Russian Chemical Reviews **77** (11) 983 – 993 (2008) © 2008 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2008v077n11ABEH003795

Organic solvent nanofiltration: prospects and application

A V Volkov, G A Korneeva, G F Tereshchenko

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Abstract. The key lines of research in a new field of the membrane science and technology, *viz*., organic solvent nanofiltration, are considered. The prospects for its use in chemical, petrochemical and food industries are discussed. Attention is focused on membranes developed for this method. The bibliography includes 123 references.

I. Introduction

In the past years membrane separation methods became widespread in different fields of industry and medicine, the number of problems solved using these methods continually grows. One of them, nanofiltration,† allows one to isolate target components with molecular weights ranging from hundreds to several thousands daltons from multicomponent solutions.[1,2] Until recently, nanofiltration has been used primarily for the separation of aqueous media (*e.g*., for water treatment); in the past one and a half decades, significant progress was achieved in the separation of components and concentration of non-aqueous solutions. Nanofiltration of non-aqueous (organic) solutions is applied to separate compounds dissolved in solvents with molecular weights ranging from 200 to 1400 Da with concomitant passing of the organic solvent through the membrane. In the literature, two main terms are used, for the designation of such process, *viz*., 'organic solvent nanofiltration' (OSN) and 'solvent resistant nanofiltration' (SRNF). The isolation of the target components with the use of both porous membranes with electric charge on the surface (as in the case of aqueous media nanofiltration[2]) and electroneutral and even dense membranes is referred to as nanofiltration.

The absence of phase transitions in the separation of compounds ensures low energy consamption of this technology compared to conventional separation methods. Sometimes nanofiltration is applied in the combination with other separation processes (distillation, extraction, pervaporation and others) as a preliminary stage of the target product concentration.[3–7] In some cases organic solvent nanofiltration is the only possible way of the separation of thermally unstable systems (the separation of intermediates during replacement of organic solvents in the course of a multistage organic synthesis[8–11] can be given as an example).

One of the examples of the application of nanofiltration in industry is the process of motor oils dewaxing (MAX-DEWAX-process, developed by 'Exxon Mobil' corporation) with the daily capacity of 11 500 m^3 with respect to the initial mixture.[3–7]

At present, the possibility of the application of organic solvent nanofiltration in homogeneous catalysis,[12–30] oil and gas, chemical and food industry is being investigated.[3–7,31–43] In the present review, the main applications of organic solvent nanofiltration are discussed along with the description of the main types of membranes designed for this method.

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Received 2 April 2008
Uspekhi Khimii **77** (11) 1053 – 1064 (2008); translated by I V Glukhov

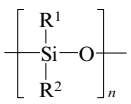
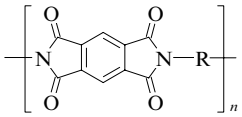
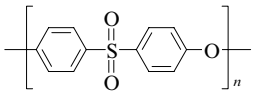
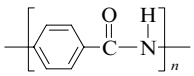
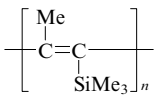
† According to the IUPAC nomenclature on membranes and membrane technology, nanofiltration is a baromembrane process of separation in which membranes reject particles and solutes larger than 2 nm.[1]

II. Membranes for organic solvent nanofiltration

Successful and efficient realisation of organic solvent nanofiltration requires that the membranes used in this process meet the following demands. They should possess mechanical and chemical resistance in organic solvents, exhibit high retention potential with respect to the target product and transmit well organic solvent. Polymeric or inorganic membranes are used for the nanofiltration of organic media.

Modern polymeric materials used to manufacture nanofiltration membranes for non-aqueous solvents can be divided into three classes (Table 1). The first class contains highly permeable rubbers, first of all, cross-linked silicon rubbers. These polymers are used to produce composite membranes in which the selective layer is deposited on the porous supporting material.[44–46] The second class comprises the low permeable polymeric glasses. These are first of all polyamides, polyimides and polysulfones. From these, membranes of asymmetric type are produced, in which selective and support layers are made of the same polymeric material.[47] The third class of polymeric materials used for the production of nanofiltration membranes contains highly permeable polymeric glasses, for example poly(1-trimethylsilylprop-1-yne) (PTMSP). The membranes of both composite and asymmetric types are manufactured on their base.[48–51]

Table 1. Polymeric materials used for the preparation of nanofiltration membranes for organic media.

Polymer	Representative	Formula
Highly permeable rubbers	silicon rubbers	 R^1, R^2 = Alk.
Low permeable polymeric glasses	polyimides	
	polysulfones	
	polyamides	
Highly permeable polymeric glasses	PTMSP	

Highly permeable silicon rubbers or polysiloxanes (see Table 1) have good thermal and chemical stability. They are used for the preparation of composite membranes with a thin continuous selective layer made of silicon rubber deposited on the porous polymeric support. The thickness of selective layer of commercial membranes MPF-50 (produced by 'Koch Membrane Systems' Germany) is $\sim$100 nm.[44] At low swelling values, the transport of liquids through the selective layer can be performed predominantly by the dissolution–diffusion model.[52]

High swelling values of rubbers in organic media ensure high transport characteristics of membranes, but adversely affect their mechanical properties and selectivity of the separation. Using chemical cross-linking of the polymer of selective layer it is possible to optimise the permeability values as well as the selectivity of OSN membranes based on highly permeable silicon rubbers.[45,46]

High chemical and thermal stability as well as good mechanical strength of low permeable polymeric glasses (polyamides, polyimides, polysulfones; see Table 1) allow producing nanofiltration membranes with asymmetric porous structure by a phase inversion method. The separation of organic compounds on such membranes occurs according to their sizes. Molecules with the size larger than the nanopore section of the selective layer cannot pass through the membrane, *i.e.*, are 'cut off' by it. A drawback is that upon the contact with different organic solvents the irreversible changes in the morphology and structure of the selective layer of membranes can occur, which affects their transport and separation characteristics.[53–56]

