not be less than 72×10^{-3} N m^{-1} for inorganic aqueous solutions.[28,29]

The critical concentrations of organic substances (alcohols, ethers, amines, ketones, and acids) in the solutions being separated are determined by the wettability of the membrane under the conditions of the separation process. The following condition for the wettability of the membrane has been proposed:[28]

$$\gamma_L = \gamma_L^p + \frac{\Delta p r_{max}}{2B}, \quad (1)$$

where γ_L is the surface tension of the liquid (solution, mixture) (N m^{-1}), γ_L^p the surface tension of the liquid (solution, mixture) at the boundary where it penetrates the pores of the microporous membrane (N m^{-1}), Δp the pressure difference (N m^{-2}), r_{max} the maximum pore radius (μm), and B the coefficient of the pore geometry.

It has been suggested that the critical concentrations of organic substances for a microporous membrane be calculated by a semiempirical method via the determination of the wetting angle of the material of the membrane.[28]

Unfortunately, the problem of the relation between the hydrophobicity of the surface of the membrane and the structure of water in the surface layers and also the structure of water within the membrane pores is not discussed in the literature.[30,31] The structure of the surface layers of water differs as a function of the nature and energy of the interaction of water molecules with membranes characterised by different surface hydrophobicities and pore dimensions, so that the physical characteristics of water (density, viscosity, phase transition temperatures, vapour pressure, etc.) also differ.[30,31] This undoubtedly must be taken into account in the study of the mechanism of the mass transfer in membrane distillation and in the optimisation of the transport characteristics of membranes.

There are few publications in the literature devoted to the preparation of special membranes for membrane distillation and to the study of their surface on structural characteristics. Among these, mention may be made of investigations[24-26] in which an attempt was made to obtain a hydrophobic layer on the surfaces of microporous cellulose acetate and nitrate membranes with the aid of methods for the radiation graft copolymerisation of styrene with pyridine and copolymerisation in plasma of octafluorocyclobutane (OFCB), CF_4, and trimethylvinylsilane $(CH_3)_3SiCH=CH_2$ (TMVS). This layer would determine the functional characteristics of the composite membrane prepared for membrane distillation. The plasma polymerisation of monomers was carried out under different conditions with the power of the discharge varying from 60 to 200 W for process durations between 5 and 90 min.[24]

In the radiation graft (co)polymerisation of the styrene–pyridine and styrene–carbon tetrachloride systems, the maximum wetting angle on the surface of a modified cellulose acetate membrane is attained for the ratios styrene : pyridine = 90 : 10 (69.5°) and styrene : pyridine : carbon tetrachloride = 85 : 10 : 5 (88.6°) (the wetting angle for the wetting of polystyrene by water is 91°). The introduction of CCl_4 into the system lowers the retention of NaCl (0.3 M) significantly to 66.7%–89.6%, whereas in the copolymerisation of styrene with pyridine the retention is 99.1%. The low retention is attributed to the formation of short grafted chains during comparatively short irradiation periods (~8 h).

The plasma polymerisation of OFCB and the copolymerisation of TMVS with tetrafluoroethylene (TFE) on the surfaces of cellulose nitrate membranes showed that the F : C ratio in the surface layer of the modified membrane and hence the wetting angle are determined by the power of the discharge. There is an extremum in the relations between the F : C ratio and the wetting angle, on the one hand, and the power of the discharge, on the other (Fig. 3, see next page). The lowest values of these quantities have been found for moderate discharge powers in the range 80–160 W. The maximum wetting angles of 113° and 120° are attained in the polymerisation of OFCB for discharge powers of 60 and 175–200 W respectively. For these parameters, a maximum retention of NaCl (0.5 M) of 92.0% is attained.

With increase in the plasma polymerisation time, an increase in the retaining capacity of the modified membranes and a decrease in their productivity are characteristic of all the systems investigated.[24-26] Electron microscope studies have shown that

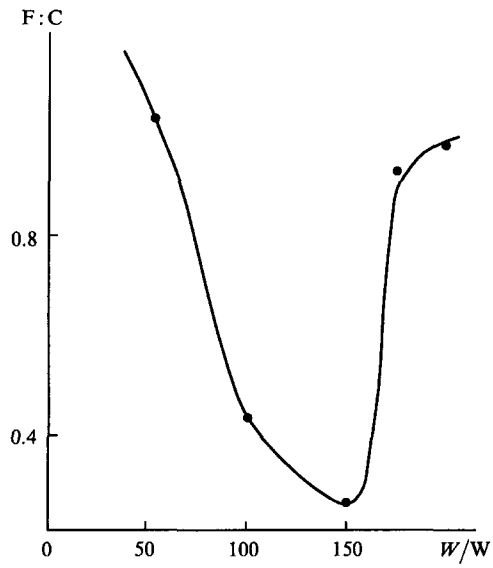


Figure 3. Dependence on the discharge power of the ratio of the contents of fluorine and carbon in the molecular structure of a cellulose nitrate membrane when the latter is modified by OFCB in a plasma.[24]

Table 1. The properties of the membranes used in membrane distillation.[24]

Membrane	Material	Permeability coefficient 10^3K/kg (m^2 h Pa)$^{-1}$	Retention (%)
Asymmetric poly(vinylidene fluoride)	poly-(vinylidene fluoride)	0.68	99.9
Modified by radiation-grafted polystyrene	cellulose acetate	0.14 0.96	99.1 66.7
Modified by OFCB in plasma	cellulose nitrate	0.82 1.32	99.5 99.1
Modified by TMVS–CF_4 in plasma	cellulose nitrate	1.81 2.22	99.9 99.4

this is associated with a decrease in the inlet diameters of the membrane pores and with an increase in the thickness of the modifying layer. Certain characteristics of the modified membranes are compared in Table 1 with those of an asymmetric porous membrane based on poly(vinylidene fluoride).

A novel membrane designed for the desalination of sea water or brines by membrane distillation has been described.[23] It has a multilayer construction based on an electrically conducting layer comprising polypropylene (25%–75%), poly(ethylene glycol) (10%–30%), graphite and ground charcoal (5%–75%), dibutyl phthalate (5%–20%), and sodium dodecyl sulfate (5%–25%). A hydrophobic polysiloxane film is deposited on this porous electrically conducting substrate from a solution or an emulsion. Such a membrane and the solution on the output side are heated by passing an electric current through the membrane.

IV. Mass and heat transfer in membrane distillation

Theoretical analysis of membrane distillation is based as a rule on the consideration of an ideal membrane, i.e. a membrane in which there are no wettable pores. In this case, the viscous flow of the liquid and thermodiffusion within the membrane pores are excluded and the diffusion of the permeated material is determined by the transport of solvent vapour by the vapour pressure gradient across the membrane. Consequently membrane distillation is a diffusion-controlled process and its phenomenological description is based on Fick's laws.

The diffusional mechanism of membrane distillation on real membranes has been confirmed in a study[32] the authors of which obtained linear relations between the flux of the permeated material and the reciprocal of the membrane thickness (Fick diffusion). Furthermore, the high retention of the involatile components of the solution (in excess of 99%) indicates the absence of convective flow in membrane distillation on real membranes. The phenomenological description of the membrane distillation process by means of Fick's laws is therefore entirely legitimate.[32–34] If the membrane pores are filled with air, the molar flux of water vapour is described by the equation[12]

$$N = -\frac{cD}{1-x}\frac{dx}{dz}, \tag{2}$$

where c is the molar concentration of the solution, D the diffusion coefficient of water vapour in the water–air mixture within the membrane pores, x the mole fraction of water vapour, and z a constant [sic. presumably a coordinate is intended (Ed. of Translation)].

The main problem arising in the solution of Eqn (2) is the difference between the diffusion coefficient within the membrane pores and the diffusion coefficient in a free medium and also the dependence of the coefficient on temperature and the vapour concentration. To simplify the problem, use has been made of the following empirical relation obtained from experimental data on diffusion in a water vapour–air mixture at ~40 °C:[12]

$$cD = 6.3 \times 10^{-5}\sqrt{T}. \tag{3}$$

Taking into account Eqn (3) and the morphology of the membrane, the following expression has been obtained for the molar flux of water (in the case of membrane distillation through a layer of gas):

$$N = 6.3 \times 10^{-5}\frac{1}{\delta/\varepsilon\sqrt{T_h} + L/\sqrt{T_c}}\ln\frac{1-x_c}{1-x_h}, \tag{4}$$

where δ and ε are the thickness and porosity of the membrane respectively, L is the thickness of the gas layer, and T_h and T_c are the temperatures on the hot and cold sides of the membrane respectively. This approach made it possible to determine the principal parameters influencing the flux and the nature of its dependence on the temperature regime and the morphology of the membrane.

Relations for the transport of gases (vapours) in porous-capillary media, based on the molecular-kinetic theory of gases, are usually employed in the description of diffusional transport of vapour in the membrane distillation process.[32,35] The general expression for the flux of permeated material, unrelated to the transport mechanism, assumes the form

$$J = \frac{K}{\sigma}(p_h - p_c) = \frac{K}{\sigma}\Delta p, \tag{5}$$

where p_h and p_c are the vapour pressures of the solvent on the hot and cold sides of the membrane respectively, and K is the permeability coefficient of the membrane. In contrast to the diffusion equation, the permeability coefficient K characterises both the properties of the gas and the morphological features of the membrane.

The diffusional transport of gases (vapours) in capillary-porous media is characterised by three flow regimes:[36-40] free-molecular (Knudsen diffusion), molecular, and transitional. The decisive parameter of the flow regime is the ratio of the mean free path of the molecules to the pore diameter.

If the mean free path greatly exceeds the pore size, Knudsen diffusion obtains. It is characterised by a greater number of collisions of the molecules with the pore wall than with one another. The molecular diffusion of vapours occurs if the free path of the molecules is smaller than the pore size, i.e. the number of collisions of the molecules with one another (or with the molecules of another kind) exceeds the number of collisions with the pore walls (viscous flow). Equations for mass transfer in capillary-porous media have been used for the transport of gases through porous membranes occurring under free-molecular and molecular diffusion conditions. For isotropic membranes, the flux of the permeated material is defined by the following equations:[35-37]

(a) for Knudsen diffusion,

$$J = \frac{2}{3}\frac{r\varepsilon}{\chi}\left(\frac{8M}{\pi RT}\right)^{1/2}\frac{\Delta p}{\delta} = \frac{K_K \Delta p}{\delta}, \quad (6)$$

where r is the membrane pore diameter, χ the tortuosity coefficient of the pores, and K_K the mass transfer coefficient under the conditions of Knudsen diffusion;

(b) for viscous flow,

$$J = \frac{1}{8}\frac{r^2\varepsilon}{\chi}\frac{1}{\eta}\frac{Mp}{RT}\frac{\Delta p}{\delta} = \frac{K_m \Delta p}{\delta}, \quad (7)$$

where η is the viscosity and K_m the mass transfer coefficient under the conditions of molecular diffusion.

