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Methods for Obtaining Polymeric Membranes

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Methods for obtaining semipermeable polymeric membranes have been described. Various aspects of the physicochemical processes taking place during the production of membranes from polymer solutions and melts have been examined. Methods for obtaining membranes by sintering polymers, and methods for transforming continuous films and the walls of hollow fibres with continuous walls into porous membranes, have been described. Data on the preparation of composite membranes have been given. Particular attention has been paid to methods which have found practical application in technical processes for obtaining membranes as films and hollow fibres.
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I. INTRODUCTION

In the present work, an attempt has been made to review the most important information on the preparation of non-ionogenic polymeric membranes. For lack of space, the review does not deal with methods for obtaining ion-exchange and liquid membranes, membranes with a relay transfer mechanism, or dynamic membranes and polymeric membranes with metallic coatings.

Membranes can be classified in different ways.[1,2] For the present purpose, it is most appropriate to classify them according to their structural characteristics. It is usual to distinguish continuous and porous membranes. Because of their technical importance, the independent types examined include asymmetric and composite membranes, in which the thin active (towards the system being separated) layers have a higher density than the remaining part, which acts as a supporting carrier. The two layers have the same chemical composition in the asymmetric membranes, and different chemical compositions in the composite membranes.

The production of membranes with a given structure is determined by the specific features of the system being separated and the mechanism of its separation. Thus continuous membranes are used to separate mixtures by the diffusion penetration of the components, and porous membranes are used to separate mixtures by the phase penetration of the components. The separating power, permeability, and stability of the operational characteristics of membranes depend on the chemical character of the polymer and on its structure, which in turn is determined by the method and conditions of preparation of the membranes, and in a number of cases by the properties of the original polymer solution or melt.

The correct choice of polymer is of considerable importance for the production of membranes for a particular purpose. An important role is played by the affinity of the polymer for the penetrating component of the mixture being separated. In particular, for the diffusion penetration of substances through a membrane, the efficiency of their sorption by the polymer acquires considerable importance. The use of block copolymers is of interest for the directed control of the sorption of gases and their diffusion coefficients. The properties of the membranes differ considerably, depending on the type of block copolymer (for a given mass ratio of the blocks). In the case of silane–siloxane block copolymers it has been shown[3] that the composition dependence of the permeability is described satisfactorily by a "disperse phase–dispersion medium" model for block copolymers of the type AB, and by an inter-penetrating polymeric network model for block copolymers of the type BAB.[4]

The treatment of amorphous–crystalline membranes with reagents bringing about their additional crystallisation with the simultaneous formation of sub-micro-pores with dimensions of ~ 1 nm also makes it possible to increase the gas permeability. As shown[5] for polyethylene–terephthalate films, the increase in permeability is brought about by an increase in the sorption of gases by the polymeric material, and this increase is different for different gases.

A sharp increase in the permeability of polymers with respect to various gases is observed when there is a specific interaction. Thus membranes of a copolymer of ethylene difluoride and ethylene tetrafluoride show an increase in their permeability with respect to ammonia during use as a result of chemical changes taking place in the polymer.[6] The permeability reaches $(0.6-1.5) \times 10^{-10}$ cm^3.cm/cm^2.s.Pa, and the separation factor reaches 5000 for the ammonia–hydrogen system, and 37 000 for the ammonia–nitrogen system.

For the effective separation of liquid systems, the wettability of the membrane material by the penetrating component of the mixture being separated is of considerable importance. If the wetting angle of the membrane is greater than 90°, part of the energy is used up in overcoming the forces of surface tension at the phase boundary. kat the same time, the polymeric material of the membrane should not undergo marked swelling in the system being separated, to avoid a change in the pore dimensions and compaction of the membrane under the influence of the pressure applied to it. The last requirement applies to a lesser extent to polymers designed for the production of dialysis membranes than to polymers used in membrane processes involving the application of pressure.

In a number of cases, particularly in the separation of liquid systems by ultrafiltration, an important role is played by the redistribution of the electron density in the macromolecules, since this factor may influence the preferential sorption by the membrane of individual components of the system being separated. Since in most

cases the membranes are produced from polymer melts or solutions, it is desirable that the polymer melt without decomposing or dissolve in available solvents.

II. THE PRODUCTION OF CONTINUOUS MEMBRANES

Continuous membranes are most frequently obtained by casting from melts or by dry forming from polymer solutions.† The production of selectively permeable membranes from polymer melts does not differ fundamentally from the production of films and fibres designed for other purposes.

Fusion and crystallisation are first-order phase transformations, that is these processes are accompanied by a discrete change in the internal energy and specific volume. When a polymer melt is cooled, long-range order may appear in it, that is ordered formations, comparable in magnitude with the segments of the macromolecules and with the length of the polymer chains, may be produced. Compact formations preserved in the melts (not broken down on fusion) often act as growth centres for the crystallites in the polymer.[7]

The diffusion permeability of polymeric membranes depends on the diffusion coefficient of the penetrating substance in the polymer and on its sorption by the polymer. The maximum values of the penetration coefficients are characteristic of highly elastic flexible-chain polymers. The permeability of the polymer generally decreases with increase in the rigidity of the chains and increase in the number of polar groups.[8] A decrease in permeability is also observed when the polymers are cross-linked, although the sorption of gases changes little.[9] The permeability of membranes is influenced by the ratio of the amorphous and crystalline phases in the polymer, where the dependence is often non-linear, and also by the structure of the amorphous regions and the morphological characteristics of the crystalline formations.

