

**PROCEEDINGS OF
FIRST INTERNATIONAL CONFERENCE ON
PERVAPORATION PROCESSES
IN THE CHEMICAL INDUSTRY**

Edited by
R. Bakish

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P.O. Box 148
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FIRST INTERNATIONAL CONFERENCE ON
PERVAPORATION PROCESSES
IN THE CHEMICAL INDUSTRY**

Atlanta, Georgia, February 23-26, 1986

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PROCEEDINGS OF
FIRST INTERNATIONAL SYMPOSIUM ON
PERMANENT LANTHANUM REFINING
IN THE LANTHANUM INDUSTRY
Atlanta, Georgia, 1985

Edited by
L. B. B.

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PREFACE

This small volume contains the papers presented at The First International Conference On Pervaporation Processes In The Chemical Industry held in Atlanta, Georgia. The conference was a milestone event which brought together virtually all the principal players in this emerging separation technology from around the world. The attendees came from Canada, France, Holland, Israel, Japan, United Kingdom, West Germany and eight States of The Union. The conference was jointly sponsored and organized by GFT of Homburg/SAAR, West Germany and Bakish Materials Corporation of Englewood, New Jersey, U.S.A.

In all eighteen papers were presented and all but three are in this volume. They have been rearranged from the order presented at the meeting in the hope of making this a more coherent volume. While we delayed publication in the hope to receive the three missing papers and print the complete record of the event, further delay would be counterproductive. The conference also hosted, under the leadership of Professor Rautenbach, the co-chairman of the conference, an exciting panel discussion among the leaders of this technology. The participants addressed numerous questions to the panelists. The discussion was exciting and most informative. It is indeed regrettable that the record of the panel could not be made part of the proceedings.

At this time we are in the process of preparing the program for The Second International Conference On Pervaporation Processes In The Chemical Industry. All those working in the field, who wish to participate or submit papers for presentation are kindly requested to forward inquiries about the event to the writer. The exact time and place for the second conference will be released as soon as the arrangements are complete.

R. Bakish,
Englewood, N.J.
July 1, 1986.

INTRODUCTORY REMARKS

Ladies and Gentlemen,

On behalf of Robert Rautenbach, the conference co-chairman, and myself I wish to extend a most cordial welcome to you on the occasion of The First International Conference On Pervaporation Processes In The Chemical Industry. This is a milestone event for this emerging technology. It is my sincere hope that you, the participant in this event, will find the content of the program and the arrangements which we have made for you to your satisfaction. This should be an event to be followed by many as this technology becomes accepted and begins to make its contributions to the chemical industry.

But before I turn the podium to Hartmund Brueschke, who will start the presentations, I do wish to use it to thank all the speakers and the academic institutions and companies which sponsored their travel, for their willingness to come from near and far to share their work with us.

I also wish to make certain that I extend on behalf of all of us gathered here to day sincere thanks to Gunter Tusel of GFT. This conference was his idea, it would not have become a reality without his help.

And now without further ado Hartmund, the floor is yours.

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STATE OF ART OF MEMBRANES FOR PERVAPORATION PROCESSES

H.E.A. Brüscke

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The term "pervaporation" is used to describe a separation process, where a liquid mixture is in direct contact with one side of a non-porous membrane, and where the permeated product, enriched in at least one of the components of the liquid mixture, is removed from the other side of a membrane as vapour. Although qualitative observations of pervaporation phenomena have been reported more than hundred years ago, scientific studies date back to 40 years only. Excellent single-stage selectivities, low operation costs due to high thermal efficiency, and the simplicity of operation have been recognized as major advantages of pervaporation over other conventional separation processes.

After intensive investigations in the 1950's, where homogeneous films were tested for the separation of various binary and multi-component mixtures, pervaporation membranes dropped out of the interest of membrane researchers for more than a decade. The availability of new membrane materials and the development of new techniques for membrane manufacturing, together with the search for energy-saving processes, intensive research in pervaporation membranes have restarted in the past years. A review of earlier studies and the state-of-the-art of pervaporation membranes will be given in this paper. Ongoing research on new membranes is reported, which allows for an evaluation of future developments and potential application of pervaporation membranes and processes.