There are a series of fundamental differences between a Knudsen flow and molecular diffusion, the main ones of which are the dependence of molecular diffusion on the average pressure.

If the free path of water molecules does not exceed 0.2 μm (in the temperature range 20–100 °C), i.e. is comparable to the size of the pores in the membranes employed for membrane distillation then the process occurs in the transitional regime. However, in certain studies the description of processes of this kind has been based on the molecular diffusion regime.[41]

The transitional regime is as a rule related not to the mixed nature of the transport but to the effects determined by the surface flow.[42] At the present time there is no single theoretical concept on the basis of which one could obtain a rigorous quantitative description of the process.

In the literature on the transport of gases in capillary-porous bodies, frequent attempts have been made to describe the mass transfer in the transitional regime by combining the equations describing the Knudsen and molecular diffusion or on the basis of empirical equations.[43]

In the study of the membrane distillation process, attempts have also been made to describe the mass transfer through porous membranes in the transitional regime. Thus it has been proposed[20] that the permeability constant be calculated from the Knudsen (D_K) and molecular (D_m) diffusion coefficients:

$$\frac{1}{K} = \frac{\chi\delta}{\varepsilon}\left(\frac{1}{D_m} + \frac{1}{D_K}\right). \quad (8)$$

An interesting approach to the description of diffusion in porous membranes in the transitional regime has been put forward.[36] On the grounds that in the Knudsen regime the flux is proportional to the pressure difference ($J \propto \Delta p$) while in the molecular regime it is proportional to the pressure difference and the pressure ($J \propto p\Delta p$), the authors suggested that in the transitional regime the permeability constant depends on different powers of the pressure:

$$\frac{K}{\delta} = a\psi^b, \quad (9)$$

whence

$$J = a\psi^b \Delta p, \quad (10)$$

where ψ is the dimensionless pressure, a the permeability constant of the membrane, and $b = 0$ for Knudsen diffusion and 1 for molecular diffusion; the constant a, characterising the properties of the membrane, is the coefficient of the proportionality between the flux and the pressure gradient. Thus, for the description of the flux of gas to the membrane, the two empirical coefficients a and b are determined from experimental data. Both parameters depend on the type of membrane and the gas transported. The permeability constant of the membrane is calculated from the relation $a = K/\delta$.

We may note that Zolotarev and Timashev[44] suggested that the permeability constant be determined from data for membrane distillation in a special cell, the receiving component of which consists of a small cylinder immersed in a vessel with a heated solution. The permeability constant is determined from the maximum height of the distillate column (h_∞) at the given temperature in the receiving component by means of the relation

$$J = K\Delta p = K\rho_d g h, \quad (11)$$

where g is the acceleration due to gravity, and h the height of the column of liquid.

An inversely proportional relation has been obtained[36] between the quantity $K/M\bar{u}$ (where $\bar{u}$ is the average velocity of the molecules) and the mean free path of the molecules. With the aid of this relation, it is possible to determine K for different gases, including water vapour, from transport data for other gases. This is important, since the determination of the transport characteristics of the membrane for the transport of water vapour in direct experiments is impossible because of the difficulties in the correct determination of the water vapour pressure in the membrane pores and of the degree of deaeration of the membrane. The latter factor is particularly important, since the presence of different molecules in the gas phase not only diminishes the partial pressure but also alters the nature of the process.

The description of the mass transfer has been based in a series of studies[37-39,45] on the equations for the transport of water vapour through a layer of air in accordance with molecular diffusion model, whereupon the molar flux is described by the equation[37,39]

$$N = \frac{1}{p_a}\frac{\varepsilon}{\chi\delta}\frac{MDp}{RT}\Delta p, \quad (12)$$

where p is the average gas pressure in the membrane and p_a the logarithmic mean pressure of air (Schofield et al.[37] suggested that the geometrical mean pressure be employed).

Ugrozov et al.[45] introduced the parameter $Kn = D_{as}/D_{Ks}$, where D_{as} is the effective coefficient of the mutual diffusion of the vapour in air and D_{Ks} the coefficient of the Knudsen diffusion of the vapour. The parameter Kn is regarded as the effective Knudsen number in the case of a porous medium and characterises the mechanism of the mass transfer. For $Kn < 0.1$, transport is effected by molecular diffusion, for $Kn > 10$ Knudsen diffusion obtains, and for $0.1 < Kn < 10$ the mass transfer takes place in the transitional regime. The flux of the permeated material is given by the equation

$$J = \frac{D_{as}pM}{RT\delta p_a(1 + Kn_0)}(p_h - p_c), \quad (13)$$

where p_a is the atmospheric pressure and $Kn_0 = D^0_{as}/D_{Ks}$ (D^0_{as} is the effective coefficient of the mutual diffusion of the vapour in air at atmospheric pressure, which depends explicitly on Kn_0; the equation can therefore also be employed for the calculation of the flux in any mass transfer regime).

The overall resistance of the membrane in the membrane distillation process is equal to the sum of the resistance of the membrane determined by its morphology and the molecular diffusion resistance.[37] In this case, the equation for the overall mass transfer is

$$J = \left(\frac{1}{a\psi^b} + \frac{p_a}{d}\right)^{-1} \Delta p , \tag{14}$$

where

$$d = \frac{\varepsilon}{\chi\delta}\frac{MD_p}{RT} .$$

This takes into account the diffusion coefficient of the gas and the morphology of the membrane. The satisfactory correlation between the experimental results and the theoretical results, predicted on the basis of the molecular diffusion of water vapour through a layer of air,[38] indicates that the latter form of diffusion predominates in the contact molecular distillation process. The analysis carried out by Schofield et al.[37] confirmed these conclusions. Only at low air pressures (under deaeration conditions) does the transport of water vapour in the membrane pores in the transition regime, described by the first term of Eqn (14), make a significant contribution.

In contact membrane distillation, the permeability to the permeated material is proportional to the difference between the vapour pressures and the porosity of the membrane and is inversely proportional to the thickness of the membrane and the air pressure in it. For the description of the process in terms of experimentally measurable parameters, the pressure distance is replaced by the temperature difference[38-40,44] (taking into account the temperature dependence of the vapour pressure and the diffusion coefficient). This approach demonstrates the dependence of the flux on the temperature regime. The vapour pressure also depends on the solution concentration, as a result of which the membrane permeability constant depends on the latter as well[38,39]

$$K = \frac{\varepsilon M}{\chi\delta R^2}\frac{pD}{T^b}\frac{\Delta H_V T^{b-3} p_m^*}{p_a}(1 - x_m) , \tag{15}$$

where $b = 1.75$ and 2.33 (Sarti et al.[38]), p_m^* is the average water vapour pressure over the pure solvent, ΔH_V the heat of vaporisation, and x_m the molar concentration of the solution.

As a consequence of the reduced vapour pressure over the solution, the transport of water through the membrane can take place only for a temperature gradient such that the vapour pressure over the hot solution exceeds that at the condensation surface. The minimum temperature difference is calculated by means of the equation[38]

$$\Delta T_0 = \frac{hT_m^2}{\lambda_m}\frac{x_h - x_c}{1 - x_m} , \tag{16}$$

where x is the mole fraction of all the dissolved substances.

The quantity ΔT_0 is used to estimate the direction of transport of water vapour in contact membrane distillation. In order to concentrate the solutions by contact membrane distillation, it is necessary that the working temperature difference should be greater than ΔT_0. When a solution with a high osmotic pressure is present on the receiving side of the membrane (osmotic distillation), the flow of water through the membrane is possible even in the absence of a temperature gradient, i.e. $\Delta T_0 < 0$.

The transfer of water from the solution in contact membrane distillation is always smaller than the transfer from the pure solvent. It has been suggested[46] that the dependence of the flux of the permeated material on the concentration be described as a function of the decrease in the flux of the permeated material from the pure solvent:

(a) at low solution concentrations (in the range where Raoult's law is valid):

$$J = J_0 - K\alpha p_h(0, T_h)c ; \tag{17a}$$

(b) at high concentrations:

$$J = J_0 K\alpha p_h(0, T_h)c + K\beta p_h(0, T_h)c^2 . \tag{17b}$$

The interpretation of experimental data in terms of the theoretical ideas described above requires the knowledge of the concentration and temperature of the solution in the near-membrane layers in order to determine correctly the driving force of the process. It is essential to note that the parameters in the near-membrane layers differ from the bulk-phase characteristics of the solution (see the temperature and concentration profiles in Fig. 2). The increase in the concentration of the involatile solutes in the near-membrane layer on the output side of the membrane is due to the phenomenon of concentration polarisation, common to all membrane processes, which exerts a negative influence on the productivity of the membrane distillation as a consequence of the decrease in the driving force of the process, as for other membrane processes. However, the relatively weak dependence of the vapour pressure on the concentration gives rise to only a slight decrease in productivity.[44]

As can be seen from Fig. 2, the temperature of the solution in the near-membrane layers also differs from the bulk-phase value owing to heat transfer through the membrane. This phenomenon has been called temperature polarisation. Like concentration polarisation, temperature polarisation has a negative influence on the productivity of the membrane distillation process as a consequence of the decrease in the temperature of the solution (the vapour pressure) on the evaporation surface and its increase on the condensation surface.

The description of the heat transfer in membrane distillation is based on the well known thermodynamic relations. The overall thermal resistance of the membrane system is then defined by analogy with the electrical resistance.[35,37,39,40] The heat transfer in the membrane distillation process takes place in three stages: heat transfer to the evaporation surface, heat transfer through the membrane, heat transfer from the condensation surface to the bulk of the distillate.

Heat transfer to and from the membrane surface is characterised by the heat transfer coefficients

$$Q = \alpha_h \Delta T_h = \alpha_c \Delta T_c , \tag{18}$$

where Q is the heat flux per unit area of the membrane and α_h and α_c are the heat transfer coefficients in the output and receiving sections respectively.

Heat transfer through the membrane takes place with the stream of vapour and as a result of transfer through a porous membrane the pores of which are filled with a gas phase. Heat transfer through the membrane represents heat losses in the membrane distillation process and is determined by the thermal conductivity of the porous polymer–gas composite structure:[35,37-40]

$$\lambda_m = \varepsilon\lambda_a + (1-\varepsilon)\lambda_p , \tag{19}$$

where λ_a and λ_p are the thermal conductivities of the vapour–air mixture and of the polymer membrane respectively.