For the nanofiltration of organic media, it is possible to create membranes based on highly permeable glassy polymers, for example, poly(1-trimethylsilylprop-1-yne) (see Table 1).[48–51] The presence of a bulky substituent and double bond in the main chain of PTMSP ensures uniquely high degree of unrelaxed free volume (up to 25%). The nanoporous structure (at a level of 1 nm) of the selective layer is spontaneously formed by casting continuous membranes in a polymer–solvent–precipitator system as in the case of the preparation of membranes based on low permeable glassy polymers. Such a unique nanoporous structure of PTMSP ensures an at least tenfold increase in ethanol permeability through the membrane based on this polymer compared to that through the membranes based on silicon rubbers.[49,50] In more detail polymeric materials and membranes used for the nanofiltration of organic media are discussed in a recent review.[57]

Inorganic nanofiltration membranes are less widespread as compared to relatively cheap membranes based on polymeric materials despite their excellent mechanical characteristics and the absence of swelling upon contact with solvents. Only descriptions of laboratory tests of inorganic membranes are available.[58–63] Thus silicozirconium inorganic membranes were prepared using sol–gel method.[58–61] The nanoporous structure of the selective layer varied in the range of 0.8–5.0 nm allowed attaining high cut-off values of 200–2000 Da in organic solvents. Using such membranes, it became possible to partially separate higher alcohols (C_6, C_8 and C_{10}) and hydrocarbons (C_6, C_{10} and C_{15}) from their solutions in ethanol at temperatures up to 60 °C and pressures up to 30 atm.

Another approach to the creation of inorganic membranes for nanofiltration of organic solvents is the modification of hydrophilic membranes based on γ-Al_2O_3/TiO_2(anatase) by grafting silyl groups containing hydrocarbon substituents of various length (C_1 and C_8).[62,63]

Using such membranes, it became possible to attain high cut-off values of 410 and 650 Da and permeability of hexane equal to 3 and 5 litre m^{-2} h^{-1} atm^{-1} for membranes with C_8 and C_1 alkyl groups, respectively.

Unfortunately the number of OSN membranes available on the market is not yet wide and it is not always possible to find the required combination of permeability and selectivity parameters, which essentially limits the scope of application of this promising separation technique.

III. The application of nanofiltration in petrochemical industry

It is well-known that the presence of long-chain saturated hydrocarbons (paraffins) essentially increases the solidification temperature of motor oils. One of the ways to extract the paraffins from motor oil is solvent dewaxing. This approach is based on cooling the solution of motor oil in an organic solvent (or a mixture of solvents) (down to -20 °C) to crystallisation of paraffins with subsequent filtration on the drum filter. The presence of an organic solvent favours the decrease in viscosity of the system at such a low temperature. After filtration, the solvent is normally regenerated by distillation. It was suggested to apply the nanofiltration at the stage of motor oil concentration before the distillation stage in order to reduce energy consumption (Fig. 1).[3–7]

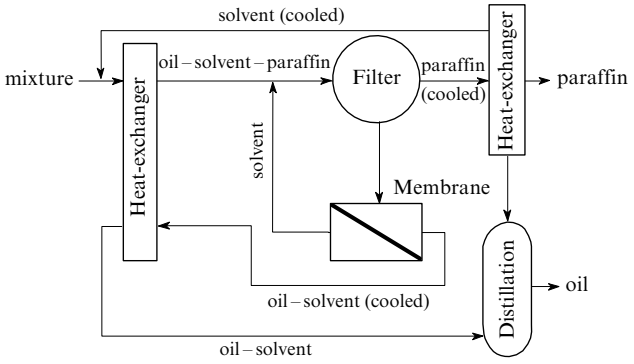


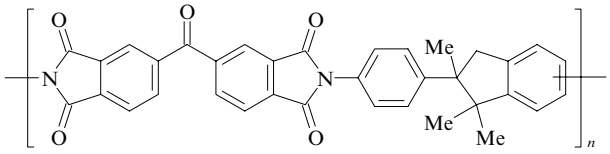
Figure 1. The flow chart of the nanofiltration separation of organic solvents for motor oils dewaxing (adopted from Ref. 4).

In the middle of the 1980s, 'Exxon Research and Engineering' (USA) patented a number of membranes based on cellulose acetate,[64,65] polyimides (reverse osmosis asymmetric membranes) [66] and polycarbonates,[67] which can be used for the separation of a wide range of solvents used for oil dewaxing.

Several big companies have implemented the process of nanofiltration-based regeneration of organic solvents used in dewaxing of motor oil at both the pilot and industrial scale. A pilot unit was built by 'Shell Oil' for the separation of mixtures of oil with widely used organic solvents in this process, *viz*., ethyl methyl ketone and toluene.[68] It was suggested to use halogen-substituted polysiloxanes with limited swelling in these media as the membrane material. The production capacity with respect to highly viscous oil was 300 t per day, and solvents mixture consumption (1 : 1) was about 1720 t per day. The active area of the applied composition membranes based on poly(3,3,3-trifluoropropylmethylsiloxane) was equal to 1400 m^2, which ensured the regeneration of the solvent mixture (1270 t per day) with residual oil content below 1%. Thus, 3/4 of the daily consumption of the solvents was taken out from the distillation recycle.

The process patented by 'Texaco Inc.' (USA) for the separation of oil and mixture of the same solvents using membranes based on cross-linked polyimines [69] and cross-linked polysiloxanes [70,71] is characterised by lower effectiveness: the permeate (filtered solution) contained up to 13 wt % of oil.[70,71]

In the framework of a pilot joint project of 'W R Grace' and 'Mobil Oil', an analogous process was carried out with the application of asymmetric membranes based on polyimide Matrimid 5218.[72–77] Compared to the previously described methods of separation [64–71] the extraction of solvents and their regeneration are performed at low temperature, which allows reducing significantly the energy consumption.