More than a century ago, it had been observed in the distillation industry that the alcohol content of beverages increased over time, when the liquid was stored in some special earthenware. This observation was in contrast to normal evaporation, where the more volatile alcohol should evaporate faster than the water, and therefore the alcohol content should decrease during storage. This strange behaviour was ascribed to a special porosity of the earthenware, by which normal volatility was changed.

In 1906 (1) Kahlenberg reported on qualitative studies on the separation of mixtures of hydrocarbons and alcohols through rubber membranes. The first quantitative investigations on the separation of organic liquid mixtures were conducted by Hagerbaum in 1955 (2), who

used a micro-porous glass membrane as a barrier. Later, Binning and co-workers (3,4) started extensive investigations on the process of separating a liquid-liquid mixture into a vapour through non-porous polymer films. For a large number of feed mixtures high degrees of separation and high permeation rates were obtained in these studies. Several patents were issued, including module design and techniques for membrane manufacturing (5).

In the beginning this process was called "liquid permeation". Because of the hybrid nature of the process, that is, the presence of both liquid and vapour phase and the phase transition of the permeate on its passage through the membrane, the term "pervaporation" was later introduced. This term is believed to be more appropriate and descriptive for a process where in fact the permeate "evaporates through the membrane".

Although all investigations recognized at early stages the excellent single-stage selectivity, the high thermal efficiency and simplicity of operation of the pervaporation process, it was not entrenched in industry. The main reasons were difficulties in a reliable, large-scale membrane production, instability of the membranes and inadequacy of module design and materials.

Not more than 10 years ago new attempts were started to develop pervaporation membranes. The availability of new polymers and techniques for membrane manufacturing, together with a much better understanding of transport mechanism in polymeric membranes allowed for the development of a first generation of pervaporation membranes and modules fit for large-scale industrial application - at least for aqueous organic mixtures.

In a pervaporation process, one side of a non-porous membrane is in direct contact with a liquid mixture, whereas the permeated product is removed from the other side of the membrane as a vapour. This is effected by keeping the partial vapour pressure at the permeate side below that of the liquid feed mixture. Composition of the permeate is determined only by the transport values of the components of the feed mixture through the non-porous membrane and may be totally different from that to be expected from liquid-vapour equilibrium curves. In other words, pervaporation is a dynamic process, operating far away from thermo-dynamic equilibrium conditions. Three closely related methods of operation are described in literature for pervaporation processes (Fig. I):

- a. an inert gas is used for continuously sweeping the permeate side of the membrane
- b. a vacuum is applied to the permeate side of the membrane and the permeating vapours are continuously pumped off
- c. a condenser is installed in the evacuated permeate compartment for continuous condensation of the permeated vapours. This method has been called "thermopervaporation" by Aptel and

co-workers (6).

For economical reasons, only method "c" is applicable in large installations. In method "a" the sweeping gas will have to be recycled, requiring condensation of the permeated vapours by cooling and pre-heating, whereas in method "b" the mechanical compression of the vapours in the vacuum pump would require too high power consumptions.

As the differences in partial vapour pressures between both sides of the membrane are the driving forces for the pervaporation process, a maximum gradient has to be maintained across the membrane. The partial vapour pressure of a component in the liquid feed mixture is determined by the concentration of this component and the temperature of the mixture, whereas at the permeate side the condensation temperature is the most important parameter. For an economical operation, this condensation temperature should not be too low; therefore, high temperatures of the feed mixture will be necessary at low concentrations of the component to be removed. Therefore, resistance against high temperatures is an essential demand for pervaporation membranes and modules.

Two data are used in order to describe the performance of a membrane in a separation process:

- a) its separation capability or selectivity
- b) the permeation rate or transmembrane flux.

