Vacuum permeate An alternative method to produce a pressure drop is the use of a vacuum on the membrane permeate. This has been shown to be highly effective in laboratory settings. However, the economics are not favourable for the large scale production of inexpensive components. Nevertheless, vacuum permeate systems may prove viable for small, high value-added systems.

Batch versus continuous Continuous reactor systems are preferred; they require less down time and have higher production rates than batch systems of similar size. However, as previously detailed, if the role of the membrane is to remove a product component, the available partial pressure difference is limited and the process will always be working with a very limited pressure drop that will require very large membrane areas. Batch and semi-batch processes allow the system to develop some limited partial pressure difference before membrane separation is attempted.

Membrane Degradation

The stability of the membrane is another important consideration. Ideally, for integrated systems, the membrane should be stable in all possible reaction environments: catalyst activation, normal reaction, catalyst regeneration and any thermal cycling experienced upon transitions. This presents specific challenges for each system and there are few materials that can satisfy all of these requirements. Thus, special engineering solutions are necessary. Even if the membrane material can fulfil these specifications, the many components needed to produce a membrane reactor module may not.

Future Possibilities

Organic Separations

A great deal of research is currently focusing on the development of membranes (either polymeric, inorganic, or hybrids of the two) for the selective separation of liquid organic mixtures. If this research is successful, it will allow for incorporation into liquid-phase membrane reactors.

Control of Reactant Addition for Intermediate Product Recovery

A second area of immense current research activity is the development of oxygen-permeable membranes to influence the conversion of methane to either methanol or syn gas. The goal in these processes is a mechanism for the conversion of natural gas to a transportable liquid that may be further converted to high valued products. Current research has shown that membranes can be developed and that the appropriate catalysts are available for these conversions. Many engineering challenges lie ahead. These membrane reactor processes operate in excess of 700°C (sometimes much higher). Sealing these ceramic membranes into a housing remains a limitation. Further, the thermal stresses, which develop when cycling from 25 to >700°C, may result in membrane damage. While these are complex problems, the incentive to succeed is large and numerous research efforts continue in this area.

Further Reading

Armour JN (1989) Catalysis with permselective inorganic membranes. *Applied Catalysis* 49: 1.

Gokhale YV, Noble RD and Falconer JL (1995) Effects of reactant loss and membrane selectivity on a dehydrogenation reaction in a membrane-enclosed catalytic reactor. *Journal of Membrane Science* 103: 235.

Govind R and Itoh N (eds) (1989) Membrane reactor technology. *AIChE Symposium Series* 85: 268.

Saracco G, Versteeg GF and van Swaaij WPM (1994) Current hurdles to the success of high-temperature membrane reactors. *Journal of Membrane Science* 95: 105.

Shu J, Grandjean BPA, Van Neste A and Kaliaguine S (1991) Catalytic palladium-based membrane reactors: a review. *Canadian Journal of Chemical Engineering* 69: 1036.

Concentration Polarization

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Introduction

All membrane separation processes are accompanied by a phenomenon called 'concentration polarization' in which the composition at the feed–membrane interface differs from the composition in the bulk of the feed mixture. This gradient in composition is generated by the separation performed by the membrane and, as such, cannot be avoided. However, it is important to minimize the effects of concentration polarization because the gradient in composition reduces the separation performance of the membrane and increases the potential for membrane fouling.

Therefore, minimizing concentration polarization is one of the most important objectives in designing and engineering membrane separation systems.

Mathematical Description of Concentration Polarization

The velocity profile of a fluid flowing in a channel is not constant across the thickness of the channel, because of friction at the fluid–channel surface interface. The fluid velocity decreases as the distance from the channel surface decreases. The same phenomenon occurs in the channels of a membrane module, and the resulting velocity gradient adjacent to the feed side of the membrane is characteristic of all membrane processes. To facilitate mass transfer analysis, the velocity gradient is usually represented by a step function, and it is assumed that a stagnant boundary layer exists adjacent to the membrane. Any component permeating the membrane must first pass through the boundary layer as illustrated in **Figure 1**.

Although the boundary layer is stagnant in the direction of the feed bulk flow, the boundary layer is subject to convective flow perpendicular to the membrane surface which is generated by the permeate flux. The convective transport of a component into the boundary layer from the bulk solution is given by the product $v_p \cdot c_p$, where v_p (cm s^{-1}) is the convective velocity and c_b (g cm^{-3}) is the concentration in the bulk of the feed. The rate at which the same component leaves the boundary layer is $v_p \cdot c_p$, where c_p (g cm^{-3}) is the permeate concentration. In general, if separation is achieved, c_p does not equal c_b, and the convective flows into and out of the boundary layer, generate a mass imbalance. This imbalance then forms a concentration gradient in the boundary layer, and the concentration gradient increases until diffusion of the component down the concentration gradient is sufficient to restore mass balance in the boundary layer.