Matrimid 5218

The pilot unit that included 36 helical membrane modules has worked for 16 months with a daily capacity of 600 m^3 per day of the initial mixture containing 20 wt % of oil.[3–6] The oil content in permeate did not exceed 1 wt %. The separation process was carried out at 41 atm and 10 °C, while the capacity of membrane unit over the operation time decreased from 6–8 $m^3\ h^{-1}$ down to 2.7–4 $m^3\ h^{-1}$ (depending on the fraction).[3,6]

After performing the pilot tests, 'Mobil Beaumont Refinery' (Texas, USA) in 1998 started the industrial production of dewaxed motor oil with the nanofiltration recycling of organic solvent mixture at low temperature.[3–6] The daily capacity on the initial mixture was 11 500 m^3. After first 14 months of running, the productivity of membranes halved (from 80 down to 40 $m^3\ h^{-1}$) but the quality of solvent purification was retained (the residual oil contents in permeate was equal to 0.2 wt %–0.8 wt % depending on the oil type). Thus it became possible to recycle up to 25%–50% of the solvent.

Optimisation of conditions of industrial dewaxing of motor oil with the application of nanofiltering separation (MAX-DEWAX-process) allowed 'Exxon Mobil' and 'W R Grace' to increase oil productivity by 25% with the concommitant decrease in paraffin contents in the final product by 3 wt %–5 wt %. The reduction of energy consumption per product unit was equal to 20% compared to the traditional production chart. In the result, the annual profit of companies increased by 6.1 million USD, and overcame capital costs (5.5 million USD) for the process optimisation in less than a year. For the creation of this membrane technology, the company was awarded one of the most prestigious world awards in industrial area, 'The Kirkpatrick Chemical Engineering Honor Award'.

IV. The application of nanofiltration in homogeneous catalysis

Transition metal complexes (Pt, Pd, Ru, Rh and others) with organic ligands are used as homogeneous catalysts in many catalytic processes of the basic organic synthesis, petrochemical and fine organic synthesis. Such processes include substantial part of transformations that involve carbon monoxide (hydroformylation, hydrocarboxylation, hydrocarbalkoxylation, carbonylation), reactions of hydrogenation, alcoholysis, positional isomerisation of an unsaturated carbon–carbon bond, hydrocyanation, hydrosilylation, *etc*. The technology of such processes requires a stage of product separation from an expensive catalyst, and for continuous modes, a recycling stage, which in many

cases is associated with high investments and energy cost. For example, in the case of oxosynthesis of butyl alcohols with the use of a homogeneous cobalt-containing catalyst (120–160 °C, 270–300 atm) the cost of catalyst recycling stage makes a significant part of all investment and operating costs.[78]

This is often the factor that limits the commercialisation of new inventions. In particular, this applies to the processes of oxosynthesis of higher fatty alcohols ($>C_6$) and their functional derivatives under conditions of homogeneous catalysis with the use of catalysts based on rhodium complexes.[79–82] Rhodium-containing catalytic systems that possess high activity and selectivity and ensure mild conditions of the process (90–100 °C, 15–17 atm) are partially or completely deactivated at the recycling stage.[83,84] Efficient separation of the catalyst from the reaction products, its rectivation and recycling is the only way to organise a homogeneous catalytic process and to increase the lifetime of the metal complex catalyst.

Several ways to solve the problem of homogeneous catalyst recycling are described.[12–14,85] All of them require the creation of systems 'catalytically active complex–reaction medium' that are specially adapted to the method of the separation of the catalyst from the product, *e.g.*, distillation, extraction or decantation. Methods for the creation of such systems can be subdivided into several types.

1. The reaction is carried out in two-(multi-)phase systems. If a catalyst is soluble in one phase and the reaction product, in another, then they can be easily separated by decantation. This approach was implemented in a number of industrial processes, such as propylene hydroformylation (Ruhrchemie/Rhöne-Poulenc process[86]) and allyl alcohol hydroformylation (Kuraray process[87]) in water–organic media, and also in the preparation of olefins with the use of non-aqueous two-phase systems (SHOP-process[88]). A major drawback of this approach is that in most cases the substrate and the reaction products are insufficiently soluble in the phase that contains the homogeneous catalyst, which dramatically decreases the reaction rate. Immobilisation of catalysts in the aqueous phase is sometimes used to increase the rate of the process. Such an approach was called SAPS (Supported Aqueous Phase Catalysts).[89] Organometallic complexes are dissolved in a thin layer of water deposited on a hydrophilic supporting material with high surface area (*e.g.*, SiO_2). This allows carrying out the catalytic reaction on the water–organic phase interface, the activity of a catalytic system being independent of the solubility of substrates in water.[90]

2. Chemical cross-linking of catalytically active complex with an insoluble support. The essence of this approach is to ensure the ease of subsequent catalyst isolation by filtration.[91,92] Insoluble small-size particles based on inorganic or polymeric materials can be used as supports. The drawback of this method is the reduction of activity of a catalytic system upon cleavage of covalent bond with the support material and dissolution of the catalyst fragments in the reaction mixture (the so-called 'leaching').

3. Cross-linking of catalytically active complex with the support (linear polymers or dendrimers) soluble in the reaction mixture.[93–96] In this case, the efficiency of catalysis compared to the previous method is increased as catalytic sites are virtually uniformly distributed over the entire system. Soluble catalytic complexes can be separated by ultra- or nanofiltration. However, this approach is yet to find its commercial application.

4. Organic solvent nanofiltration, which allows effective retention of homogeneous catalysts, including organometallic complexes, with molecular weights of about 300–1200 Da with simultaneous removal of reaction products and the solvent. The advantage of this approach is that the optimised catalytic complex based on transition metals can be used directly, without additional modification mentioned above.

An effective way to solve the problem of homogeneous catalyst recycling without their deactivation is the use of a chemical reactor combined with nanofiltration separation unit (Fig. 2). The separation process can be performed either in a continuous mode together with the chemical reaction in the reactor or in a periodic mode. In the latter case the reaction mixture is supplied into the nanofiltration unit after completion of the chemical reaction, and the isolated catalyst is loaded into the reactor again.