Both these values are in general rather complex functions of a number of variables, like temperature, feed composition, membrane material and feed side and permeate side pressures. Therefore, it is difficult to find values of general validity which specify the performance of a membrane and allow for comparison of different membranes.

Two different definitions are used in literature in order to specify the selectivity of a pervaporation membrane:

$$= \frac{C_{1,p}}{C_{1,f}} \quad (1)$$

and

$$= \frac{\frac{C_{1,p}}{C_{1,f}}}{\frac{C_{2,p}}{C_{2,f}}} = \frac{C_{1,p}}{C_{2,p}} \cdot \frac{C_{2,f}}{C_{1,f}} \quad (2)$$

where

C_1 denotes the better permeating component in a binary mixture and p and f stand for permeate and feed, respectively. In both definitions, α and β are dependent on the composition of the feed mixture. Experimental evaluation of a large number of membranes have shown that α and β are indeed functions of the respective feed concentrations; therefore, both values can be used for evaluation of the membrane only when this feed composition is given.

Only slight changes of the separation characteristics of pervaporation membranes have been found when the temperature of the feed mixture was changed (7). For practical purposes it can be assumed that selectivity is independent on temperature. At feed side pressures below 10 bar, no influence of this pressure on selectivity was observed either. Permeate side pressures do influence the selectivity of the membrane, however, maximum selectivity is obtained at permeate side pressures below 20% of the respective partial vapour pressure of the feed mixture.

It has been tried to predict the separation characteristics of a pervaporation membrane for a specified mixture by determination of the permeation rates of the single components of the mixture, as it is common in gas separation through membranes. These attempts have failed, as high-coupled effects occur in pervaporation because of the non-ideal behaviour of liquid mixtures. In some cases, the addition of low concentrations of a third component to a binary mixture may change significantly the separation characteristics of a pervaporation membrane.

Similar complexities have to be faced in describing permeation rates or transmembrane fluxes through pervaporation membranes. For the temperature dependence of the flux usually an arrhenius relation is found, whereby the activation enthalpy includes two terms: one relating to the increase in the partial vapour pressure of the components of the liquid mixture with temperature and the second term describing the temperature dependence of the mass transport through the membrane.

Permeate and feed side pressures show a similar influence on flux as on selectivity. That means, as long as feed side pressures are low and permeate side pressure is significantly below the partial vapour pressure of the liquid mixture, these influences can be neglected.

A strong influence on transmembrane flux is observed with changes in the composition of the liquid feed mixture. This is understandable if one is aware of the fact that any changes in feed concentrations will change the activity of the respective component, thereby changing the driving force for the separation process. In some cases linear relations between concentration and flux have been reported for binary mixtures over certain concentration ranges; however, because of the non-ideality of the liquid mixtures, this cannot be expected for all concentration ranges and different feed mixtures. Therefore, today performance data of a pervaporation membrane for the separation of a liquid mixture cannot be predicted theoretically or derived from single component data at sufficient accuracy, but tests will be needed in most

cases.

Mass transport through pervaporation membranes is generally described by a "solution-diffusion model". It is assumed that those components which can permeate through the membrane are dissolved in the membrane material and transported through it by diffusion along a concentration gradient, similar to the mass transport through gas separation membranes. It has to be considered, however, that the side of the membrane in direct contact with the liquid feed is swollen, whereas the permeate side is "dry". Diffusion coefficients, therefore, will change across the membrane and would need to be determined at different swelling degrees of the membrane. At this time it cannot yet be decided which one of the two consecutive steps of mass transport through a non-porous membrane, solubility of the components in the membrane material or diffusional transport is the more important and finally determining the separation characteristics of the membrane.

When the first investigations in pervaporation processes were started, only rather thick films were available as a membrane. With the development of asymmetric membranes, thinner, non-porous separating layers could be used and today's technology of composite membranes allows for the manufacturing of non-porous membranes of thicknesses between 0,05 to several microns with sufficient mechanical stability for large-scale uses.