For heat transfer as a result of thermal conductivity, we have

$$Q_1 = \left(\frac{\lambda_m}{\delta}\right)\Delta T_m = \lambda_1 \Delta T_m , \tag{20}$$

where λ_1 is the thermal conductivity of the membrane.

The heat transfer associated with the flow of vapour through the membrane is determined by the magnitude of the flux and the heat of vaporisation:

$$Q_2 = J\Delta H_V = \lambda_2 \Delta T_m , \tag{21}$$

where λ_2 is the heat transfer coefficient related to the vapour flux.

The heat balance equation is

$$Q = Q_1 + Q_2 . \tag{22}$$

Having solved Eqn (21) for J using Eqns (18)-(20) and (22), we obtain

$$J = \frac{\lambda_2}{\Delta H_V} \frac{\lambda}{\lambda_1 + \lambda_2 + \lambda} (T_h - T_c) , \tag{23}$$

where

$$\lambda = \left(\frac{1}{\alpha_h} + \frac{1}{\alpha_c} \right)^{-1} , \tag{24}$$

$$\lambda_1 = \frac{\varepsilon k_B + (1 - \varepsilon) k_m}{\delta} . \tag{25}$$

Eqn (23) reflects the influence of the heat transfer conditions on the productivity of the membrane. When account is taken of Eqn (20), Eqn (23) can be reduced to the form

$$\frac{\Delta T_m}{T_h - T_c} = \frac{\lambda}{\lambda_1 + \lambda_2 + \lambda} . \tag{26}$$

The ratio $\Delta T_m/(T_h - T_c)$ has been called the coefficient of temperature polarisation (CTP) and reflects the fraction of the overall driving force $T_h - T_c$ which ensures the operation of the true driving force ΔT_m. In the ideal case, the CTP should be unity, which corresponds to the equality of the temperatures in the surface layers and in the bulk phase.

The level of temperature polarisation depends both on the properties of the polymer membrane (λ_1) and on the heat transfer regime in the liquid flow (α_h, α_c). From the standpoint of the heat transfer through the membrane, an increase in the thickness of the latter tends to decrease the level of temperature polarisation. However, this entails an increase in the diffusion path for the water vapour. Hence, in order to attain the maximum productivity of the membrane distillation process, optimisation with respect to the thickness of the membrane is needed, as already stated.

The estimates carried out in a number of studies[35, 37, 47, 48] indicate that temperature polarisation is influenced mainly by the heat transfer conditions in the liquid streams, which are determined by the hydrodynamic conditions governing the flow of liquids within the channels of the membrane module. The level of temperature polarisation decreases with increase in the degree of turbulence of the streams within the channels.

The heat transfer in liquid streams depends on the orientation of the membrane and the Earth's gravitational field. The best conditions for heat transfer are achieved when the direction of natural convection coincides with the direction of heat transfer. Natural convection then influences the stability (thickness) of the near-membrane layer, which increases if the direction of natural convection coincides with the concentration profile and the temperature polarisation.[49] It has been confirmed experimentally[27, 38] that, for a horizontal disposition of the membrane and of the hot chamber (the hot chamber is located below), the maximum productivity of membrane distillation is attained.

The extremely high retention coefficients of involatile substances in the membrane distillation process were noted above. However, in practice the retention of involatile substances nevertheless does not attain 100%, which makes it necessary to take into account this fact in theoretical analysis. Thus the level of concentration polarisation in membrane distillation is estimated taking into account the incomplete retention of the solute.[34] The following expression has been obtained[34]:

$$\frac{c^0}{c} = (1 - \varphi) + \varphi \exp\left(\frac{Jl}{D} \right) , \tag{27}$$

where c and c^0 are the concentrations of the solution being separated on the surface of the membrane and in its bulk respectively. φ is the retention coefficient, l is the thickness of the near-membrane layer, and D is the diffusion coefficient.

According to Eqn (27), in order to minimise concentration polarisation it is desirable to maintain the flux at the level of l/D.

It has been suggested that the diffusion model of the selectivity of the established membrane distillation process be used for the description of the retention in the membrane distillation process on the basis of the hypothesis that a hydrophobic microporous membrane contains both hydrophobic and hydrophilic pores.[50, 51] The 'breakthrough' of the volatile solutes in membrane distillation is possible owing to their diffusion via the solution-filled hydrophilic pores. It is assumed that the hydrophilic pores have a smaller diameter than the hydrophobic ones. In our view the possibility of a decrease in selectivity as a consequence of the wetting of the largest pores owing to the pressure drop is less probable. Since the pores in membranes have submicron dimensions, even slight pressure drops lead to a significant convective flow of the solution. As a result, the retention coefficients should be lower than the experimental values and should depend on the concentration of the initial solution, which is not observed in practice.

Thus the relative hydrophilic porosity is the parameter of the nonideality of the membrane:[50]

$$\varepsilon_f = \frac{m_f}{m_0} = 1 - \frac{m}{m_0} , \tag{28}$$

where m_0 is the fraction of the membrane surface corresponding to all the pores, both hydrophobic (m) and hydrophilic (m_f) ($m_0 = m + m_f$).

According to the analysis carried out by Starikov,[50] the retention coefficient is a function of the nonideality of the membrane and of the hydrodynamic parameters of the system:

$$\varphi = \left[1 + \frac{m_1 D}{J\delta} \exp\left(\frac{Jl}{D} \right) \right]^{-1} . \tag{29}$$

In the presence of hydrophilic pores and a nonstirred near-membrane layer, the selectivity of the flux of permeated material passes through a maximum at $J = D/l$. We then have

$$\varphi_{max} = \frac{\delta}{\delta + l m_f e} . \tag{30}$$

Calculations have shown that the retention coefficient increases with increase in the flux and with decrease in the thickness of the unstirred layer.[50] Similar dependences of the selectivity are characteristic also of a multilayer membrane consisting of a hydrophobic microporous membrane with a thin hydrophilic surface layer.[51, 52]

The selectivity coefficient in membrane distillation for systems containing more than one volatile component is determined by the vapour–liquid equilibrium, which the membrane hardly affects. The description of the mass transfer, including the selectivity parameters, is hardly discussed in the relevant communication, as is the description of transvaporisation processes.[53]

V. Experimental studies on membrane distillation

The results of theoretical studies on heat and mass transfer in the membrane distillation process can serve as a basis for the treatment of experimental data and a satisfactory prediction of the possibilities of membrane distillation.

In the initial stage of the development of studies on membrane distillation, attempts were made to reconcile the experimental data obtained with the mathematical description of heat and mass transfer.[10, 12, 19, 54-64] The attempt to elucidate the influence of all factors on the principal process characteristics

was self-evident and entirely comprehensible.[10,12,15,54-61] Thus membrane distillation on microporous hydrophobic [polypropylene, poly(vinylidene fluoride), polytetrafluoroethylene], planar, and hollow-fibre membranes was investigated with the aid of model aqueous solutions of sodium chloride, glucose, or sucrose. Such studies[10,12,54-58,62-64] showed that the most important factors influencing the productivity with respect to the permeated material are the temperature, the temperature drop (vapour pressure drop) on either side of the membrane, the pore size, the overall porosity and thickness of the membrane, and the concentration of the initial solution. It was established that, for a constant temperature drop, the productivity of the membrane distillation process increases with increasing concentration of the initial solution and, when the latter is constant, the productivity increases with increase in the temperature drop (Fig. 4).

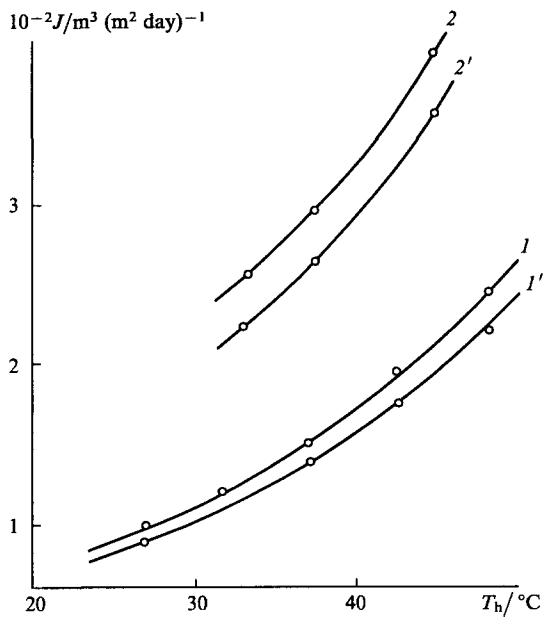


Figure 4. Dependence of the flux of the permeated material on the temperature of the hot sodium chloride solution.[64] ΔT/°C: (*1*) and (*1'*) 5.0; (*2*) and (*2'*) 9.5; c_{NaCl}/mol litre^{-1}: (*1*) and (*2*) 0.05; (*1'*) and (*2'*) 0.50.

Later investigations confirmed the general characteristics of the membrane distillation process and its dependence on the principal factors indicated above. At the same time, in these studies more continuous attention was devoted to individual factors influencing the process. Furthermore, whereas a distinct applied trend could be traced in the early studies (they dealt as a rule with simplified models of the process), in later investigations attempts were made to develop the theoretical foundations of membrane distillation with the aid of new revised experimental data (in particular, account was taken of heat exchange and of the nature and velocities of the fluxes in membrane cells, the temperature and concentration polarisations, etc.).[46,65-72]

The membrane distillation of solutions of sodium chloride and glucose at very high concentrations of the latter (up to 5 and 50 g litre^{-1} respectively) has been investigated in detail.[46] Analysis of the dependence of the productivity on concentration was based on the approximate Raoult's law, according to which the vapour pressure of the solvent was defined by the expression

$$p(c, T) \approx p(0, T)(1-\alpha c), \quad (31)$$

where $p(0, T)$ is the vapour pressure of the solvent at $c = 0$ for dilute solutions and c is the concentration of the solute. The coefficient α is then always positive.

On the other hand, at fairly high concentrations of the solution, a nonlinear dependence of the partial pressure of the solvent on concentration is observed:

$$p(c, T) \approx p(0, T)(1-\alpha c+\beta c^2). \quad (32)$$

The coefficient β can be both positive and negative. This corresponds to a positive or negative deviation from Raoult's law, which occurs at high solution concentrations.

It has been established[46] for a wide range of solution concentrations that there is a linear dependence of the flux of permeated material on the concentration [see Eqn (17b)]. It is important to note that the concentration of the substance not in the bulk phase but at the interface of the membrane, which is higher than the bulk phase concentration, should be employed in Eqns (17a), (17b), and (32).[41] The decrease in productivity with respect to permeated material with increasing solute concentration should be less appreciable, according to Eqn (32), if $\beta > 0$ and should be more applicable if $\beta < 0$.