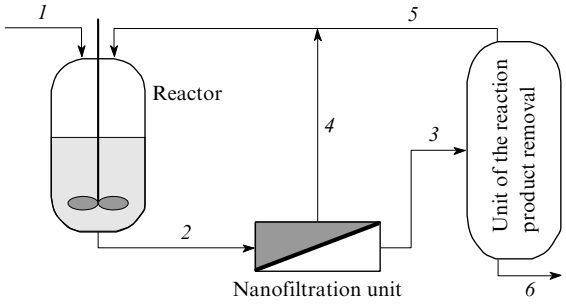


Figure 2. The flow chart of the integration of chemical reactor with the unit of nanofiltration concentration of a homogeneous catalyst and the unit of the target reaction product removal.
(*1*) substrate, (*2*) reaction mixture, (*3*) permeate enriched in the target product, (*4*) retentate enriched in the catalyst, (*5*) mixture of substrate and solvent, (*6*) target product.

It should be noted that the realisation of this process in the continuous mode has a number of limitations. First of all, the reaction rate and, consequently, the degree of conversion of the substrate should be as high as possible because the substrate and the reaction products are simultaneously removed from the reaction volume through the membrane due to insignificant difference in their sizes. Second, the necessity of combining the parameters for the realisation of chemical transformation and nanofiltration separation of the reaction mixture (temperature, pressure *etc.*) limits the number of possible reactions due to the limited interval of operating conditions of the existing nanofiltration membranes.

In the patent literature, one can find a number of examples of baromembrane methods of separation of homogeneous catalysts from non-aqueous media using different polymeric membranes. The first works on the separation of homogeneous catalysts from reaction mixtures using baromembrane processes started half a century ago. For example, in 1959 'American Oil' patented a method of membrane isolation (reverse osmosis) of acid catalysts employed in hydrocarbon conversion processes using hydrophobic continuous membranes based on polyethylene.[15]

In 1971 'British Petroleum' patented an ultrafiltration method for the separation of transition metal (rhodium, nickel, vanadium, *etc*.) complexes from olefin dimerisation and propylene hydroformylation products with the use of membranes based on cellulose acetate.[16] The same company obtained in 1974 a patent for the method of separation of organoelement compounds (metals of Groups V, VI and VII of the Periodic Table) with the concentration being in the range of 1 ppm to 10 wt % from non-aqueous media (in particular, from reaction mixture after completion of alkene hydroformylation reaction). The process was carried out using membranes based on silicon rubber at the temperatures 0–200 °C and the pressure up to 277 atm.[17]

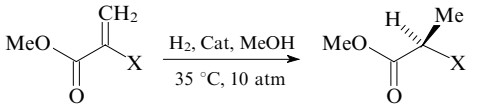
The use of asymmetric membranes based on aromatic polyamides and polyimides for the reverse osmosis separation of organoelement catalysts from organic media containing compounds with nitrile groups was patented by 'E I du Pont de Nemours' company in 1974.[18] In 1992 the German company 'Hoechst Aktiengesellschaft' realised the process of concentration of a wide range of organoelement compounds and metal carbonyls that can be used as catalysts from organic media with membranes based on aromatic polyamides.[19]

In 1993 'Membrane Products Kiryat Weitzman Ltd' obtained patents for nanofiltration membranes of MPF series stable in organic solvents and based on silicon rubbers [*e.g*. polydimethylsiloxane (PDMS)] for the isolation of different solutes from organic media, *viz*., catalysts, organoelement compounds, pigments, oils, *etc*.[20, 21] One of the first practical applications of such membranes was the separation of homogeneous catalyst based on rhodium complexes and non-bonded organophosphorus ligands from the reaction mixture containing enantiomeric aldehydes (patent of 'Union Carbide Chemicals and Plastics Technology'[22]). After the hydroformylation reaction was over, the authors managed to reduce the catalyst concentration in the mixture of aldehydes (30%) and acetone as a solvent (70%) from 389.3 down to 5.6 ppm in three stages of consecutive separation with MPF-50 membranes.

As the result of the investigation of the same catalytic system based on rhodium complexes and a mixture to be separated with similar composition (aldehydes in solution of acetone or butyric aldehyde), a patent[23] was issued in 1997 for the method of the membrane isolation of homogeneous catalysts. Examples given in the patent show that the retention‡ of a rhodium catalyst is 92.8% in the case of polydimethylsiloxane membranes MPF-50 in the form of a helical unit (unit active area 0.25 m^2) at a pressure of 27.5 atm.

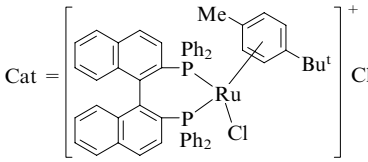
For the first time, a model of the integration of a chemical reactor with a unit for nanofiltration separation of non-aqueous media has been presented.[24] The characteristics of this model were designed for the application of a hydrophobic MPF-60 membrane stable in solvents and molecular weight cut-off (MWCO) at 400 Da. It was shown that for a number of reactions typical of fine organic synthesis parallel application of nanofiltering separation in a continuous mode allows increasing the yield of a target compound, reducing the time of reaction and increasing the selectivity of the process up to the full elimination of side reactions.

The first experimental proof of the efficiency of a combination of nanofiltration separation with chemical reactor in a continuous mode was obtained in 2001 by the research group of professor Vankelecom.[25] Enantioselective hydrogenation of dimethyl itaconate and methyl 2-acetamidoacrylate (MeOH, 35–37 °C, 10 atm) was carried out in the presence of homogeneous catalysts Ru-BINAP (929 Da) and Rh-EtDUPHOS (723 Da), respectively (1).

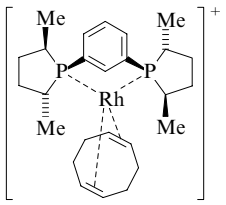


(1)

X = CH_2CO_2Me;



Cl^- (Ru-BINAP),



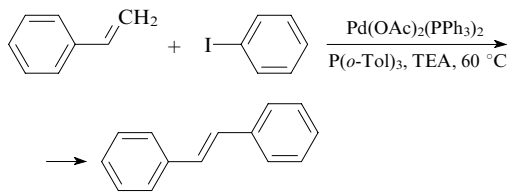
TfO^- (Rh-EtDUPHOS), X = NHAc.