Whereas the first researchers had to use rubber films as membranes, it was tried in a very early stage to use membranes, originally developed for desalination, in pervaporation. One reason was simply the availability of these membranes, but in addition to that, it had been very easily recognized that there was a large potential demand for a membrane easily permeating water, as desalination membranes are expected to do. A large number of widely used organic solvents do dissolve water to any or only a limited extent and the removal of this water may be difficult in certain concentrations. A lot of work was therefore concentrated on what was summarized for the sake of simplicity as "dehydration of alcohol". As it is well-known, ethanol is miscible to any extent with water and this mixture forms an azeotrope at a concentration of 95,6% b.w. Removal of this last portion of water requires rather complicated means, formation and separation of a ternary azeotrope after the addition of a third component known as an entrainer, which then needs to be recycled.

A number of membranes developed for desalination were found to be suitable in principle for a pervaporation process for dewatering. These membranes were partially developed for electrodialysis and for Reverse Osmosis, and experimental data obtained with these membranes will be reported in several papers during this conference. Closer investigation of the performance of these membranes reveals, however, that even for the dehydration of ethanol, their usage is rather limited. Cellulose acetate membranes, for example, exhibit high fluxes and good selectivities at lower ethanol concentrations. With

increasing alcohol concentrations, however, selectivity decreases and becomes low at concentrations close to or above the azeotropic point. The use of cellulose acetate membranes in ethanol dehydration will therefore require high recirculation rates of the water-enriched permeate, in order to reduce losses of ethanol. In addition, operation temperatures will be limited because of the solubility of cellulose acetate even in alcohols and the extension of the use of such a membrane to the dewatering of other solvents will be impossible.

Membranes comprising either fixed cations or anions are also suitable for pervaporation processes. A number of commercially available ion-exchange membranes have been widely tested for dewatering of solvents. The selectivities of these membranes are influenced by both the charge of the fixed ions and by charge and nature of the respective co-ions, thus they were found to be superior over cellulose acetate membranes. Again, however, chemical stability of commercial ion-exchange membranes is limiting usage of these membranes for the dewatering of solvents. Efforts have therefore been started to implant ionic groups into very thin films of polymers of high thermal and chemical stability. Films of partially or perfluorinated polymers were used as base materials together with radiation-induced grafting. In this technique, the film is exposed to a certain dose of γ or electron radiation, which produces excited spots or radicals in the polymeric matrix. In a second step, a reactive monomer with an additionally suitable functional group (usually either a basic or an acidic one) is reacted with the excited spots and radicals. A new polymer is thus formed, which has now a new and different solubility and diffusivity towards water and organic solvents but still exhibits nearly the same chemical and thermal stability as that of the original basic polymer. Again co-ions, necessary to neutralize the electrical charges in the polymer matrix, influence selectivities and transmembrane fluxes in pervaporation processes. Excellent selectivities and water removal have been reported for a large number of these membranes together with satisfying chemical and mechanical stabilities. In some cases, however, co-ions, obviously responsible for the performance of the membrane, have been washed out during operation, requiring frequent regeneration by being flushed with suitable solutions. Long-term stability of these membranes for dewatering may therefore need still further development.

Because of the possibility to place a thin, non-porous layer of a selective polymer onto the surface of an otherwise non-selective but rigid and stable porous substructure, researchers have focused a lot of work towards the development of composite membranes. By this technique a membrane could be developed, which comprises a layer of polyvinyl-alcohol, cross-linked to insolubility even in boiling water onto a thermally and chemically stable porous support. The PVA-layer is only permeable to water but retains organic molecules. Even at low water concentrations in the feed mixture, it exhibits high selectivities, allowing an economical dehydration of organic solvents to final water contents as low as 10 ppm. This membrane is, at this time, the only one fit for large-scale applications and is already in use in a number of

commercial plants for the dehydration of alcohols, ethers, esters and multi-component mixtures of these solvents with water.