A decrease in the crystallinity of the polymer usually leads to an increase in the permeability of the membranes.[10,11] An exception is provided by membranes of poly-4-methylpent-1-ene, whose density is lower in the crystalline state than in the amorphous state.[12] Up to a definite limit, the dimensions of the spherulitic formations have no significant influence on the gas permeability, which increases significantly only with further increase in the size of the spherulites, as a result of the development of micro-cracks.[13]

To decrease the crystallinity of membranes, branched polymers are used. Thus the crystallinity of branched polyethylene is 50 to 60%, whereas that of the non-branched analogue reaches 70 to 80%.[14] A decrease in the crystallinity of the polymer can apparently be brought about by marked superheating of the melt (50 to 55 K above the melting point), which leads to the formation of a completely isotropic system and to the disappearance of the crystallisation nuclei.[15]

An important role in the control of the crystallinity of the material is played by the rate of cooling of the melt.[16] If the melt is cooled rapidly to the vitrification temperaturre of the polymer, the rate of crystallisation approaches zero, and its duration tends to infinity. According to Avrami's equation:[17]

$$a = 1 - \exp(-k' t^{n_A})$$

where a is the degree of crystallinity; k' the crystallisation rate constant; t the time; and n_A the Avrami coefficient, which varies from 1 to 4 and characterises the morphological features of the crystal formed, and also the mode of production of the crystallisation centres (thermal or athermal). For the slow formation of structures with three-dimensional order, $n_A = 4$, and for the instantaneous formation of one-dimensional structures, $n_A = 1$. Intermediate values correspond to the instantaneous formation of structures with three-dimensional order, the slow formation of structures ordered in two dimensions, and other cases.[18]

Homogeneous (continuous) membranes can be obtained by dry forming from polymer solutions by analogy with the processes involved in the production of cinematographic films and acetate textile fibre. In this case the original system (solution) does not separate into phases, but remains single-phase until the solvent is completely removed; as the solvent is removed, the viscosity of the system increaes by several orders of magnitude, and the system loses its fluidity. The increase in the viscosity as a result of the increase in the concentration of the polymer in the system can be described by the equation[19]

$$\lg \eta = \nu c^{\alpha}$$

where η is the viscosity; c the polymer concentration; and ν and α are constants which depend on the nature of the polymer and the solvent.

The rate of evaporation of the solvent influences the properties of the membranes formed. Thus when crystallising polymers are used, slow evaporation of the solvent facilitates crystallisation, often leading to a decrease in the permeability of the membranes. The rate of evaporation of the solvent depends on its vapour pressure above the solution p_1 decreases. This is observed in the first stage of the evaporation of the solvent from a liquid film or a stream of solution (in the production of membranes in the form of a hollow fibre). The difference in the chemical potentials in different layers of the solution leads to diffusion of the solvent from the inner layers, and the rate of diffusion gradually decreases, accompanied by an increase in the concentration of the polymer in the solution and an increase in the solution viscosity. For solutions with medium concentration, this process is described approximately by the equation[20]

$$Q/t = bc^{r/s}$$

where Q/t is the rate of diffusion of the solvent in the solution, and b a constant which depends on the nature of the polymer and the solvent, temperature, and other factors.

The difference in the rates of removal of the solvent from different layers of the liquid film or fibre leads to non-uniformity of the structure along the thickness of the membrane.[21] For example, in films produced on rigid supports it is possible to distinguish three layers: a compact upper layer, a loose intermediate layer, and a plane-orientated lower layer. In the production of membranes in the form of hollow fibres, the polymer molecules are oriented in the channels of the holes in the die. After the jets leave the holes, the induced orientation of the polymer is partly reduced as a result of relaxation processes, but usually it cannot be eliminated completely. The influence of orientation on the gas permeability of the polymer is indeterminate. The permeability depends on the relative quantity of cavities in the material. For example, the cold stretching of polyethylene by 297% leads to a decrease in the number of cavities.[8] There is a simultaneous decrease in the sorption, diffusion

†The terms "dry" and "wet" forming are taken from chemical fibre technology. In dry forming, the solvent is removed by evaporation, and in wet forming it is removed by mixing with a precipitant.

coefficient, and permeability. On the other hand, when nylon-66 is stretched, the number of cavities increases, leading to an increase in the permeability, and this effect overlaps the influence of the increase in crystallinity. A five-fold increase in the orientation of polypropylene, although leading to loosening of the structure, a decrease in the crystallinity, and a decrease in the diffusion rate, does not bring about a significant change in the sorption and permeability.[8] A decrease in permeability was observed[22] as a result of the uniaxial stretching of polyethylene, and is attributed to the rearrangement of the spherulitic and micro-spherulitic structures in the highly oriented material and to the significant deviation from thermodynamic eqiuilibrium in the amorphous regions in the layers between the crystallites.