Experimental studies on the membrane distillation of concentrated sodium chloride and glucose solutions confirmed satisfactorily the theoretical considerations described above (Figs 5*a* and 5*b*): at low solute concentrations, the relation $J = f(c)$ is linear, while at higher concentrations it is nonlinear. These effects are associated not only with deviations from Raoult's law but to a considerable extent also with the manifestation of concentration and temperature polarisations, which has been confirmed by experiments designed to investigate the $J = f(c)$ relation with and without stirring of the solution being separated (see curves *1* and *2* in Figs 5*a* and 5*b*).

A more rigorous study of the dependence of the productivity of the membrane distillation process on temperature and on the temperature difference on either side of the membrane confirmed[38,45,73,74] that the specific productivity of the contact membrane distillation process increases with increasing temperature difference for a fixed temperature T_x and also with increase in the average bulk-phase temperature. It has been shown that intensification of the stirring of the solution makes it possible to increase significantly (by a factor greater than 2) the productivity of the contact membrane distillation process, which is associated with the partial elimination of temperature and concentration polarisations.[34,38,45,46,69-75]

The influence of temperature and concentration polarisations on the functional characteristics of the membranes and on the membrane distillation process is always negative. A partial elimination of such polarisations can be achieved by altering the velocity and nature of the solution and permeated material fluxes at the output and receiving surfaces of the membrane.[72] The procedure in which the flow of the solution to be separated was rendered turbulent proved to be extremely effective, lowering the negative influence of concentration and temperature polarisations and intensifying the membrane distillation process, especially in flat chamber apparatus. The flow of the solution was rendered turbulent by stirring, and with the aid of pressure channels in apparatus and turbulators of different design. The movement of the membrane element relative to the solution being separated (when the membranes are arranged on rotating discs), as well as vibration and ultrasound, can be used.[72]

Analysis of experimental data on the effect of turbulent flow on the specific productivity of membranes showed[72] that, for $Re > 1500-2000$, an increase in the flux through the membrane is not observed. Here one should note that the procedure in which the flow solution is rendered turbulent is more effective than the one in which the flow of the permeated material is made turbulent.

The dependence of the separating characteristics of microfiltration membranes in the membrane distillation process on the average pore diameter has been noted.[75] This has been explained by the influence on the mass transfer by the predominant Knudsen or molecular mechanism of the diffusion of vapour through pores having different diameters and lengths. In real membranes with a

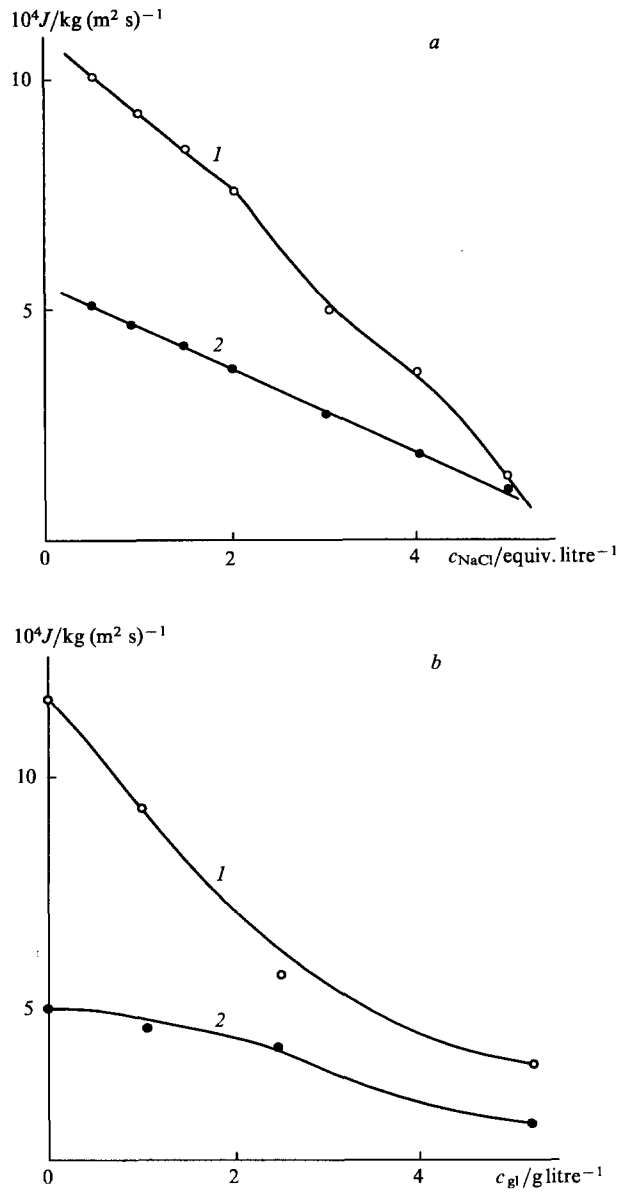


Figure 5. Dependence of the productivity of the contact membrane distillation process on the concentrations of NaCl (*a*) and glucose (*b*) in the solution:[73] (*1*) with stirring (600 rev min^{-1}); (*2*) without stirring (temperature of the hot solution 70 °C, temperature of the distillate 30 °C).

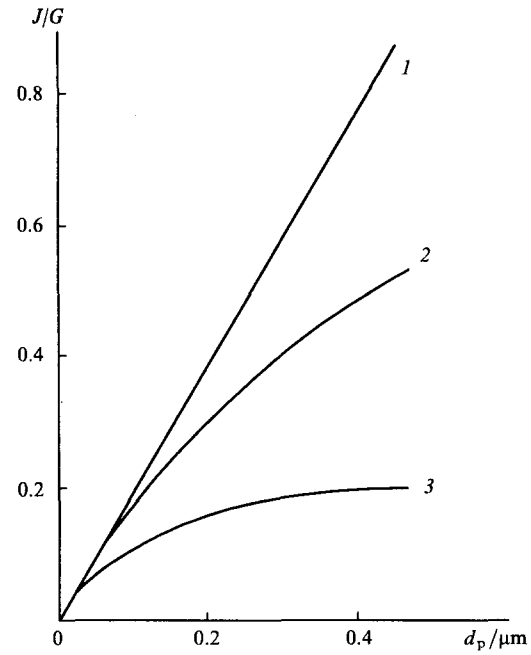


Figure 6. Dependence of the flux in the membrane distillation process on the pore size at different partial pressures of air (kPa): (*1*) 0; (*2*) 20; (*3*) 80.[72]

complex porous structure, a combined mass transfer takes place, i.e. with different contributions by both mechanisms, which has in fact been demonstrated experimentally and theoretically in a number of investigations.[37,45,72] Here one should take into account the fact that the presence or absence of an air layer in the membrane pores affects the mass transfer. The air in the membrane pores prevents the diffusion of water vapour and diminishes its flux through the membrane. Indeed, Fig. 6 shows that the dependences of the specific productivity of the membrane on the pore size are different for different partial pressures of air in the pores. For small pores, where the transfer is effected predominantly via Knudsen diffusion, the removal of air promotes only slightly an increase in the flux, whereas for membranes with a large pore diameter the flux to the membrane can be increased by 50% by deaeration.[72]

It has been noted that deaeration diminishes the heat transfer through the membrane by 10%–25%.[37,72] However, the hydrodynamic conditions, the pore structure, and the thickness of the thermophysical properties of the membranes are most important for the reduction of the influence of temperature polarisation on the intensity of the membrane distillation process.

The characteristics of the heat and mass transfer through PTFE membranes in the membrane distillation process have been determined experimentally with the aid of the $H_2SO_4-H_2O$, $HCl-H_2O$, NH_3-H_2O,[75] $NaCl-H_2O$,[55,56,75] and $C_2H_5OH-H_2O$ [53,69] systems at different temperatures and for different flow rates of the solution and the permeated material. It was established that the extents of heat and mass transfer are proportional to the temperature difference on either side of the membrane and depend on the porosity and thickness of the latter.[53,75,76] Expressions based on the material and heat balance equations for determining the flux of transferred substance have been obtained with the aid of mathematical modelling of the membrane distillation process. It is believed[75,76] that the calculated data agree well with the experimental results and that the membrane distillation process can be used to concentrate solutions such as juices, milk, sugar syrup, [aqueous] alcohol, etc.

Among the factors influencing the intensity of the membrane distillation, the hydrophobicity (wettability) of the membrane surfaces by the substances being separated has been considered in some investigations (see, for example, Yoshishige and co-workers[77,78]). The special importance of this factor is manifested for systems the concentraion of which leads to an appreciable decrease in surface tension (surfactants, alcohols, and certain water-soluble organic compounds).[28,29,77,78] Special procedures (modification of the membrane surfaces by more hydrophobic polymers or substances, a change in the size of the pores in the selective hydrophobic layer, etc.) make it possible to employ membrane distillation for the concentration of, for example, dilute solutions of alcohol. In such cases, it is possible to employ only membrane distillation through a gas (vapour) layer or vacuum membrane distillation.[15,17,19,53] The deposition of a layer of silicone rubber or poly-(1-trimethylsilyl-1-propylene) on the surface of microporous poly(vinylidene fluoride) membrane lowers the permeability to water and increases the selectivity of the membrane with respect to ethanol, acetone, acrylonitrile, and 1-butanol dissolved in water.[77,78] Not only the hydrophobicity of the membrane but also is asymmetry, the mechanism of the

sorption-desorption of the substances being separated, and also the changes in temperature gradient associated with the asymmetry and chemical composition of the membrane layers play a significant role in this process.

Studies of the membrane distillation process on different aqueous systems demonstrated the practical importance of this separation method and its advantages compared with other procedures, primarily the baromembrane methods. These advantages are associated with the possibility of separating concentrated and highly concentrated solutions, which as a rule do not require a complex preliminary purification.

VI. Modules and apparatus for membrane distillation

Membrane modules with all the existing configurations of membranes — flat, hollow fibre, and tubular — are employed for the membrane distillation process.

In contrast to baromembrane elements, two enforced flows are established within the channels of the membrane distillation modules (MDM) — the flow of the concentrate and the flow of the distillate (in the case of contact membrane distillation) or a gas (in the case of membrane distillation with a flow of gas). Furthermore, a cooling agent channel, separated from the gas space by the impermeable condensation surface, is essential for membrane distillation with a gas space.