In this experiment, the transmembrane pressure (10 atm) was created using hydrogen which was also a reactant of the chemical reaction. For the separation of reaction mixtures, MPF-60 membranes ('Koch International B V'; cut-off value 400 Da) were used. The obtained retention values for these catalysts were equal to 97%–98%. It was shown that in the course of nanofiltration process it becomes possible to recycle the organoelement catalyst in the active form, as even after 10 consecutive reaction–separation cycles the yield of the target enantiomer remained high. A slight decrease in the conversion degree of the esters with the time was explained by incomplete rejection of the catalyst by the membrane. Turnover numbers of the catalysts§ Ru-BINAP and Rh-EtDUPHOS in a hybrid chemical reactor–nanofiltration unit were equal to 1950 and 930, respectively.

A possibility of a semi-continuous mode for the nanofiltration separation of a homogeneous catalyst by an example of the Heck reaction (2) has been demonstrated.[26] This reaction was carried out in three different solvents: ethyl acetate–acetone system (1 : 1), *tert*-butyl methyl ether and tetrahydrofuran. Following arylation, the homogeneous catalyst was separated from the reaction mixture and recycled with the use of asymmetric solvent-resistant polyimide membranes (W R Grace) (pressure 30 atm). Depending on the solvent, the following fluxes (J) through the membrane and retention values (R) of the catalyst were obtained:

‡ Retention coefficient is the difference in concentration of the target product in the initial solution and the filtrate divided by its concentration in the initial solution.

§ Turnover number of a catalyst is the number of moles of a substrate that are converted by one mole of the catalyst into the target product during the entire time of the catalyst tests.



(2)

o-Tol is Tol, TEA is triethylamine.

Solvent	J /litre m^{-2} h^{-1}	R (%)
Ethyl acetate – acetone (1 : 1)	32.3	90
tert-Butyl methyl ether	11.3	96
Tetrahydrofuran	45.8	96

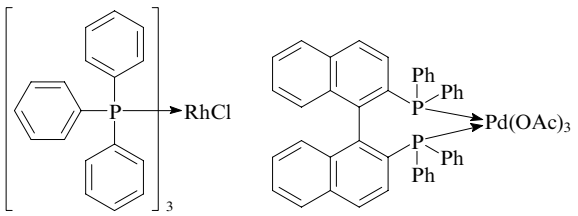
The minimum time required for the completion of the reaction (25 h) was observed for the ethyl acetate – acetone mixture. After 5 recycles, the turnover numbers were almost identical for all solvents, equalling about 1200.

The nanofiltration recovery of phase transfer catalysts was described.[27] As a model reaction, the conversion of heptyl bromide (179 Da) into heptyl iodide (226 Da) under the action of potassium iodide has been selected. The process was carried out in a two-phase system, water – toluene, in the presence of a catalyst, tetrabutyammonium bromide (TBABr, 322 Da, solubility in toluene 1.6 g litre^{-1}) or tetraoctylammonium bromide (TOABr, 546 Da, solubility in toluene 380 g litre^{-1}). For the first time, organic solvent nanofiltration through a range of commercial nanofiltration membranes was compared to that through membranes based on silicon rubber and terpolymer of ethylene, propylene and diene (EPDM-resin), each being 0.6 mm thick. The membrane characteristics are given in Table 2. It should be noted that all membranes studied except for Desal-5 asymmetric membrane are hydrophobic.

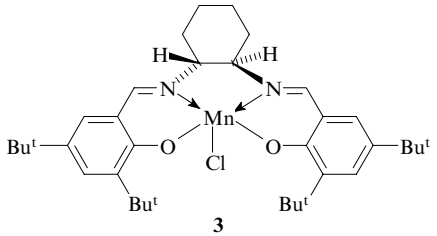
The following conclusions could be drawn. First of all, in all cases (except for the membranes based on rubber) the initial decrease in permeability in pure toluene was observed, which can be attributed to the partial membrane compaction under high pressure. Second, upon the introduction of the catalyst (0.05 M salt solution) into the mixture to be separated, the total flux through the membrane reduced by 20% – 65% due to fouling of the membrane surface with the homogeneous catalyst. Third, the manufacturer's data on molecular weight cut-offs do not always correspond to the values obtained in different solvent – model compound systems.

The highest productivity and retention of both catalysts in toluene were obtained with asymmetric membranes of the STARMEM series.[27] Using STARMEM 122 membranes in three consecutive reaction – separation recycles, identical conversion rate of the substrate was obtained over the same time and without addition of the catalyst (rejection > 99%). At the same time, low retention of reaction product by the membrane (22%) facilitated its isolation from the reaction mixture in a reasonably pure state, with minimum catalyst content.

Scarpello *et al.*[28] used an analogous range of commercial nanofiltration membranes (MPF-50, Desal-5 and STARMEM 120, 122 and 240) for the separation of three catalysts — complexes of ruthenium (**1**), manganese (**2**) and palladium (**3**) — from a number of solvents, which are often used in organic synthesis: dichloromethane, tetrahydrofuran and ethyl acetate.



1 **2**



3

Compound	M /Da	Name	Reactions
1	925	The Wilkinson catalyst	hydrogenation, reduction
2	849	Pd-BINAP	asymmetric C – C-addition
3	622	The Jacobsen catalyst	chiral epoxidation

It was shown,[27] that membranes of STARMEM series are preferable for the nanofiltration of solutions in ethyl acetate (the highest fluxes and catalyst rejection > 95%). Unfortunately, in dichloromethane and tetrahydrofuran the

Table 2. Nanofiltration characteristics of membranes: cut-off value (manufacturer's data), flux (J /litre m^{-2} h^{-1}) and catalyst rejection [(R (%)] at the transmembrane pressure of 30 atm (adopted from Ref. 27).