The dependence of the permeability of polymeric materials on the degree of biaxial stretching is complex, and in a number of cases extremal. Polyethylene–terephthalate films are more sensitive to biaxial than to uniaxial stretching. Polypropylene and polyethylene show a slight decrease in permeability at low deformations, and an increase at deformations exceeding a certain critical value. This can be attributed to the appearance of sub-micro-cracks or to recrystallisation. Polyethylene tetrafluoride, whose macromolecules are highly rigid, shows an increase in permeability on even slight biaxial orientation.[8]

All these relationships must be taken into account in the production and application of membranes. Dry forming can be used to obtain ultra-thin membranes (thickness 300–500 nm) from polymer solutions with low concentrations (0.5–2%) on a liquid surface (mercury, water). The volatile solvent should not be miscible with the liquid support.[23] The membrane formed is practically isotropic, and has a high permeability. Considerable difficulties arise, however, when these membranes are used. To avoid these difficulties, asymmetric and composite membranes have been developed, and have found extensive application.

III. THE PRODUCTION OF POROUS MEMBRANES

Porous membranes are obtained by different methods. In particular, continuous membranes can be made porous by "bombarding" them with the ions of heavy elements, for example ^{136}Xe, ^{84}Kr, and ^{40}Ar,[24] or with radioactive decay products.[25] The starting materials are continuous films of polyethylene–terephthalate, polyamide, polycarbonate, etc. When they strike the polymer film, the ions bring about cracking degradation of the polymer. The density of the breakdown brought about by the particle is proportional to the square of its electrical charge and approximately inversely proportional to the square of its velocity. Since the maximum possible critical rate of loss of energy by the particle in the polymer dt/dx increases with increase in the atomic mass of the particle, there exists a lower limit of the mass of the ions capable of forming "traces". The beam of ions is collimated to ensure that the direction of the "traces" is perpendicular to the membrane surface. The film treated with the ions is subjected to strong ultraviolet irradiation to intensify the subsequent etching, which is carried out using solutions of alkalis or acids, depending on the nature of the polymer. During etching, pores are formed in the film; the form of the pores depends on the ratio of the rate of extraction of the material along the axis of the "trace" v_t to the rate of extraction of the material from the undamaged surface v_s. The form of the pores is close to cylindrical when $v_t > v_s$; when $v_t \simeq v_s$, a conical depression is formed in the film. These membranes, which are usually called nuclear filters, are most widely used in microfiltration processes.

Another method for converting continuous into porous membranes involves swelling the original membrane, with a cryptoheterogeneous structure, and then fixing the resulting pores.[26]

Methods for obtaining porous membranes by stretching continuous membranes under strictly controlled conditions have been used increasingly in recent years. These processes can be carried out in two ways. One involves the use of the familiar Rebinder effect. Stretching continuous films in adsorption-active media makes it possible to produce membranes with a developed system of continuous connecting pores.[27] This principle has been used, for example, to obtain a porous hollow polyethylene fibre.[28] For this purpose, the fibre was subjected to thermal treatment for 30 min at 90–120°, after which it was kept in trichloroethylene or perchloroethylene at a temperature above the vitrification temperature of the polymer. The fibre was then stretched by 200–300%, and then subjected to thermal fixation at 85–120°, when it was allowed to shrink by 5%. A similar process has been carrried out for films of polytetrafluoroethylene[29,30] and polyethylene–terephthalate.[31] In particular, when films of vitreous polyethylene–terephthalate were stretched by 200% in n-propanol, the quantity of pores was brought to 3.2×10^{12} cm^{-2}, with average dimensions of $\sim$4.6 nm.

Continuous membranes of crystallising polymers can also be made porous without using adsorption-active media.[32–37] The process usually involves the stages of preliminary heating of the material, stretching to produce a system of pores in the material, and thermal fixation of the porous structure. The formation of pores when the membrane is stretched can be represented as an increase in the distance between the lamellae; when an external force field is applied to the system, the "through" chains are partly "drawn out" from the lamellae into amorphous region.

The degree of stretching influences the pore dimensions.[32] The stretched membrane is subjected to thermal fixation at the temperature of the preliminary heating or a slightly higher temperature. The thermal fixation is carried out under slight tension, which controls the partial shrinkage of the material. Since this is accompanied by the relaxation of a considerable proportion of the internal stresses, the membrane subsequently does not undergo appreciable shrinkage deformation, and its porosity is preserved.

This method of producing porosity has been most widely used in the preparation of hollow fibres of polyalkenes,[33–36] poly-*p*-phenylene sulphide,[37] etc. Porous polyalkene membranes can be used to separate gas mixtures as a result of the difference in the rates of penetration of the individual components through the pores by a Knudsen flow mechanism. These materials appear promising for removing contaminants from liquid fuel and oils by ultrafiltration, and also for carrying out membrane distillation, a process in which increased interest has recently been shown.[38,39]

When porous polyalkene membranes are used in the separation of aqueous systems, the polymer is often made hydrophilic, for example by treating it with sulphuric acid or by grafting hydrophilic monomers.[40] Membranes can be made hydrophilic by treating them with a gas mixture containing SO_2 and F_2.[41]

One method of producing porous membranes is by sintering powders or by calendering finely dispersed polymers. A detailed analysis and description of the processes involved in the production of micro-filtration membranes by this method have been given.[42] It is particularly appropriate to use this method with polymers which cannot be brought into the viscous-flow state by fusion or solution.