The effectiveness of membrane distillation and other membrane processes is determined by the properties of the membranes and the design of the module. The principal parameter in the optimisation of the design of the MDM is the level of temperature polarisation. It was noted above that heat transfers in liquid streams exert an appreciable influence on such polarisation. The heat transfers are determined by the hydrodynamics of the flow of liquids within the channels of the membrane module, which depends on the design characteristics of the latter. The level of temperature polarisation can be estimated on the basis of the Nusselt number.[35,75]

From the standpoint of heat transfer, the most successful configuration is that of hollow-fibre membranes for which, at an internal diameter of 0.3 mm, a coefficient of temperature polarisation of 0.8 is already attained for $Re = 300$ (Table 2). However, with increase in the internal diameter to 1 mm, the attainment of CTP = 0.85 requires $Re = 3000$. For flat channels, the CTP increases with decrease in the thickness of the channel. Modules which are effective from the standpoint of the decrease in the level of temperature polarisation can be created on the basis of both hollow fibres and flat membranes (Table 2). This is indicated by the present state of development of the equipment for membrane distillation processes.

Spiral membrane distillation modules were proposed as early as 1982,[79] but we have been unable to find experimental data on the membrane distillation process carried out on MDM of this type. In our view, the lack of such data cannot be regarded as evidence that modules of the spiral type are unlikely to be useful. In such modules, it is entirely possible to create sufficiently narrow channels and to ensure enforced flows in the latter. Furthermore, the presence of spiral heat exchangers ensures effective heat exchange in MDM of this kind.

The Swedish cassette elements should probably be regarded as the first flat-frame MDM.[3,80,81] They consist of plastic plates with an internal channel for the stream of heated initial water in contact with two membranes. The working area of the membrane surface is 0.3 m^2. The membrane in the cassette is fitted on a porous base, which protects it from damage during the assembly of the module. The module is assembled from cassettes of the filter-press type. This entails the formation of a condensation channel (a gas space with a condensation surface) and a cooling water channel as a result of the employment of additional plates. This apparatus was created for membrane distillations through a gas layer or at a reduced pressure.

Unfortunately, apart from the above studies,[3,80,81] there have been no publications describing adequately the design of a flat-frame MDM. There is in fact no information whatever about the working parameters of the module, the hydrodynamic regime, the principles governing the organisation of the streams, etc.

Somewhat later, the membrane distillation process began to be carried out on hollow-fibre elements.[82–85] A hydrodynamic regime within the capillaries favourable for heat transfer is characteristic of MDM of this type.[37] However, it is fairly difficult to ensure effective heat and mass exchange on the outer side of the capillaries when a large number of bunches of capillaries are present.[75] It is important that stagnant zones should not form on the outer surface of the fibres.

Studies have been made on the hollow-fibre MDM with three types of packing of the capillaries:[75] parallel fibres, bunches of twisted fibres, and bunches of intertwined fibres. The packing comprising parallel fibres is made from a fabric material in which transverse filaments serve for the fixation of the hollow-fibres in the parallel direction. Such fabrics are rolled up and the rolls are packed in a jacket. The highest productivity has been observed for bunches of twisted and intertwined fibres. The highest packing density of the fibres, reaching 40% – 50%, occurs in the latter type of MDM. Bunches of intertwined and twisted fibres act as devices causing a turbulent flow within the shell of the hollow fibre MDM. Overall, the hydrodynamic regime established in the hollow-fibre MDM ensures the maximum productivity even for the laminar flow of liquids ($Re \approx 450$).[84]

Table 2. *Temperature polarisation for different membrane distillation systems.*[35]

Geometry of membrane	Characteristics of flow	*Nu*	Hydraulic diameter of channel/mm	Heat transfer coefficient/W(m² K)⁻¹	CTP[a]
Internal diameter/mm					
1	$Re = 5000$	29	1.0	19 000	0.90
	$Re = 3000$	20	1.0	13 000	0.85
	$Re = 1000$	4.4	1.0	2900	0.54
0.3	$Re = 300$	4.4	0.3	9700	0.80
External diameter 0.6 mm	nearly laminar regime	~5	0.9	3700	0.60
Channel 0.5 m long	flow rate 2 m s⁻¹	970	500	1300	0.51
Channel thickness/mm					
2	laminar regime	5.4	8	450	0.15
0.5	"	5.4	2	1800	0.4
0.1	"	5.4	0.4	8900	0.7

[a] CTP on one side of the membrane.

Table 3. Membrane distillation on a hollow fibre pilot module.[82]

Temperature/ °C				Flow rate/m min^{-1}		Flux/kg $(m^2\ h)^{-1}$	Heat transfer coefficient $10^{-7}K/W\,(m^2\ K)^{-1}$	Permeability constant/ kg $(m^2\ s\ Pa)^{-1}$
solution		distillate		solution	distillate			
inlet	outlet	inlet	outlet					
52.0	36.9	32.9	48.1	2.44	2.43	2.1	3280	3.31
55.0	33.5	26.5	48.2	2.94	2.93	3.5	3260	3.39
60.2	32.0	24.4	53.1	2.46	2.43	4.1	3140	3.44
65.0	29.3	21.8	59.1	1.70	1.63	3.7	2620	3.15
69.0	41.6	35.2	63.4	2.44	2.38	5.1	3090	3.44
70.7	38.7	32.4	66.3	2.83	1.73	4.6	2870	3.51

Note. The module consists of 2000 polypropylene fibres with internal and external diameters of 300 and 600 μm respectively and with a length of 400 mm. The area of the membranes is 1 m^2.

The flow of liquid media in hollow-fibre MDM is organised on the basis of the countercurrent principle. The temperatures at the inlet to and outlet from the module are then different. As can be seen from Table 3, the temperature differences are significant even for relatively short fibres (with a length of 400 mm). This leads to differences between the average temperatures in different sections of the fibre, i.e. the mass transfer conditions vary as a function of the length of the fibre. The differences between the inlet and outlet temperatures increase with the increasing length of the fibres and with decrease in the flow rate. Tests have been made hitherto on hollow-fibre MDM with fibre lengths up to 2 m and an internal diameter of the jacket of 250 mm. The area of the membrane for such MDM varies from 50 to 100 m^2.[84]

It is noteworthy that the differences between the mass transfer conditions for different sections of the membranes are equally characteristic of MDM of any configuration, but in the literature this problem has been discussed explicitly only in relation to the hollow-fibre MDM. It must be emphasised that the length of the membrane channel in the MDM is an important design feature, which requires optimisation both in the construction of modules and in the development of apparatus and technology.

In our view, the use for membrane distillation of the tubular modules with a low packing density of the membranes, which are as a rule very thick, is justified only in individual instances. Tubular MDM can probably be used to concentrate viscous solutions, characterised by impairment of heat transfer. Tubular MDM can ensure a satisfactory hydrodynamic regime in the flow of viscous liquids, particularly within the tubes.

Hitherto the available information about tubular MDM is limited. They are used predominantly for the desalination of water or for the concentration of aqueous solutions of low-molecular-mass substances.

A Japanese patent application[86] describes an unusual design of a tubular MDM. In this device, the evaporation system is separated from the condensation system, i.e. this is an apparatus for membrane distillation processes with a gas space. The evaporation and condensation systems consist of parallel tubes for the supply and removal of liquid media connected by a multiplicity of tubes in the condensation system or via tubular membranes in the evaporation system. A heated concentrated solution is supplied to the evaporation system, while a cooling liquid is supplied to the condensation system. The vapour which has passed through the tubular membranes condenses on the surfaces of metallic tubes of the condensation system and the distillate flows spontaneously into the collector.

Cartridge filters with a folded configuration of flat membranes have come to be fairly widely used to microfiltration processes. Cartridge elements based on polytetrafluoroethylene membranes with areas of 0.3 and 0.15 m^2 have been tested for membrane distillation.[87,88]

Apparatus for membrane distillation is, as a rule, of the circulation type, which ensures an increase in the degree of concentration and a more rational use of heat as a result of the decreased heat consumption in raising to its working temperature the solution being concentrated.

Depending on the heat transfer conditions and the length of the membrane channel of the MDM, the temperatures of the streams at the inlets and outlets differ to such an extent that the outlet temperature of the distillate may be higher than the inlet temperature of the solution being concentrated. In this case, it is possible to use part of the heat of the distillate to heat the solution undergoing concentration (Fig. 7*a*). However, in apparatus with heat recovery, the temperature difference between the two sides of the membranes, i.e. the specific productivity of the process, is small and this is why membranes with a high surface area are used in them.

In a number of cases, the problem of heat recovery is not formulated, for example if the membrane distillation is used to obtain water for boilers. In apparatus of this type (Fig. 7*b*), it is endeavoured to attain large temperature differences. Therefore the attainable specific selectivity of apparatus without recovery is higher, which lowers the capital expenditure and the expenditure on membranes.

From the standpoint of energy expenditure, the membrane distillation process is characterised by the energy efficiency parameter E, which is defined as the ratio of the part of the heat consumed on vaporisation to the overall heat introduced into the apparatus:[17,41]

$$E = \frac{JS\Delta H_V}{Fc_p(T_{in} - T_{out})}, \tag{33}$$

where S is the area of the membrane and F the flow rate of the initial solution with a heat capacity c_p and the temperatures T_{in} and T_{out} at the inlet to and outlet from the MDM.

As a consequence of the heat losses, E is always less than unity. The cost of the water purified by the membrane distillation method diminishes with increase in the temperature of the initial solution.[82]

The component which is always present in apparatus for membrane distillation processes is heat exchange equipment needed to heat the initial water to the working temperature and then maintain this during the membrane distillation process, and additionally for the utilisation of the heat from the distillate. Problems of heat exchange (outside the MDM) and of energy supply (source of energy) have scarcely been considered in studies on membrane distillation. In practice, these problems are solved by traditional engineering procedures.[85]

In discussing the economics of membrane distillation, Hanbury and Hodgkiess[89] noted that the process does not withstand competition when it is carried out on expensive tetrafluoroethylene membranes. This problem may be solved by employing polyalkene membranes or membranes made from chlorinated polyalkenes. The conclusion that Teflon membranes

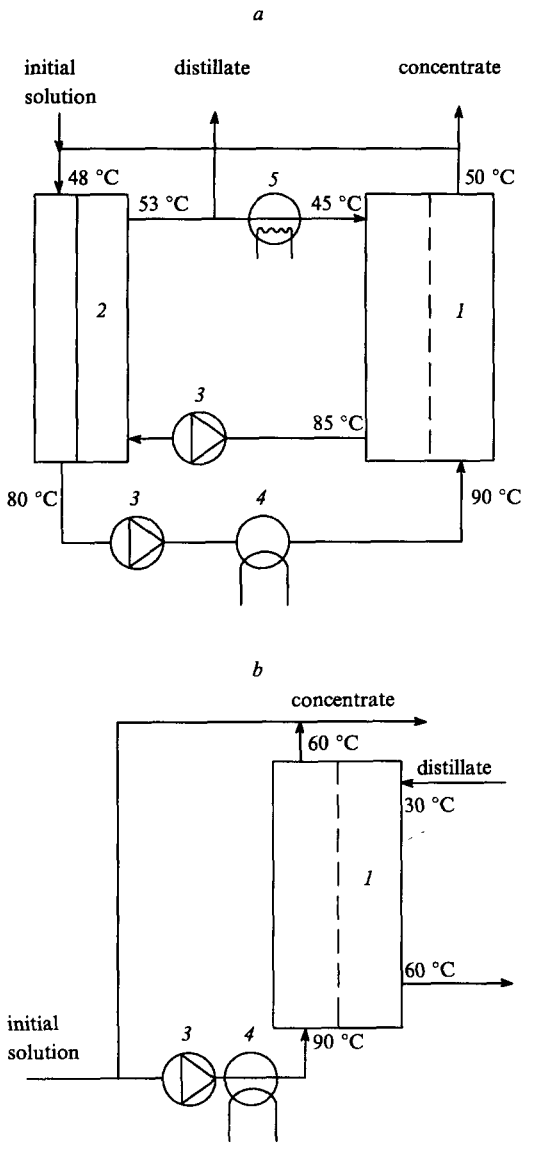


Figure 7. Schematic illustration of apparatus for membrane distillation with (*a*) and without (*b*) recovery of heat:[84] (*1*) membrane distillation module (MDM); (*2*) heat exchanger; (*3*) pump; (*4*) heater; (*5*) cooling unit.

are not competitive is not incontrovertible, bearing in mind the possible extended use of such membranes in membrane distillation.