Membrane		MWCO /Da	Manufacturer	Pure toluene	0.05 M TBABr in toluene		0.05 M TOABr in toluene	
name	type[a]			J	J	R	J	R
MPF-50	Com	700	Koch	21	19	61	19	48
MPF-60	Com	400	Koch	5	5	89	2	86
Desal-5	A	350	Osmonics[b]	6	3	55	4	62
STARMEM 122	A	220	W R Grace	39	23	> 99	26	> 99
STARMEM 120	A	200	W R Grace	34	20	> 99	24	> 99
STARMEM 240	A	400	W R Grace	38	28	80	16	> 99
Silicon rubber	Con	–	Silex	0.8	0.3	> 99	0.2	> 99
EPDM-Rubber	Con	–	William Warne	0.3	0.2	> 99	0.3	> 99

[a] Notations: Com is composite membrane, A is asymmetric membrane, Con is continuous membrane; [b] at present, 'General Electrics'.

polyimide STARMEM 240 membranes are unstable, while STARMEM 120 and 122 membranes have low permeability. Significantly better transport characteristics in CH_2Cl_2 were shown by Desal-5 membrane, while in THF, by MPF-50 one (with comparable catalyst rejection for each type of solvent).

The effectiveness of nanofiltration separation of a phase transfer catalysts (TOABr, 546 Da, ethyl acetate – acetone, 1 : 1) and the Heck reaction catalyst [$Pd(OAc)_2(PPh_3)_2$ + $Pd(o\text{-Tol})_3$, 749 Da, toluene] using STARMEM 122 membrane was studied.[29] In the former case, high rejection of the salt was achieved (> 99%), while the turnover number of catalyst was equal to 28 after two recycles. In the later case, after four recycles of the catalyst (turnover number was equal to 1220) the reaction rate decreased fourfold. The reason for the slowing-down of the reaction was the destruction of the catalyst during the process where fragments with lower molecular weight were formed, including palladium black.

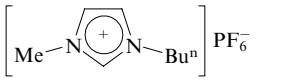
In the synthesis of *trans*-stilbene according to the Heck reaction [see reaction (2)] in THF – water system at 60 °C in the presence of the above-mentioned catalytic system, a fivefold decrease in the reaction rate was observed as well as precipitation of palladium black.[30] The use of STARMEM 122 (20 °C, 30 atm) membranes allowed only 6 recycles of the catalyst to be carried out (the turnover number was equal to 689 in 120 h). The most efficient recycling of the catalyst was achieved in the catalysis of reaction (2) by the complex $Pd(OAc)_2 \cdot PPh_4Br$. The solvent exchange (THF – water system → acetonitrile) increased the thermal stability of the catalyst (reaction was carried out at 160 °C), prevented the precipitation of palladium and decrease in the reaction rate in the subsequent recycles. It was shown [30] that with acetonitrile as solvent and a resistant MPF-60 membrane, it is possible to achieve high turnover numbers of the Heck catalyst (1062 after 10 recycles in 46 h).

A relatively low reaction rate during the first cycle is the result of the slow formation of the catalytic complex $Pd(OAc)_2PPh_4Br$ in the reaction medium from palladium acetate and tetraphenylphosphonium bromide. A number of investigations [97–103] is dedicated to the application of nanofiltration membranes for the separation of bulkier homogeneous catalysts from organic media. These include dendrimer-type catalysts;[97–100] catalysts cross-linked with soluble polymeric supports;[101] 'sandwich-like' organic salts based on metal oxides [102] and gold salts. In most cases, the preferability of nanofiltration separation in comparison to the ultrafiltration is caused by the necessity of high separation efficiency (> 99.5%) and catalyst recycling in real chemical processes, as even for the retention value equal to 99.8%, the loss of homogeneous catalyst (without account for the deactivation) due its partial permeation through the membrane after 50 recycles will be equal to 10%.

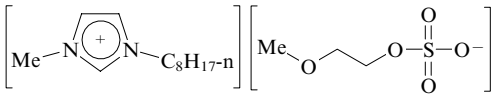
At the end of this section, it should be noted that the combination of the chemical reactor with nanofiltration separation is one of the most actively developing branches of the membrane technology.[12–30,97–103] The efficient recycling of a homogeneous catalyst allows reducing its consumption and, consequently, the cost of the final product. Besides, a significant reduction of catalyst contents in the post-reaction mixture is important from the point of view of the subsequent purification of the final product from by-products, for example, in pharmaceutical industry.

V. The application of nanofiltration for the separation of ionic liquids

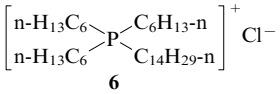
Ionic liquids are a new generation of environmentally friendly solvents.[104–106] These compounds are non-volatile organic salts (*e.g.*, **4**–**7** [107]), which are usually liquid at room temperature.



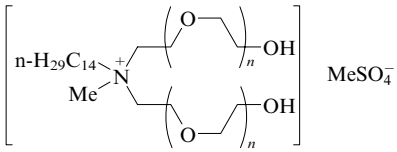
4



5



6



7

Compound	Commercial name	*M*/Da
4	$[BMIM]PF_6$	284
5	CYPHOS IL 101	519
6	ECOENG 48M	395
7	ECOENG 500	868

Ionic liquids do not mix either with water or with the majority of organic solvents, while many catalysts based on organoelement complexes are well soluble in them, which ensures the prospects of their use in organic synthesis. In addition in such organic salts the ions are most often not fully coordinated, that is why ionic liquids are very popular as non-coordinating solvents. The fact that the active site of a catalyst is virtually non-solvated in ionic liquids results in substantial increase in stability, efficiency and selectivity of a catalytic system, especially with the optimally selected ionic liquid. In this case, one can use an organic solvent as a non-miscible phase. In the result, such a medium has numerous advantages over conventional water – organic system:

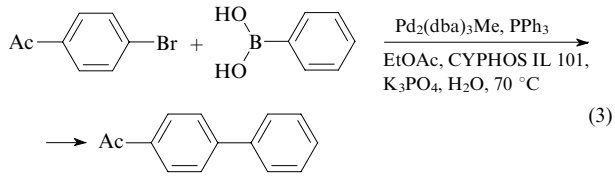
— reaction products are extracted into organic phase, while the catalyst predominantly remains in the ionic liquid;

— homogeneous catalyst does not require additional modification that would ensure its solubility, *e.g.*, in an aqueous phase.