The primary example of polymers of this kind is polytetrafluoroethylene, which has a high chemical stability and can withstand temperatures above 200°, Polytetrafluoroethylene membranes are obtained by sintering its powder in pure form[43–45] or in mixtures with binding agents, including other fluorine-containing polymers. A number of petroleum products have been used as binding agents.[46,47] The mechanical strength of polytetrafluoroethylene membranes not containing a binding agent is usually insufficient. To eliminate these disadvantages, membranes with a fibrous filler are prepared.[2] These membranes, with a thickness of 0.12–0.15 mm, have pores with dimensions up to 500 Å. They are hydrophobic, and therefore impermeable to water at low pressures (up to 1.2 MPa).

Examples of the production of membranes by sintering are also known for other polymers, in particular polyalkenes, with the introduction into the mixture of materials which can be removed by water, for example starch.[48] The sintering is carried out at a temperature above the vitrification temperature of the polymer. Interdiffusion of the macromolecules of the particles in contact with one another takes place. The adhesion of the particles leads to a decrease in the specific surface of the system, and hence to the liberation of free energy:[42]

$$\Delta E = \sigma_{pa}(1/r - 1/R) \qquad (1)$$

where σ_{pa} is the surface tension of the polymer at the boundary with air, r the radius of the contact surface, and R the radius of the particle.

During the technical process, it is extremely important not to allow complete merging of the particles, since this naturally leads to closure of the pores. It is important to stop the process at the first stage of the sintering. The duration of this stage (τ) for a number of systems can be determined if the familiar Frenkel' equation[49] is written in the form: $\tau = 2\pi r^2\eta/3R\sigma_{pa}$, where η is the viscosity of the melt.

The method of obtaining porous membranes by separating polymer solutions into phases has been most widely used. This method opens up extensive possibilities for the directed control of the structure and operational properties of membranes.

Solutions of macromolecular compounds are not ideal. For these solutions, the following relationship applies: $\Delta G_{rs} = \Delta G_i + \Delta G^E$, where ΔG_{rs} is the free energy of the real solution, ΔG_i the free energy of the ideal solution, and ΔG^E the excess free energy. Positive values of the deviation ΔG_{rs} correspond to poor miscibility of the components.[50] When ΔG^E reaches $\sim 0.5\ RT$,[51] the solution separates into phases.

The decomposition of polymer solutions into phases can take place by two mechanisms—nucleation and spinodal. Analysis of the equilibrium diagram of a polymer–solvent system (Fig.1) leads to the following basic postulates.[52] The region lying above the binodal corresponds to a thermodynamically stable single-phase solution. This region is characterised by the inequality $(\partial^2 g/\partial x^2)_{pT} > 0$, where g is the average free energy of the system, and x the molar concentration of one of the components. The region lying between the binodal and the spinodal corresponds to a metastable state of the system. For the range of metastable states, the inequality $(\partial^2 g/\partial x^2)_{pT} > 0$ is again applicable. In this region, the diffusion fluxes of the components are directed in such a way that they decrease the fluctuations. The formation of a new interface is energetically unfavourable, and the work of formation of the nuclei of the new phase provides a measure of the metastability of the solution.[52] Thus the system is unstable only with respect to heterophase fluctuations exceeding a certain critical value.[53] If this critical value is exceeded, a spontaneous increase in the fluctuations takes place.

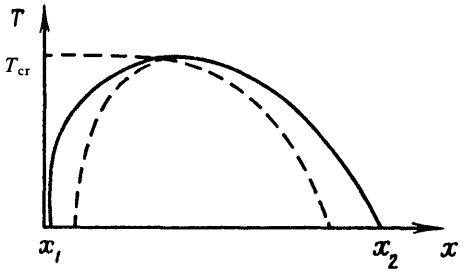


Figure 1. Equilibrium diagram of a polymer–solvent system (continuous line–binodal, broken line–spinodal): T–temperature, x_1–concentration of the solvent, x_2–concentration of the polymer.[52]

As the nuclei of the new phase are formed, the concentration of the polymer in the solution decreases. At the same time there is an increase in the coefficient of self-diffusion of the macromolecules,[54] and it follows from scaling theory that this increase for concentrated solutions shows a cubic dependence on the mass fraction of the polymer in the solution. The increase in the coefficient of self-diffusion of the macromolecules leads to the growth of the nuclei of the new phase. The rate of the formation and growth of the nuclei depends on the degree of supersaturation of the solution. The degree of supersaturation in turn can be controlled by changing the temperature, using precipitants with different compositions, and changing the concentration of the polymer in the original solution. The development of the growth of the nuclei of the new phase when there is a sufficient quantity of polymeric material in the system leads to the nucleation breakdown of the polymer solution into phases, that is to the formation of a polymeric framework including regions of a phase with a low polymer concentration (this is usually a mixture of the solvent and the precipitant in which a small quantity of the polymer, mainly its low-molecular-weight fractions, is dissolved).[55] The polymeric framework formed as a result of the breakdown of the solution into phases is subjected to syneretic contraction, as a result of which it becomes more compact, with the simultaneous partial separation of a liquid phase. The polymer is converted from a highly fluid into a highly elastic (and sometimes vitreous) state.