According to the estimate of Fane et al.,[82] the expenditure on the operation of membrane distillation apparatus with a moderate power (5000 kg h^{-1}) is comparable to the expenditure on the operation of similar apparatus based on reverse osmosis. For less powerful apparatus, the expenditure is higher compared with the reverse osmotic apparatus. However, an advantage of membrane distillation is that it requires a less thorough preliminary purification of water.

VII. Applications of membrane distillation

The experimental data described above (see Section V) outline the range of technological processes in which membrane distillation may be employed. However, at the present time one is dealing only with the potential possibilities of the process. Despite the almost ten year history of the development of the equipment for membrane distillation, there are in fact no literature data on its long-term tests. The longest tests concern the treatment of artesian well water over a period of 18 weeks,[84] which indicate the stable operation of the apparatus.

It is possible to differentiate the following principal applications of membrane distillation: the preparation of pure water; the concentration of solutions of involatile substances; the purification of waste water; the isolation of volatile components from solutions containing also involatile substances; the separation of dilute water–organic liquid mixtures. Such subdivision is to some extent arbitrary. For example, the concentration of solutions of involatile substances leads to the simultaneous formation of pure water, whereas purification of waste water may involve the concentration of contaminating involatile substances, etc.

Preparation of pure water. When any aqueous solutions containing involatile substances are treated, highly pure water is obtained as the permeated material. Thus it has been shown[75] that the electrical conductivity of the distillate obtained on treating aqueous solutions of NaCl, H_2SO_4, and NaOH does not exceed 5 μS cm^{-1}. In the first place, membrane distillation is used[38,62,63,81] to obtain pure water from sea water and artesian well water.[84] The high quality of the water, which is almost independent of the concentration of the feed solution, has been noted. For example, when the electrical conductivity of artesian well water varied from 350 to 35000 μS cm^{-1}, the quality of the filtrate remained stable.[84] In carrying out the process, provision was made for only preliminary elimination of mechanical impurities. The long term operation is generally accompanied by a decrease in productivity as a function of time as a consequence of the contamination of the membranes. The recovery of the productivity in the treatment of artesian well water is achieved by washing the membranes with hydrochloric acid solution.[84] It is essential to note that, owing to the lack of results of long-term tests, the problems of the contamination and purification of membranes have been hardly described in the literature.

The use of membrane distillation for the final treatment of water in order to obtain sterile apyrogenic water is of interest.[87,88] It has been established that the content of endotoxins in the distillate obtained by membrane distillation is less than 1.0 ng $litre^{-1}$ when their content in the initial water is 11.3 ng $litre^{-1}$. Water of this quality is characterised as apyrogenic. Bacteria were not detected in the distillate. Membrane distillation ensures better elimination of particles than the usual distillation particularly the elimination of particles the size of which is less than 1 μm. The content of low-molecular-mass organic impurities, for example carbon, in water falls from 417 μg (on treatment of deionised water) to 280–290 μg per litre. The proposed apparatus with polytetrafluoroethylene membranes having a folded configuration (with areas of 0.30 and 0.15 m^2) makes it possible to obtain 20 kg of apyrogenic water per hour. Tests carried out over a period of 1000 h demonstrated the stability of the apparatus both as regards productivity and the quality of water.

Concentration of solutions of involatile substances. Membrane distillation is a promising method for the concentration of aqueous solutions of involatile substances. The possible concentration limits of the membrane distillation process greatly exceed those when reverse osmosis is used.

The membrane distillation method can be employed to concentrate aqueous solutions of sugars.[64,75] When a solution of glucose is concentrated, a sharp decrease in productivity is observed at a concentration in excess of 25 g $litre^{-1}$,[75] which is probably due to an increase in the viscosity of the solution, impairing the heat exchange conditions, and not to a decrease in the vapour pressure over the solution. In the treatment of viscous solutions, it is necessary to intensify the turbulence of the stream or to carry out the process at higher temperatures. Thus concentration of a sugar syrup at 86 °C is characterised by a productivity with respect to the distillate of 20–28 kg $(m^2\ h)^{-1}$ in the syrup concentration range from 10% to 40%.

The problem of the impairment of heat transfer as a consequence of the increase in concentration arises also when solutions of high-molecular-mass oligomeric substances are concentrated. For example, a fairly sharp decrease in productivity has been observed when a solution of gelatine was concentrated.[75] At the same time, one should note that the vapour pressures over solutions of high-molecular-mass compounds depend only slightly on the mass concentration of the polymer (owing to the low molar concentration of the solutions). As a result of this, water-soluble polymers may be concentrated in the presence of effective heat and mass exchange in the MDM channels, for example in a tubular MDM. We may note the high stability of the productivity in the concentration of oligomeric substances (Fig. 8), characterised by a low viscosity.

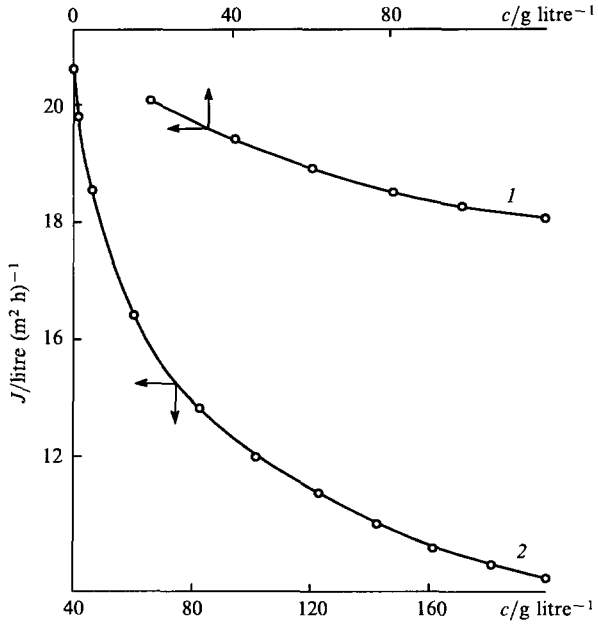


Figure 8. Dependence of the productivity of the membrane distillation process with respect to the permeated material on the solute concentration during the concentration of a solution of poly(ethylene glycol) with a molecular mass of 6000 (curve *1*) and waste water from a coke-chemical factory (curve *2*).

The problem of concentrating liquid products containing high-molecular-mass components frequently arises in the food industry. Thus it has been shown that membrane distillation is more effective in the concentration of mandarin juice as compared with reverse osmosis.[75] Membrane distillation makes it possible to attain threefold concentration with a gradual decrease in productivity as the degree of concentration rises from 10 to 7 kg $(m^2\ h)^{-1}$. On the other hand, reverse osmosis is characterised by a sharp decrease in productivity: after concentration by a factor of only 1.5, the productivity is 5 kg $(m^2\ h)^{-1}$. We may note that the treatment of mandarin juice by membrane distillation was carried out at 48 °C, i.e. under fairly mild conditions, which makes it possible to preserve the properties of the thermolabile components of the juice.

Even milder treatment conditions are attained is osmotic distillation, where the vapour pressure in the receiving part of the MDM is reduced as a result of the employment of solutions with a high osmotic pressure. Thus the concentration of orange, apple, and grapefruit juices at a temperature of 29 °C (40 °C in individual experiments) with the aid of a flat-frame module having a membrane area of 0.7 m^2 (a 28% solution of an inorganic electrolyte was passed through the receiving channels) has been described.[22] As in the case of contact membrane distillation, the productivity of osmotic membrane distillation depends on the hydrodynamic conditions in the flow within the capillaries of the apparatus; the absolute productivity did not exceed 2.5 litre $(m^2\ h)^{-1}$ as a consequence of the small temperature difference. The juices were concentrated until the attainment of a 50% content of the solutes.

Overall, the likely usefulness of membrane distillation for the concentration of solutions of thermolabile substances must be specially emphasised.[61] Studies on mass transfer in the concentration of solutions of vitamins C and B_1 by the contact membrane distillation method in the temperature range 50–60 °C showed that it is possible to obtain supersaturated (at room temperature) solutions of the vitamins: 50%–55% for vitamin C (the concentration of the saturated solution at 20 °C is 25.3 mass%) and 60%–65% for vitamin B_1 (the concentration of the saturated solution at 20 °C is 50 mass%). After cooling, the concentrated solutions of the vitamins and their crystallisation, the deposited vitamin may be separated and the solution can be again concentrated with the aid of membrane distillation. After the attainment of the concentrations indicated, the productivity of the contact membrane distillation is 6–8 litre $(m^2\ h)^{-1}$. It has decreased compared with the initial value by a factor of not more than 2–3.

The formation of supersaturated solutions in the membrane distillation process is not exceptional.[90,91] Thus membrane distillation has been suggested for the isolation of lanthanum compounds from a sulfuric acid extract of phosphogypsum.[91] The extract obtained on treatment of phosphogypsum contains 16% of sulfuric acid, 1.6% of Ln_2O_3, and 3.5% of CaO as the main components. The concentration of such an extract by membrane distillation was from 16% to 44% in terms of sulfuric acid, with a productivity of 215 and 80 litre $(m^2\ day)^{-1}$ at an extract temperature of 60 °C. After cooling the concentrate, a deposit containing up to 25% of lanthanum compounds was isolated. The formation of $CaSO_4$ crystals on the membrane surface has been observed when the process is carried out by a periodic procedure, this being a consequence of crystallisation from supersaturated solutions remaining on the membrane surface.