However, partial dissolution of anionic liquid and the catalyst in the organic phase makes topical the problem of their separation from reaction products and solvent for subsequent recycling. This is performed, in particular, by organic solvent nanofiltration.[107–109] Thus it was suggested to use nanofiltration membranes of the STARMEM series with the cut-off in the range of 200 – 400 Da for the separation of ionic liquids **4**–**7** from methanol, toluene and ethyl acetate at 30 °C and pressures 30 and 50 atm.[107] It was shown that STARMEM 120 and STARMEM 122 membranes ensure rejections of CYPHOS IL 101 (**5**) and ECOENG 500 (**7**) ionic liquids in methanol and ethyl

acetate of >95% (in a flowing mode) and of about 80%–90% in toluene.

Nanofiltration separation of the final product of the Suzuki reaction, 4-acetylbiphenyl, and organic solvent using STARMEM 122 membranes was studied.[108]



(3)

dba is dibenzylideneacetone.

Performing the reaction (3) in a homogeneous system (1:1 ethyl acetate–ionic liquid mixture) led, on the one hand, to an increase the reaction rate and mass transfer due to the reduction of viscosity of the system, and on the other hand, to reduction of the destruction of the catalytic complex based on palladium compared to the reaction in pure organic solvent. As a result, the total loss of catalyst after all recycles decreased from 73.4% down to 15.9%. The minimum loss of the catalyst and stable high yields (>60%) of the final product during 12 recycles of the reaction (3) were obtained in the case of ionic liquid CYPHOS IL 101 (**5**), and the maximum turnover number of the catalyst for this system exceeded 5000.

In the hydrogenation[109] of dimethyl itaconate [see reaction (1), X = CH_2CO_2Me] in a homogeneous system CYPHOS IL 101 (**5**)–methanol, high yields of the target product were also obtained (~80%) in each recycle with high enantioselectivity (>95%). The rejection of the catalyst Ru-BINAP by STARMEM 122 membrane was ⩾95%, and that of ionic liquid CYPHOS IL 101 (**5**) ⩾92%.

Thus, the simultaneous efficient nanofiltration recycling of ionic liquids and homogeneous catalysts extends the possibilities of the practical application of these media in organic synthesis.

VI. Nanofiltration as a method of the solvent exchange in multistep organic synthesis

As is well-known, in the pharmaceutical industry significant part of pharmaceuticals is produced in a multi-step chemical synthesis, so a problem exists of solvent exchange on transition from one step to the next. This problem is usually solved by vacuum distillation, the major part of the first solvent is distilled off, then the second solvent is repeatedly added to, and distillated from, the residue. Such an approach has a number of limitations and cannot be used in the following cases: if the second solvent has a lower boiling point than the first one, if the solvents form azeotropic mixture and if the reaction product is thermally unstable.

As an alternative approach, one can use organic solvent nanofiltration. In this case, the solvent parmeates through the membrane, while the intermediate, which has a higher molecular weight, is rejected (Fig. 3). The process of solvent exchange proceeds as follows: 70%–90% of the initial solvent is removed and then the second solvent is added. If needed, the process is repeated. By varying the number of nanofiltration–dilution cycles, on can reduce the concentration of the first solvent in the mixture down to the required level.

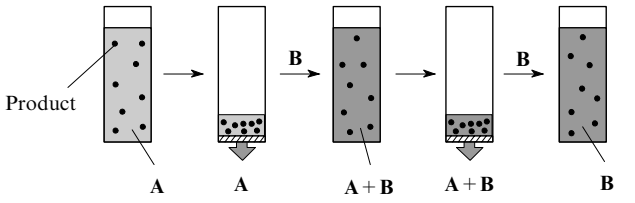


Figure 3. Schematic diagram of replacement of solvent **A** by solvent **B** without significant loss of the intermediate product using organic solvent nanofiltration.

Livingston *et al.*[8, 9, 11] have shown experimentally the applicability of nanofiltration for the replacement of a wide range of organic solvents. As an example the substitution of methanol for toluene and of ethyl acetate for methanol is given using STARMEM 122 and MPF-50 membranes, which reject the dissolved catalyst (TBABr or TOABr). After 5 cycles of filtration with STARMEM 122 membrane with the cut-off of 220 Da, the contents of toluene in methanol decreased down to 0.3%, and that of methanol in ethyl acetate, to 0.4%. At the same time, rejection of TBABr and TOABr, >99.5% and 99.9%, respectively, remained unchanged. Using MPF-50 membranes (the cut-off of 700 Da), it was possible to reduce the contents of methanol in ethyl aceate down to 0.9% in a shorter period of time but with higher losses of the catalyst TBABr (with each cycle of filtration, the rejection gradually decreased from 94.1% to 79.4%). In all experiments, the nanofiltration process was stopped when the volume of permeate reached 90% of the initial volume.

The possibility of using MPF-50 and MPF-60 membranes for the substitution of methanol for ethyl acetate in a model mixture typical of the pharmaceutical industry, was investigated.[10] The antibiotic erythromycin (734 Da) was used as a solute. The final percentage of ethyl acetate in the flux that does not pass through the membrane after 3 cycles of separation at pressure of 30 atm was equal to 4% (the volume of each retentate was equal to 40% of the initial value). Both types of membranes exhibited relatively high rejection of erythromycin: 87% and 96% for MPF-50 and MPF-60 membranes, respectively.

VII. The application of nanofiltration in food industry

In the food industry, vegetable oil is usually prepared by two ways: seeds pressing or solvent extraction (most often, with hexane). If the contents of oil in seeds is higher than 25%, the extraction method is economically profitable; it is generally used for the preparation of sunflower and soy oil. One of the most energy-consuming stages (up to 50% of the entire energy used) of the process of vegetable oil preparation is the distillation recycling of an organic solvent (hexane). If was suggested to use nanofiltration for partial removal of solvent and concentration of the oil solution before the final distillation.