On the spinodal, the work of formation of the nuclei of the new phase is equal to zero; the equation of the spinodal is $(\partial^2 g/\partial x^2)_{pT} = 0$.[52] Under the spinodal lies a region corresponding to a thermodynamically unstable state of the system. This state corresponds to the inequality $(\partial^2 g/\partial x^2)_{pT} < 0$. In the initial stage of the spinodal decomposition of the system into phases in the homogeneous solution a set of concentration fluctuations is produced, and these can be regarded as a set of sinusoidal waves with a fixed length λ equal to the dimensions of the structures formed. The fluctuations may not reach the critical value, as in the nucleation process of breakdown into phases. Subsequently, at the points where the fluctuations are

produced, as a result of the existence of a component flux directed against the concentration gradient, micro-regions of the heterogeneous structure are enriched in these components, and begin to coalesce.[56] The temperature at which the rate of formation of the interconnected micro-regions of phase separation is a maximum corresponds to a definite composition. If the volume fraction of one of the components is greater than 15%, then in the final stage of the process, the coalescence initiated by hydrodynamic factors ensures that each phase is connected.[51] At this stage, the dimensions and composition of the structures may be the same as in the nucleation mechanism of the breakdown, that is two phases with concentrations of a given component x_1 and x_2 may coexist in equilibrium. When the change in temperature is rapid, however, a non-equilibrium system with a matrix (continuous) phase may be preserved.[57] The structures formed in this case differ from those produced in nucleation breakdown. In the coalescence process, the initially spherical particles form either cellular or network structures,[58,59] which form the basis of the highly porous membranes.

The theory of spinodal decomposition applied to polymeric systems was developed by De Gennes.[60] Spinodal breakdown has been studied experimentally by a number of workers.[56–59,61,62]

In practice, semipermeable membranes are produced mainly by the breakdown of solutions into phases by the nucleation mechanism. The original (forming) solution is converted to the metastable state by changing either its temperature or its composition. The latter is achieved either by evaporating the solvent from the three-component solution containing the polymer, the solvent, and the precipitant (spontaneous gel formation method) or by using the method of wet forming to obtain the membranes.

The method of spontaneous gel formation is widely used to obtain film membranes for ultra-filtration and micro-filtration. Its essential features are as follows. A solution of the polymer is prepared in a mixture of a solvent with a non-solvent, which should be less volatile than the solvent. The solvent is then evaporated from a film of the liquid deposited on a stationary or moving support. As a result of the change in the composition of the system, it breaks down into phases with the production of a gel which forms the basis of the highly porous membrane.

To analyse the processes taking place, it is appropriate to examine the equilibrium diagram of a three-component polymer–solvent–non-solvent (precipitant) system, represented in general form in Fig.2.[63] The solid phase (polymer) can be isolated from the solution with the composition A by different methods. For systems with an upper critical temperature of mixing, $T_1 > T_2$, and for systems with a lower critical temperature of mixing, $T_1 < T_2$. If the solution A contains a solvent whose vapour pressurre is higher than that of the precipitant, the decomposition of the solution into phases takes place as a result of the evaporation of the solvent. At the point B_2, the system loses its homogeneity, and decomposes into phases with compositions x_1 and x_2, after which, as a result of the evaporation of the solvent and the precipitant, it acquires the composition P. If however the precipitant is more volatile than the solvent, the composition of the system changes along the path AGP, and the system remains homogeneous throughout.

To obtain membranes by the wet forming method, the original system is enriched in the precipitant by diffusion processes, with a simultaneous decrease in the concentration of the solvent. At the point B_1 below the temperature T_2 (or at the point B_1' below the temperature T_1), the solution breaks down into phases with compositions x_1 and x_2 (below the temperature T_2) or x_1' and x_1' (below the temperature T_1). On subsequent "elution" of the solvent by the precipitant, the system arrives at the composition C_1 or C_2, and then, as a result of drying along the paths C_1P or $C_1'P$, at the composition P.