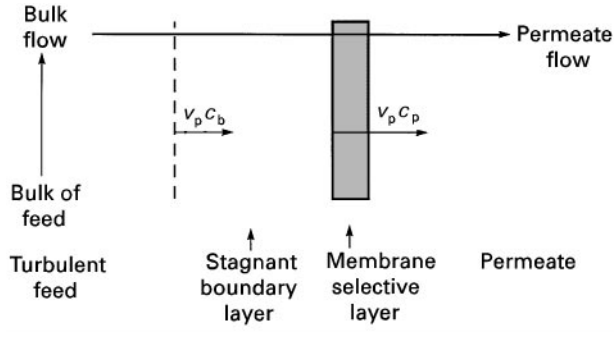

Figure 1 Schematic of the boundary layer adjacent to the membrane surface. If $c_p > c_b$: component is enriched in permeate. If $c_p < c_b$: component is depleted in permeate.

At steady state, the sum of convective and diffusive transport in the boundary layer equals the amount permeated through the membrane. This steady state is expressed for each component by the equation:

$$v_p c_i - D\mathrm{d}c_i/\mathrm{d}_x = J_i^w \qquad [1]$$

where D (cm^2 s^{-1}) is the diffusion coefficient, x (cm) is the coordinate perpendicular to the membrane surface and J_i^w (g cm^{-2} s^{-1}) is the mass flux of i permeating through the membrane.

In liquid-phase separations (including pervaporation) concentrations are typically expressed as a weight fraction, $w_i = c_i/\rho$ where ρ (g cm^{-3}) is the density of the liquid. Assuming that the density of the feed is constant in the boundary layer:

$$v_p \cdot w_i \cdot \rho - D \cdot \rho \frac{\mathrm{d}w_i}{\mathrm{d}x} = J_i^w \qquad [2]$$

and assuming that the feed density is equal to the density of the permeate:

$$J_i^w = w_p \cdot J_{tot}^w = w_p \cdot v_p \cdot \rho \qquad [3]$$

where w_p (g g^{-1}) is the weight fraction of i in the permeate and J_{tot}^w (g cm^{-2} s^{-1}) is the combined mass flux of all components permeating the membrane. Combining eqns [2] and [3] and eliminating the density ρ gives:

$$v_p \cdot w_i - D \frac{\mathrm{d}w_i}{\mathrm{d}x} = v_p \cdot w_p \qquad [4]$$

which, integrated over the thickness δ (cm) of the boundary layer, yields the polarization equation:

$$\frac{w_m - w_p}{w_b - w_p} = \exp(v_p \cdot \delta/D)$$

$$= \exp(v_p/k_{bl})$$

$$= \exp(J_{tot}^w/\rho \cdot k_{bl}) \qquad [5]$$

where w_m and w_b are the weight fractions of i at the membrane surface and in the bulk of the feed, respectively, and $k_{bl} = D/\delta$ (cm s^{-1}) is the mass-transfer coefficient in the boundary layer.

In gas-separation applications, concentrations are typically expressed as mole fraction n_i, which is equal

to the volume fraction, assuming the gas mixtures are ideal. Starting again with eqn [1], the mole fraction n_i can be substituted for c_i by using:

$$n_i = c_i \cdot 22\,400 \cdot T/(M_i \cdot p_f \cdot 273) \qquad [6]$$

where 22 400 (cm^3 (STP) mol^{-1}) is the molar volume of an ideal gas, T (K) is the gas temperature, M_i (g mol^{-1}) is the molecular weight of i, p_f (bar) is the feed gas pressure, and 273 K is the standard temperature. Also, the volume flux J_i^v (cm^3 (STP) cm^{-2} s^{-1}) can be substituted for the mass flux J_i^w using:

$$J_i^v = J_i^w \cdot 22\,400/M_i \qquad [7]$$

Elimination of the term $M_i/22\,400$ gives:

$$v_p \cdot n_i \cdot p_f \cdot 273/T - D \cdot p_f \cdot 273/T \frac{dn_i}{dx} = J_i^v \qquad [8]$$

Since $J_i^v = n_p \cdot J_{tot}^v$ and:

$$v_p = J_{tot}^v \cdot T/(p_f \cdot 273) \qquad [9]$$

elimination of the term $p_f \cdot 273/T$ gives:

$$v_p \cdot n_i - D \frac{dn_i}{dx} = v_p \cdot n_p \qquad [10]$$

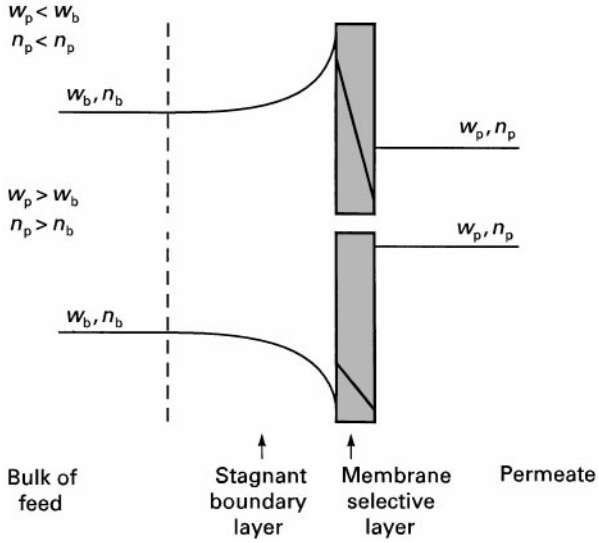

Figure 2 Schematic of the concentration polarization phenomenon. The concentration profiles in the boundary layer result from the separation achieved by the membrane. The type of concentration profile formed depends on the value of w_p relative to w_b (or n_p relative to n_b).