Energy saving and perspectiveness of the application of organic solvent nanofiltration in the production of vegetable oil was described.[110, 111] It was estimated that the annual energy savings can be equal to ~2 Btu. However, low chemical stability of membranes available at that time was noted.[111]

In 1996 the German company 'GKSS' patented the method of preparation of membranes with selective layer based on radiation-induced cross-linked PDMS for nanofiltration of 10% solution of corn oil in hexane.[31] Upon radiation-induced cross-linking of selective layer of membranes, it was possible to increase the oil content from 66% up to 90% with the concomitant decrease in the permeability of membranes by 20%.

Later, Stafie *et al.*[32] have investigated nanofiltration separation of hexane from its mixtures with sunflower oil using laboratory samples of composite nanofiltration membranes based on cross-linked PDMS (the effective thickness of a selective layer was equal to ~ 2 μm). These membranes exhibited stable selectivity characteristics in the filtration of 8% solution of sunflower oil in hexane (the total flux was equal to ~ 12 litre m^{-2} h^{-1}, while the rejection was more than 90%) at the pressure of 7 atm and temperature of 20 °C during 4 days (6 h per day). It was shown that with the concentration of sunflower oil equal to 30%, the osmotic pressure of the solution at room temperature is equal to 4.3 atm. Hence, it is advisable to apply the organic solvent nanofiltration only at the step of the initial concentration of oil solutions, before the step of the distillation separation. The increase in oil retention upon the increase in the pressure is explained by the fact that the solvent flux through the membrane is increased to a greater extent as compared to the transport of bulky oil molecules. This results in the increase in hexane content in the permeate upon increase in pressure.

Since different triglycerides are the main components of vegetable oils, these compounds are often used as models of oil. Thus the rejection of a number of triglycerides was investigated for their solutions in hexane (concentration was equal to 500 mg $litre^{-1}$) at different pressure and temperature.[33] Nanofiltration was performed through commercial composite membranes based on silicon rubber (Membrane D, 'Osmonics'). As one can see from Table 3, the rejection of triglycerides is increased with the increase in their molecular weight, while the cut-off of Membrane D in hexane is estimated as 900 Da.[34]

Table 3. The rejection of triglycerides in the nanofiltration of their solutions in hexane through Membrane D (45 °C, 41 atm) (adopted from Ref. 33).

Triglyceride	*M* /Da	*R* (%)
Tricaprin	554	72
Trilaurin	639	81
Trimiristin	723	83
Tripalmitin	807	92
Tristearin	890	90

It is known that alcohols, ethanol in particular, can be used for the extraction of oils and other valuable components from plant raw materials.[35,112–117] The fermentative preparation of alcohols (bioethanol and biobutanol) from biomasses, which includes the pervaporation separation of alcohols using membranes based on PTMSP is described.[118–122] Considering that the reserves of fossil raw materials are being depleted and prices for hydrocarbons will unavoidably grow, the prospects of this class of extractants is evident. Besides, the replacement of hexane by alcohols allows usage of a wider range of polymeric membranes,[47–51,111,115] including industrial membranes for the nanofiltration of aqueous media. For example, the use of polyamide membranes (Desal DK, TFC-SR1 and TFC-SR2) made it possible to increase the concentration of corn oil in ethanol from 5 to 100 g $litre^{-1}$ (Ref. 35).

Another important and actively investigated problem of nanofiltration purification of vegetable oil is the removal of free fatty acids from them.[36–43] There are several main approaches to the solution of this problem with the help of membrane technology. One of the methods implies partial removal of fatty acids at the stage of the nanofiltration concentration of vegetable oil.[36] The second method is the addition of organic solvent (*e.g.*, acetone) into oil. This solvent increases the overall flux through the membrane; predominantly the transport of free fatty acids is enhanced, the transport of triglycerides changes insignificantly.[37,38] The third way is based on the extraction separation of fatty acids with alcohols (*e.g.*, methanol) with subsequent nanofiltration separation and recycling of the solvent.[39,40] The fourth method is the nanofiltration separation of triglycerides and free fatty acids itself, without addition of an organic solvent.[38,42]

As is estimated by Ebert and Cuperus,[43] in the production of coleseed and soy oil in the European Union, up to 20 000 t of organic solvents are emitted into the environment every year. The application of nanofiltration at different stages of purification of vegetable oil allows reduction of these wastes by 95%. Thus, the application of membrane technology allows enhancement of the economics and environmental safety of the process of vegetable oil preparation.

VIII. Conclusions

Among known membrane methods of separation, the organic solvent nanofiltration is relatively new, but promising low energy demanding technology. To the present moment, the greatest practical application was found for nanofiltration in petrochemical, chemical and food industries.

At the industrial scale, nanofiltration is applied for dewaxing of motor oils. The application of this method of separation at the concentration step, before distillation, allowed increasing the productive capacity of the process by 25% and decreasing the energy costs per production unit by 20% with the capital cost repayment period in less that 1 year.

Nanofiltration changes dramatically the solution of a complicated problem of chemical technology *viz.*, optimisation of synthesis–separation stages. Thus selecting the components of a catalyst–solvent–nanofiltration membrane system it is possible to achieve fair results of the separation and recycling of a catalyst and thus to lower significantly the limiting barriers in the commercial application of homogeneous catalysts. One should specially stress the prospects of this approach for the application of ionic liquids, which represent new solvents for chemical technology .

It was shown that distillation and rectification processes, which are commonly used for the solvent exchange in multistep processes can successfully be replaced by lower energy-demanding nanofiltration technologies, especially in the cases where intermediate products are thermolabile.

The wide industrial application of nanofiltration is still restricted by a small assortment of commercially available membranes. It is evident that the variety of chemical processes requires widening of membrane assortment,

which will cause the intensification of investigations in this field. In the course of preparation of this manuscript for publication, a critical review was published,[123] which considers the organic solvent nanofiltration from the point of view of separation process at a molecular level.

Authors would like to thank Dr. A A Svitzov for the fruitful discussion of this paper. The work was carried out with the partial support in the framework of the national contract No. 02.513.11.3358. A V Volkov expresses his gratitude to the Fund of Support of Russian Science for the partial financial support.

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[a] — *Mendeleev Chem. J. (Engl. Transl.)*