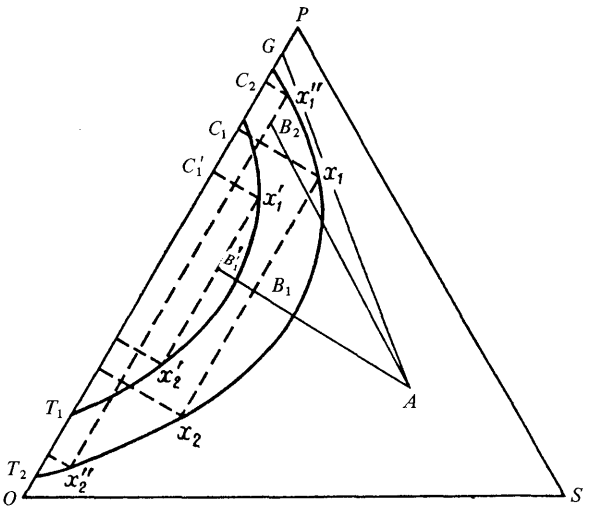


Figure 2. Equilibrium diagram of a three-component system (for explanation see text).[63]

Analysis of the diagram shows that for systems with an upper critical temperature of mixing, the concentration of the polymer in the framework phase increases with decrease in the temperature of the phase separation. This is important for controlling the parameters of the porous structure of the membranes.

In addition to thermodynamic factors, it is also necessary to take account of kinetic factors, which have a considerable effect on the structure and properties of the membranes. For example, the change in composition along the path AB_2C_2P may take place so rapidly that the breakdown of the system into phases cannot take place.[64] Because of the very high viscosity of the gel, the conversion of the system from the heterogeneous to the homogeneous state on the section C_1P (paths $C_1'P$; C_2P) is extremely difficult, so that after the removal of the precipitant from the gel, the system may remain heterogeneous for an unlimited time.

One of the most widely used technical methods for controlling the degree of supersaturation of the forming solutions is by using precipitant baths with different composition, in particular with different ratios of the precipitant and the solvent. In practice, baths containing a small quantity of solvent are called "hard", and baths containing a large quantity of solvent are called "soft". The use of hard precipitant baths, which bring about extensive supersaturation of the solution, leads to the production of a large quantity of nuclei of the new phase in the system and to their rapid growth. Steric hindrance, however, restricts the growth of the particles of the new phase. As a result, a membrane with fine pores is formed. A similar effect can be achieved by increasing the polymer concentration in the solution and by changing the temperature of the system.

The influence of these factors on the structure and properties of membranes obtained from cellulose esters has been studied by many workers.[65–74]

In the study of the wet forming of membranes from aromatic polyamides, polyacrylonitrile, and other polymers it has been shown[75,76] that the morphological characteristics of the membranes vary considerably, depending on the polymer precipitation conditions. Soft precipitation of the polymer from highly concentrated solutions gives a regular spongy material. Hard precipitation of the polymer from solutions with a low concentration gives a membrane permeated by large rod-shaped pores. In the formation of these pores, a decisive influence is assigned[77–80] to local convection currents in the liquid, arising as a result of the exothermic character of the interaction of the solvent with the precipitant.

Breakdown of solutions into phases by the spinodal mechanism is as yet very rarely carried out in technical practice. In this connection, mention may be made of the process carried out by the West German firm "ENKA Membrana" for obtaining tubular and capillary membranes, known by the trade name "Accurel", from solutions of polypropylene in an organic oil (other solvents may also be used). The heated solution is extruded through a specially designed die, after which it is rapidly cooled. This gives a highly porous isotropic membrane, which can be used successfully as a micro-filter.[81]

IV. THE PRODUCTION OF ASYMMETRIC MEMBRANES

The different conditions of formation of the structure of the films and fibres in different layers leads to the formation of asymmetric membranes. Since the preparation of the first asymmetric membranes,[82,83] the most widely used but not the only method for obtaining them has been by dry–wet forming. In this process, the solvent is partly evaporated from the surface layer of the solution, after which the solution (in the form of a liquid film or filament) is placed in a precipitating bath, where it breaks down into phases. As a consequence of the higher concentration of the polymer in the surface layer, a compact polymeric sheath is formed on the surface of the membrane, giving it its high separating power. At the same time, the loose polymeric matrix formed from the layer with the lower concentration ensures that the membranes are highly permeable to the penetrating components of the system being separated. The active (selective) layer usually corresponds to a small fraction of the thickness of the asymmetric membrane. The absolute thickness of the active layer varies from 0.1 μm^2 to 0.25 μm,[84,85] although thicker layers up to 4 μm are also encountered.[10]

The parameters of the process of the partial evaporation of the solvent from the surface of the liquid film or filament (chiefly the rate of evaporation) play an important role in the production of the structure of the asymmetric membrane.[86,87] The lower the rate constant of the evaporation of the solvent, the higher the permeability of the membranes for a given selectivity. Since the rate constant of the evaporation of the solvent depends on several factors (the concentration of the solvent vapour in the evaporation zone, temperature, etc), it is possible to obtain membranes with identical properties for different parameters of the technical process. A necessary condition, however, is a constant value of the solvent evaporation rate constant, which has an optimum value for each composition of the forming solution.

An important role in the formation of asymmetric membranes is played by surface phenomena.[88] If the surface tension σ_1 at the boundary between the solvent and air containing the solvent vapour is lower than the surface tension σ_2 at the boundary between the solution and air containing the solvent vapour, then the surface of the forming solution in contact with air is enriched in the solvent, and the polymer is sorbed on the support, forming an asymmetric membrane with the compact layer in contact with the support. If however $\sigma_1 > \sigma_2$, then the surface in contact with air is enriched in the polymer, and after the breakdown of the solution into phases, the compact selective layer is formed on this surface.