As pervaporation processes can be used to remove small quantities of water (the water content usually not exceeding 20 - 30% b.w.) from organic liquid, the reverse should be possible as well, that is, the removal of small quantities of organic substances from water. Whereas in the first case water-absorbing membranes are required, in the second case the membranes should preferentially absorb the organic component and exclude water. A number of polymers are known, which have these desired properties. As the bulk of the liquid in direct contact with the membrane is mainly water, requirements for chemical stability are less stringent than in processes for the dewatering of solvents. In addition, most of the organic components to be removed from water by means of pervaporation processes exhibit sufficiently high vapour pressures at moderate temperatures, thereby reducing the resistance needed by the membrane against high temperature. Consequently, in the past years a number of common polymers have been tested for their separation capacities as well as for their potentiality of being produced as membranes. Several polyesters, polyvinylchlorides, and especially silicones seem to be the most likely candidates as materials for this type of pervaporation membranes. Most tests insofar were performed, using ethanol as the organic component to be removed, originating from the wish to develop a continuous fermenter, from which the product alcohol is continuously removed. Such membranes, however, may even find a much wider application in the removal of organic solvents, such as hydrocarbons or lightly chlorinated hydrocarbons from wastewater streams. Tests have shown that final concentrations of several ppm of the chlorinated hydrocarbon can be obtained, started at the saturated solution as a feed. Selectivities of these membranes are very high, thus only less than one percent of the water will be removed with the permeate.

As stated in the introduction, already in the very beginning of pervaporation studies it had been observed that non-porous membranes have a high potentiality in organic-organic separations. Binning proposed the removal of normal paraffins through membranes from gasoline, in order to raise its octane number. Separation of aromatic isomers by pervaporation has been tested as well as separation of aromatics from paraffins. In the development of membranes for dewatering of organic solvents, membranes with high water-sorption capabilities had to be found, whereas for the removal of organics from water, hydrophobic membranes are needed. In organic-organic separations no simple relation of this kind can be expected. However, sorption measurements in polymers will at least allow for a first judgement of the separation capabilities of a membrane.

Large series of tests of this kind are performed especially in Japan for the development of these second generation membranes. But even those membranes which are originally developed for dewatering processes, show very promising capabilities for organic-organic separa-

tion. As the number of potential organic-organic mixtures to be separated is very large, numerous tests have to be performed in order to gain more information.

Rapid development of new membranes for pervaporation processes can be expected in the next future. In contrast to membranes for gas separation and Reverse Osmosis, membranes of the Loeb-Sourirajan type are not very likely to be used in pervaporation. As only very small pressure losses at the permeate side of a pervaporation membrane can be tolerated, the structure and resistance to flux of the porous part of such an asymmetric membrane has an important influence on the overall performance of a pervaporation membrane. In membranes of the Joeb-Sourirajan type it is very difficult to combine a very thin but pore-free active layer with a porous substructure with low resistance to flux. In the development of pervaporation membranes, three different routes can be distinguished today:

- a) Development of films grafted by radiation.
Although these films may rather be thick and homogeneous, however, after preparation they will become asymmetric in a pervaporation process, as one side of the film is in contact with the liquid feed, whereas the other side is exposed to a vacuum.
A gradient in the swelling of the membrane will thus be established and the layer by which separation and transport are limited, may be very thin.
- b) Thin-film composite membranes.
On a porous substructure, selected with respect to low flow resistance and stability, a thin film of a second polymer is deposited, responsible for the separation of the feed mixture. Active layer and porous substructure are bound together by chemical bonds; the active film is deposited either out of a solution or out of the gas phase and cross-linked by heat treatment or by radiation.
- c) Film membranes, which are produced as such, without an integrated porous substructure, although they may need some mechanical support. This type of membranes can especially be quite useful in the development of capillary modules.

In summary it can be expected that in the next few years pervaporation processes will become state-of-art unit operations. As is the case with other membrane processes, they will not totally replace conventional separation processes, but will be used for all separation problems where conventional processes consume too much energy or are difficult to be operated.

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