Purification of waste water. Water of very high quality is obtained in the purification of waste water by membrane distillation, whereas the concentrate may contain valuable components or even the target product of the manufacturing process at a high concentration up to supersaturated solutions. Thus the concentration of water from the manufacture of taurine (2-aminoethanesulfonic acid), containing taurine and sodium chloride, is accompanied by the crystallisation of taurine.[91] The deposit segregated contains up to 60% of taurine and impurities (sodium chloride). The product may be purified by recrystallisation.

Membrane distillation may become the principal procedure for the creation of closed water supply systems. Laboratory studies on systems for the recovery of water under conditions of space stations have been reported.[92]

Membrane distillation is perhaps the only alternative to vaporisation processes in the treatment of highly concentrated waste waters, including those from undertakings in different branches of industry. Experiments have been carried out on the purification of waste waters from the textile industries containing dyes.[41] It has been noted that membrane distillation can be best employed to concentrate further already concentrated waste water and it is therefore recommended that, in the purification of waste waters from textile undertakings, preliminary concentration by reverse osmosis be carried out with subsequent treatment of the concentrate by membrane distillation.[41]

The possibility of a high degree of concentration of aqueous salt solutions, in particular solutions of heavy metal salts, has been investigated.[93] The authors employed membrane distillation through a gas layer. In the concentration of nickel salts, a weak variation of the productivity with respect to permeated material

was noted. The productivity reached 25–30 litre $(m^2\ h)^{-1}$. The high quality of the permeated material was noted, which makes it possible to employ membrane distillation in combined schemes for the purification of wash waters and for the processing of spent solutions from the electroplating industry.

In the purification of waste waters from processing plants in the food industry, it is possible to obtain concentrated solutions of valuable food components. Thus treatment of whey by membrane distillation made it possible to obtain a concentrate containing 300 g $litre^{-1}$ of lactose for a process productivity with respect to the distillate of 0.43 m^3 $(m^2\ day)^{-1}$.[94]

As a rule, waste waters are complex multicomponent mixtures. Thus the waste water from the coke-chemical industry (water from the gas collector) contains up to 40 g $litre^{-1}$ of ammonium chloride, inorganic electrolytes, and various organic substances (phenols, pyridines, etc.). Such water is highly corrosive, especially at high temperatures, which makes problematical the employment of evaporation processes to be carried out at the critical temperatures.

Waste waters may be concentrated by membrane distillation up to a content of inorganic electrolytes of 200–250 g $litre^{-1}$ (Fig. 8). It is noteworthy that the waste waters from the coke-chemical industry contain volatile organic impurities, which also permeate through the membrane. After the treatment of such waste waters by membrane distillation, the permeate therefore contains volatile organic impurities (phenols, pyridine). These impurities can be made harmless by biological methods. The vital activity of the corresponding microorganisms is suppressed in the biological treatment of highly mineralised waste waters.

Isolation of volatile components from solutions of involatile substances. The example involving the concentration of waste waters partly demonstrates the possibility of using membrane distillation for the isolation of volatile components from solutions of involatile substances. For example, phenols can be removed from a concentrate of inorganic salts. However, so far there are no literature data on the deliberate technological employment of this approach. A system which makes it possible to isolate volatile substances from aqueous solutions by membrane distillation, before their analysis, has been described.[95] In this scheme, specimens with a volume not exceeding 6 ml are introduced into plastic tubes, their contents are boiled, and the vapour passes through a hydrophobic membrane and is then condensed. The method allows 100% isolation of substances in less than 60 min. It has been tested in experiments with cyanides, cyanide complexes, sulfides, phenol, and ammonia.[96]

Separation of water–organic solvent mixtures. The use of membrane distillation for the separation of water–organic solvent mixtures is an alternative to the transvaporisation and fractional distillation methods in the treatment of mixtures with a low content of the organic substances. Membrane distillation has been tested primarily in the separation of water–ethanol mixtures.[15,53,69,77,78,97] In the stationary regime, the concentration of ethanol in the permeated material increases by a factor of 2–3.[69,97] The productivity with respect to the permeated material then reaches 10 kg $(m^2\ h)^{-1}$ and more,[96] which greatly exceeds the productivity in transvaporisation. However, it has been shown[69] that the permeability of the membrane and its selective properties vary with time owing to the wetting of the pores.

VIII. Conclusion

Analysis of the available publications on membrane distillation supports the view that the method is promising for the solution of a series of technological problems. The advantages of membrane distillation compared with other membrane methods are associated with the low requirements which must be met in the preliminary purification of waste and other saline waters, the absence of excess working pressures, a satisfactory productivity even at high and very high concentrations of the solutes close to the solubility limit, the possibility of using low-energy heat in combination with the possibility of its recovery, the relative simplicity of the design of the modules and apparatus, the high quality of the permeated material (water), including the possibility of obtaining in one stage a pyrogenic sterile water, and the extensive possibilities for the technological employment of membrane distillation in many branches of industry.

The following disadvantages of membrane distillation may be noted: the impossibility of using it for the purification of water and the concentration of solutions containing surfactants and other water-soluble organic compounds with a low surface tension and a low boiling point (for example alcohols), the limited selection of hydrophobic materials suitable for the formation of membranes, and the high cost of such materials and of the membranes based on them. The last factor may not be quite so significant if the operating life of the membrane is sufficiently long (3–5 years).

Analysis of the advantages and disadvantages of membrane distillation compared with other membrane as well as physico-chemical purification and concentration methods leads to the conclusion that membrane distillation has on the whole significant advantages over the baro- and electro-membrane methods employed for such purposes both independently and in hybrid technological schemes involving other methods.

Bearing in mind that hitherto membrane distillation is still a little investigated process, the growth of interest in the method and in its extensive practical use is to be expected in the future. At the same time, problems which require consideration in the immediate future have already become apparent. In our view, they include the theoretical and experimental solution of problems of mass and heat transfer in relation to the real macrostructure of the membranes and the physical properties of the materials from which they are made. Hence follows the need to optimise the pore and geometrical characteristics of the membranes and modules and also for a rational search for materials with the required physical, physicochemical, and mechanical properties. A more thorough and purposeful study of problems of the hydrophobic-hydrophilic properties of the membrane surfaces and of their influence on the structure of water in thin surface layers and also on the nature of the interaction of the components of the solution with the membrane surface is required. Hitherto, this problem has not been solved for membrane distillation, although it may be important for the treatment of experimental data on the retention of components of the solutions and on the productivity of membranes with respect to the permeated material. Yet another special problem, associated with the possibility of the contamination of the membrane surfaces by sorbed solution components and with the formation of deposits on the hydrophobic surface and in the pores of the membrane, is related to the above problem. It has not been discussed in the literature, although its practical importance is evident especially for the estimation of the potential possibility of the use of membranes and of the time intervals at which they are to be regenerated and the development of procedures for such regeneration.

Experimental studies on the characteristics of the membrane distillation of solutions mixtures containing readily volatile and volatile components (wetting and not wetting the surfaces of hydrophobic membranes) and the determination of the critical concentrations and other physicochemical parameters of such systems are needed. In our view, kinetic studies on the membrane distillation process under the conditions of variable characteristics of the mixtures being separated are also important.

The above list of problems associated with the development of membrane distillation is incomplete, but we hope that the analysis of the available literature data will serve the purpose of a deeper study of membrane distillation and of its extensive practical employment.