Since the structure and properties of the membranes depend on the structure of the forming solutions, the rates of their breakdown into phases, and the surface properties of the system, the importance of the correct choice of solvent is obvious. Frequently, the solvent used is a two-component mixture, one of whose components is an effective solvent, while the other is a swelling agent.

A noteworthy procedure developed by a number of workers[89–93] involves the selection of the solvent from the magnitude of the Hildebrand solubility parameter δ. It is known[94,95] that $\delta = (\Delta E/v)^{1/2}$, where v is the molar volume, ΔE the energy of cohesion, $\Delta E = \Delta E_d + \Delta E_p + \Delta E_h$, and ΔE_d, ΔE_p, and ΔE_h the components of the energy of cohesion due to the action of dispersion forces, polar forces, and hydrogen bonds respectively.

From the equations given it follows that $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$.

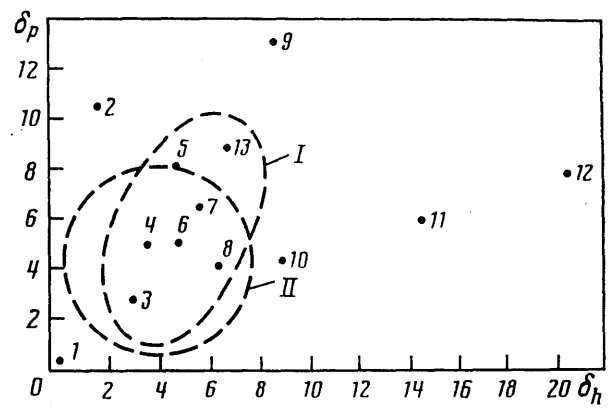


Figure 3. Solubility diagrams of cellulose acetate (*I*) and polysulphone (*II*):[89] *1*) carbon tetrachloride, *2*) ethylene carbonate, *3*) methylene chloride, *4*) acetone, *5*) dimethyl sulphoxide, *6*) dimethylacetamide, *7*) dimethylformamide, *8*) acetic acid, *9*) formamide, *10*) ethanol, *11*) glycerol, *12*) water, *13*) mixture of acetone and formamide (6:4).

The range of solubility of substances can be represented in the form of a sphere on coordinates $\delta_d - \delta_p - \delta_h$.[96,97] Since for most substances the values of δ_d are similar,[96] it has been proposed that the mutual solubility of substances be characterised using two-dimensional diagrams on coordinates $\delta_p - \delta_h$ (Fig.3). The action of weak forces can be taken into account by a generalised parameter $\delta_v = (\delta_d + \delta_p)^{1/2}$.[98] The range of solubility can then be represented on coordinates $\delta_v - \delta_h$. The fraction of each component of δ can be

represented as follows:

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h}; \; f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h}; \; f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h}$$

The range of solubility can then be represented on a triangular Hashimoto diagram[93] (Fig.4).

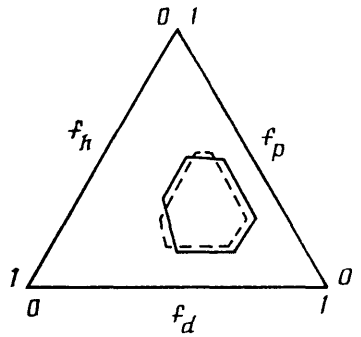


Figure 4. Diagram of secondary cellulose acetate (continuous line) and cellulose triacetate (broken line) on Hashimoto coordinates. For explanation see text.[93]

To obtain a highly permeable asymmetric membrane, the orioginal solution should satisfy the following requirements:[89] all the components of the dissolving mixture should be compatible with the precipitant; the composition of the solution before the breakdown into phases should correspond to the range lying at the solubility boundary; the concentration of the structure-formation centres in the solution before the breakdown into phases should be high, to ensure the rapid precipitation of the polymer; when the volatile component of the dissolving mixture is removed, the solubility of the polymer should decrease.

The breakdown of the forming solution gives the so-called "primary gel". To give the membrane a compact structure, it is subjected to annealing involving thermal treatment in a liquid medium, which produces shrinkage deformations in the polymeric material. A necessary condition for effective shrinkage is the devitrification of the polymer.[63] For cellulose acetate in an aqueous medium, the devitrification temperature is 90–95°.[99] Thus the annealing temperatures of 75–85° given by Brock[100] for cellulose acetate membranes are too low.

The shrinkage of the polymer takes place to a greater extent in the surface layer than in the loose matrix. This is due to the higher concentration of stresses in the surface layer of the membrane as a result of the more rapid precipitation of the polymer on the surface of the liquid film, compared with the volume. Annealing leads to an increase in the salt-retention power of membranes designed for reverse osmosis, and increases their water permeability.

The membranes obtained in this way have an ultraporous structure, and are extensively impregnated by liquid. When the liquid evaporates, the forces of capillary contraction bring about closure of the pores, as a result of which the membrane may lose phase permeability. To avoid this, the membrane is usually impregnated with glycerol, a liquid with a low volatility. This membrane retains its operational properties for a time interval sufficient for the preparation of the separating module.

Asymmetric membranes are used for the separation of both gas mixtures and mixtures of solutions by reverse osmosis and ultrafiltration. An example is a gas-separating membrane of polyvinyltrimethylsilane, which has permeability coefficients with respect to O_2 and N_2 of 15.0 x 10^{-15} mole.m/m^2.s.Pa and 3.5 x 10^{-15} mole.m/m^2.s.Pa respectively.[1] Asymmetric membranes are widely used as ultra-filters with molecular-mass retention limits from 1000 to 300 000, and also to separate solutions by reverse osmosis.[77–87]

V. THE PRODUCTION OF COMPOSITE MEMBRANES

In recent years there has been an increase in interest in the production of composite membranes. This development is regarded as particularly promising.[101] Composite membranes are obtained by depositing a layer of another polymer on a porous base. The first successful attempts were made in the early nineteen-seventies,[102] and in recent years the method has been developed on the industrial scale. Membranes with unique properties have been obtained. It is suggested that composite membranes undergo less deformation on the application of pressure, compared with asymmetric membranes. Polymers with unique properties can be used to obtain the selective layer of composite membranes. Since the coating is thin, the quantity of polymer used for the production of the membrane is small, so that the cost of the polymer is not usually a limiting factor.

Several methods can be used to obtain composite membranes. A popular method involves the deposition of the active layer by plasma polymerisation in a glow discharge.[103–108] Various organic compounds can be subjected to plasma polymerisation, including compounds which cannot be polymerised by ordinary methods, for example benzene. In the glow discharge, benzene is apparently converted into acetylene, which then polymerises.[109] The monomers used include acetylene, allylamine, 4-vinylpyridine, N-vinylpyrrolidone, 4-picoline, 4-ethylpyridine, 4-methylbenzylamine, 3,5-dimethylpyridine, and other compounds.[109]

Plasma polymerisation can be carried out by electrodeless and electrode methods. To establish the electrodeless discharge, the discharge tube is placed inside a solenoid, through which the electric current passes. The discharge takes place when definite values of the current strength and frequency have been reached. The polymer formed is deposited on a porous support in the zone of the glow discharge. The supports used include ultra-filters with pore dimensions of ~25 nm,[109] hollow fibres, porous glass, and other porous materials.

When the electrode method is used, the polymer is deposited on the electrodes, which may be porous plates; the distance between the plates is 5–40 mm.[109] Before the stream of monomer is supplied, the air is evacuated from the plasma polymerisation chamber to a residual pressure of ~10^{-1} Pa. The monomer vapour is then introduced into the chamber to a pressure of 10 Pa, after which an inert gas is added to increase the pressure to 25 ± 5 Pa. A high-frequency generator is then used to create a glow discharge, which brings about the polymerisation of the monomer.

The water permeability of the membrane obtained naturally depends on the hydrophilic character of the polymer formed. Thus if methacrylic acid is used as the original monomer, the water permeability of the membrane is 5.85 x 10^{-6} m^3/m^2.s, and when vinyl

acetate is used, the water permeability is 2.02 x 10^{-6} $m^3/m^2.s$, and the selectivity towards sodium chloride is almost the same in both cases. A highly selective and highly permeable membrane for reverse osmosis can be obtained by treating a porous polyacrylonitrile membrane with a plasma with the introduction of He, H_2, and O_2 into the discharge zone.[110] This gives a cross-linked surface layer containing $-OH$, $>C=O$, and $>NH$ groups.

Composite membranes are also obtained by the vacuum deposition of a thin (0.05 μm) active polymer layer on a porous support,[111] and also by depositing polymer solutions with a low concentration on a porous base and then evaporating the solvent.[112,113] In the last case, the adhesion interaction between the polymer and the material of the support is of considerable importance. The thermo-dynamic characteristic of the adhesion is the loss of free energy per unit surface area of contact between the solids in contact. The work of adhesion is given by

$$W_a = \sigma_{sa} + \sigma_{la} - \sigma_{sl}$$

where σ_{sa}, σ_{la}, and σ_{sl} represent the surface tension at the solid base–air, solution–air, and solution–solid base boundaries respectively. This equation shows that to improve the adhesion of the solution to the porous base, it is necessary to select systems for which the surface tension at the boundary with one another is a minimum. Composite membranes obtained by depositing polyelectrolyte complexes on a porous base have found practical application.[114]

Methods for obtaining composite membranes by depositing on a porous base a thin film formed as a result of interphase polycondensation are of considerable interest.[115–117] This method has been used to obtain membranes for reverse osmosis with a selectivity (with respect to sodium chloride) of up to 99% with a specific permeability of 0.40–0.55 $m^3/m^2.d$.[117]

In the near future, technical development will be directed towards the search for new polymers for the production of highly effective gas-separating membranes and membranes with functions analogous to those of biological membranes.

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"Khimvolokno" (Chemical Fibre)
Scientific and Industrial Combine,
Mytishchi