References

1. US P. 4 419 187; *Ref. Zh. Khim.* 2 I 83P (1985)
2. Jpn. Appl. 58-51 906; *Ref. Zh. Khim.* 12 I 326P (1984)
3. Swed. Appl. 452 451; *Ref. Zh. Khim.* 24 I 501P (1988)
4. K Schneider, T S Van Gassel *Chem. Ing. Tech.* **56** 514 (1984)
5. M E Findley *Ind. Eng. Chem., Process Des. Dev.* **6** 226 (1967)
6. M E Findley, V V Tanna, Y B Rao, C L Yem *AIChE J.* **15** 483 (1969)
7. A Vanhaute, Y Henderyckx *Desalination* **3** 169 (1967)
8. Y Henderyckx *Desalination* **3** 237 (1967)
9. E Drioli, V Calabro, Y Wu *Pure Appl. Chem.* **56** 1657 (1986)
10. Y Wu *Inyun Khuasyue (Ying Yung Huaxue?)* **3** 1 (1986)
11. A-S Jonsson, R Wimmerstedt, A-C Harrysson *Desalination* **56** 237 (1985)
12. E Drioli *J. Membr. Sci.* **33** 275 (1987)
13. S Ripperger *PT/Procestech.* **41** 50 (1986)
14. G S Sarti, C Gostoli, in *Proceedings of the International Congress on Membrane and Membrane Processes, Tokyo, 1987* p. 488
15. M Tomaszewska, M Gryta *Inz. Chem. Proc.* **13** 359 (1992)
16. Yu I Dytnerskii, A A Akobyan, in *Zamknutye Tekhnologicheskie Sistemy Vodopol'zovaniya i Utilizatsii Osadkov Promyshlennykh Stochnykh Vod (Tez. Dokl. 3 Resp. Nauch.-Tekhn. Konf., Kishinev 1990)* (Abstracts of Reports at the Third Scientific Conference on Closed Technological Water Consumption Systems and Head-Recovery of Sediments from Industrial Waste Water, Kishinev, 1990) p. 113.
17. K Smolders, A S M Franken *Desalination* **72** 249 (1989)
18. Yu I Dytnerskii, I R Bykov, A A Akobyan, V T Smekalov, in *Razdelenie Zhidkikh Smesei Ispareniem cherez Membranu i Membrannoi Distillyatsiei* (Separation Liquid Systems by Evaporation through a Membrane and by Membrane Distillation) (Moscow: NIITEKhIM, 1989) p. 49
19. C Gostoli, G C Sarti, S Matulli *Sep. Sci. Technol.* **22** 855 (1987)
20. L Basii, G D'Angelo, M Gobbi, G C Sarti, C Gostoli *Desalination* **64** 245 (1987)
21. Aust. P. 587 407; *Ref. Zh. Khim.* 15 I 67P (1990)
22. Sh Jin, R A Johnson, M S Lefebvre *Desalination* **80** 113 (1991)
23. Br. Appl. 2 229 379; *Ref. Zh. Khim.* 8 I 382P (1992)
24. Y Wu, Y Kong, X Lin, W Liu, J Xu *J. Membr. Sci.* **72** 189 (1992)
25. Y Kong, X Lin, Y Wu, J Cmen, J Xu *Gaofenzi Xuebao (Acta Polym. Sci.)* (2) 158 (1993)
26. Y Kong, X Lin, Y Wu, J Xu *J. Appl. Polym. Sci.* **46** 191 (1992)
27. R R Nigmatullin, A F Burban, A F Mel'nik, M T Bryk, V V Kondratyuk *Zh. Prikl. Khim.* **66** 1328 (1993)
28. A C M Franen, J A M Nolten, M H V Mulder, D Bargeman, C A Smolders *J. Membr. Sci.* **33** 315 (1987)
29. N Chlubek, M Tomaszewska *Environ. Prot. Eng.* **15** 95 (1989)
30. S Roland (Ed.), in *Water in Polymers* (Translated into Russian; Mir: Moscow, 1984) p. 556
31. M T Bryk, I D Atamanenko *Khim. Tekhnol. Vody* **12** 398 (1990)
32. Yu I Dytnerskii, A A Akobyan *Khim. Promst. (Moscow)* (8) 22 (1990)
33. P P Zolotarev *Khim. Tekhnol. Vody* **12** 681 (1990)
34. P P Zolotarev *Khim. Tekhnol. Vody* **13** 675 (1991)
35. R W Schofield, A G Fane, C J D Fell *J. Membr. Sci.* **33** 299 (1987)
36. R W Schofield, A G Fane, C J D Fell *J. Membr. Sci.* **53** 159 (1990)
37. R W Schofield, A G Fane, C J D Fell *J. Membr. Sci.* **53** 173 (1990)
38. G S Sarti, C Gostoli, S Matulli *Desalination* **56** 277 (1985)
39. S Bandidni, C Gostoli, G S Sarti *Desalination* **81** 91 (1991)
40. V A Kozlov, L L Tovazhnyanskii, V V Kutovoi *K Opredeleniyu Mekhanizma Techeniya Para v Poristykh Sredakh dlya Sluchaya Membrannoi Distillyatsii* (Determination of the Mechanism of Vapour Flow in Porous Media in Membrane Distillation) Article deposited at the State Scientific and Technical Library (GNTB) of Ukraine, Kharkov, No 836-Uk93 (1993)
41. V Calabro, E Drioli, F Matera *Desalination* **83** 209 (1991)
42. N I Nikolaev *Diffuziya v Membranakh* (Diffusion in Membranes) (Moscow: Khimiya, 1980)
43. S-T Hwang, K Kammermeyer *Membranes in Separations* (Translated into Russian; Moscow: Khimiya, 1981)
44. P P Zolotarev, S F Timashev *Teor. Osnovy Khim. Tekhnol.* **24** 252 (1990)
45. V V Ugrozov, P P Zolotarev, S F Timashev *Teor. Osnovy Khim. Tekhnol.* **25** 17 (1991)
46. P P Zolotarev, V V Ugrozov, I B Elkina, V N Nikulin *Khim. Tekhnol. Vody* **14** 501 (1992)
47. V A Kozlov, L L Tovazhnyanskii *Vliyanie Poperechnogo Potoka Veshchestva na Teplo- i Massoobmen v Protsesse Membrannoi Distillyatsii, 1993* (Influence of the Transverse Flow of Material on Heat and Mass Exchange During Membrane Distillation) Article deposited at the State Scientific and Technical Library (GNTB) of Ukraine, Kharkov, No 837-Uk93 (1993)
48. C Gostoli, G C Sarti, in *Synth. Polym. Membr. (Proceedings of the 29th Microsymposium on Macromoles, Prague, 1986)* (Berlin, New York: Springer, 1987) p. 515
49. A Slezak *J. Membr. Sci.* **26** 115 (1986)
50. E N Starikov *Kolloidn. Zh.* **53** 902 (1991)
51. E N Starikov *Teor. Osnovy Khim. Tekhnol.* **26** 50 (1992)
52. USSR P. 1 126 306; *Byull. Izobret.* **44** 20 (1984)
53. C Gostoli, G C Sarti *J. Membr. Sci.* **41** 211 (1989)
54. E Drioli, N Chlubek, A Punzo *Chim. Ind.* **66** 147 (1984)
55. E Drioli, Y Wu *Desalination* **53** 339 (1985)
56. E Drioli, Y Wu *Pr. Nauk. Inst. Ochr. Srodowiska Politech. Wroclaw.* (57) 177 (1986)
57. Kh Kurokava, I Koseki, A Yamada, K Ebara, S Takakhashi *Kagaku Kogaku Rombunsyu* **14** 330 (1988)
58. E Drioli, V Calabro, in *Third World Congress of Chemical Engineers, Tokyo, 1986* Vol. 3, p. 276
59. R Leysen, W Doyen, R Geens *Mol. Res. Div. Rept.* (602) 100 (1987)
60. A A Akobyan, E S Tsetsura, in *6 Vsesoyuz. Konf. Molodykh Uchenykh i Spetsialistov po Fiz. Khimii: "Fizkhimiya-90" (Tez. Dokl.) Moscow, 1990* (Abstracts of Reports at the Sixth All-Union Conference of Young Scientists and Specialists in Physical Chemistry: "Physical Chemistry-90", Moscow, 1990) Vol. 3, p. 3
61. Yu I Dytnerskii, S P Agatichev, A A Akobyan, G G Falileeva, in *Membrannye Metody Razdeleniya Smesei (Tez. Dokl., Vladimir)* [Membrane Methods for Separation of Mixtures (Abstracts of Reports, Vladimir)] (Cherkassy, 1991) p. 95
62. K Ohta, K Kiuchi, I Hayano, T Okabe, T Goto, S Kimura, H Ohya *Desalination* **78** 177 (1990)
63. K Ohta, I Hayano, T Okabe, T Goto, S Kimura, H Ohya *Desalination* **81** 107 (1991)
64. E Drioli, Y Wu, V Calabro *J. Membr. Sci.* **33** 277 (1987)
65. P P Zolotarev, V V Ugrozov, in *Membrannye Metody Razdeleniya Smesei (Tez. Dokl., Vladimir, 1991)* [Membrane Methods for Separation of Mixtures (Abstracts of Reports, Vladimir)] (Cherkassy, 1991) p. 4
66. P P Zolotarev, V V Ugrozov, S F Timashev, S Yu Zinevich, in *14 Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii, Moskva, 1989 (Ref. Dokl. i Soobshch.)* (Abstracts of Reports at the XIVth Mendeleev Congress on General and Applied Chemistry, Moscow, 1989) Vol. 2, p. 259
67. V P Litkhov, I V Landa, V A Malyusov, N N Kulov, in *14 Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii, Moskva, 1989 (Ref. Dokl. i Soobshch.)* (Abstracts of Reports at the XIVth Mendeleev Congress on General and Applied Chemistry, Moscow, 1989) Vol. 2, p. 284
68. S Yu Zinevich, in *3 Resp. Konf. Molodykh Uchenykh-Khimikov, Posvyashch. 80-letiyu Akad. M F Nagieva, Baku, 1988* (The Third Republican Conference of Young Chemists Commemorating Acad. M F Nagiev's 80th Birthday, Baku, 1988) p. 156
69. A C M Franken, J A M Nolten, M H V Mulder, C A Smolders, in *Synthetic Polymer Membranes (Proceedings of the 29th Microsymposium on Macromolecules, Prague, 1986)* (Berlin, New York: Springer, 1987) p. 531
70. H Kurokava, K Eboa, O Kuroda, S Takahashi *Sep. Sci. Technol.* **25** 1349 (1990)
71. M Ortiz de Zarate Jose, Garcia-Lopez Frutos, J Mengual Juan *J. Chem. Soc., Faraday Trans.* **86** 2891 (1990)
72. Yu I Dytnerskii, G G Falieeva *Khim. Promst. (Moscow)* (8) 474 (1992)
73. I B Elkina, P P Zolotarev, V N Nikulin, V V Ugrozov *Khim. Tekhnol. Vody* **14** 498 (1992)
74. S Yu Zinevich, V V Ugrozov, P P Zolotarev *Teor. Osn. Khim. Tekhnol.* **26** 793 (1992)
75. S Kimura, S-T Nako, S-I Shimatani *J. Membr. Sci.* **33** 285 (1987)

76. Kh Kurokava, T Sava, K Mitani *Kagaku Kogaku Rombunsyu* **17** 1168 (1991)
77. F Yoshishige, K Shoji, J Hidetsugu, A Masatoshi *J. Membr. Sci.* **72** 53 (1992)
78. F Yoshishige, K Shoji, J Hidetsugu, A Masatoshi, F Yoshinari *J. Membr. Sci.* **72** 73 (1992)
79. D W Gore, in *Proceedings of the 10th Annual Convention of Water Supply Improvement Association, Honolulu, Hawaii, 1982* p. 34
80. L Carlsson *Desalination* **45** 221 (1983)
81. S I Anderson, N Kjellander, B Rodesjo *Desalination* **56** 345 (1985)
82. A G Fane, R W Shofield, C J D Fell *Desalination* **64** 231 (1987)
83. T J Van Gassel, K Schneider, in *Membrane and Membrane Processes* (Eds E Drioli, M Nakagaki) (New York: Plenum Press, 1986) p. 343.
84. K Schneider, W Holz, R Wollbeck *J. Membr. Sci.* **39** 425 (1988)
85. P A Hogan, Sudjito, A G Fae, G L Morrison *Desalination* **81** 81 (1991)
86. Jpn. Appl. 2-14 719; *Izobret. Stran Mira* **11**(2) (1991)
87. M Tamura, in *Proceedings of the 1990 International Congress on Membranes and Membrane Processes, ICOM '90, Chicago, 1990* Vol. 1, p. 71
88. M Tamura *Desalination* **80** 105 (1991)
89. W T Hanbury, T Hodgkiess *Desalination* **56** 287 (1985)
90. M Tomaszewska *J. Membr. Sci.* **78** 277 (1993)
91. Y Wu, Y Kong, J Liu, J Zhang, J Xu *Desalination* **80** 235 (1991)
92. A Ashida, K Mitani, K Ebara, H Kurokawa, I Sawada, I Kashiwagi, T Tsiji, S Hayashi, K Otsubo, K Nitta *Adv. Space Res.* **7** 73 (1987)
93. P P Zolotarev, B V Ugrozov, I B Belkina, V N Nikulin *Ross. Khim. Zh.* **37** 105 (1993)
94. N Chlubek, M Tomaszewska *Environ. Prot. Eng.* **13** 17 (1987)
95. S Scott, in *Pittsburg Conference Presents PITTCON '92, New Orleans 1992 (Book Abstr.)* p. 285
96. S Kiyotaka, S Takeshi, M Toshihito, T Makio *Chem. Eng. J.* **38** B 33 (1988)
97. T Nakane, H Yanagishita, M Tamura, Y Takahashi, T Hakuta, H Yoshitone, in *Proceedings of the 1987 International Congress on Membranes and Membrane Processes, 1987* p. 588