Integrating eqn [10] in the same way as eqn [4] gives:

$$\frac{n_m - n_p}{n_b - n_p} = \exp(v_p \cdot \delta/D)$$

$$= \exp(v_p/k_{bl})$$

$$= \exp(J_{tot}^v \cdot T/p_f \cdot 273 \cdot k_{bl}) \qquad [11]$$

where n_m and n_b are the mole (or volume) fraction of i at the membrane surface and in the bulk of the feed.

Eqns [5] and [11] describe the concentration profiles that develop in the boundary layer, as illustrated in **Figure 2**. Any component enriched in the permeate will be depleted in the boundary layer and any component depleted in the permeate will be enriched in the boundary layer.

Factors Determining the Extent of Concentration Polarization

The ratio of the concentration of a component at the membrane interface to the concentration in the bulk of the feed is called the 'concentration polarization modulus' and is a measure of the influence of concentration polarization on the separation process. The following expression for the modulus can be obtained from eqn [5]:

$$\frac{w_m}{w_b} = \frac{\exp(v_p/k_{bl})}{1 + E_o[\exp(v_p/k_{bl}) - 1]} \qquad [12]$$

where $E_o = w_p/w_m$ is the intrinsic enrichment achieved by the membrane (and equal to the actual enrichment if concentration polarization were absent). An equation equivalent to eqn [12] but expressed in mole fractions can be derived from eqn [11].

Eqn [12] allows the concentration polarization modulus to be calculated as a function of v_p/k_{bl} for different values of the intrinsic enrichment factors, E_o. The ratio v_p/k_{bl} is a Peclet number and is a measure of the influence of convection relative to the influence of diffusion in the boundary layer. The results of this calculation are shown in the very informative **Figure 3**, which confirms that the concentration polarization modulus is smaller than 1 (boundary layer depletion) if the permeating compound is enriched in the permeate and larger than 1 (boundary layer build-up) if the permeating compound is depleted in the permeate. The concentration polarization modulus increasingly deviates from unity as the ratio v_p/k_{bl} increases, that is, as the flux through the membrane increases or as the turbulence

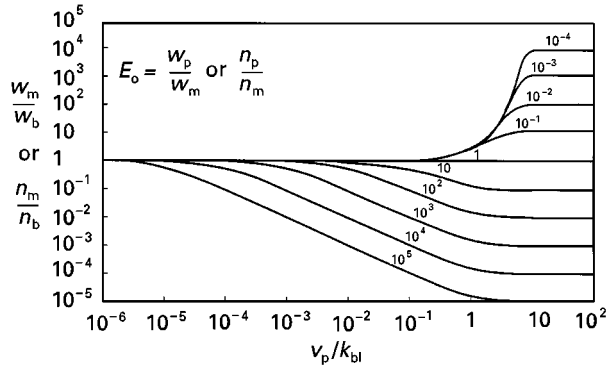

Figure 3 Concentration polarization modulus, w_m/w_b, as function of v_p/k_{bl} for a range of values of the intrinsic enrichment factor E_o. Lines calculated through eqn [12]. This figure shows that compounds that are enriched by the membrane ($E_o > 1$) are more affected by concentration polarization than compounds that are rejected by the membrane ($E_o < 1$).

of the feed fluid decreases. At high values for the ratio v_p/k_{bl}, the concentration polarization modulus, w_m/w_b, approaches the limiting value $1/E_o$. At this point, the boundary layer completely negates the separation power of the membrane permeation step. The concentration polarization modulus also increasingly deviates from unity as the intrinsic enrichment increasingly deviates from unity, that is, as the separation power of the membrane increases.

A striking feature of Figure 3 is the asymmetry with respect to enrichment and rejection. For example, when the term v_p/k_{bl} has a value of 10^{-1}, concentration polarization is essentially nonexistent for a component rejected by the membrane with an intrinsic enrichment E_o of 10^{-4}. On the other hand, concentration polarization is very severe for a component enriched by the membrane with an intrinsic enrichment E_o of 10^4. The reason for this asymmetry is that the concentration polarization effect is generated by the difference in concentration between the permeate and the feed, $w_p - w_b = w_b(E - 1)$, where $E = w_p/w_b$ is the actual enrichment factor. It is clear that the absolute value of $w_p - w_b$ is significantly larger if $E > 1$ than if $E < 1$.

A second feature of the calculations shown in Figure 3 is that the concentration polarization modulus values are independent of the bulk concentration, w_b. This means that at a constant enrichment factor, E, the influence of concentration polarization is the same, no matter whether the component is present in the feed at a concentration of one part per hundred, one part per million, or one part per billion. Thus, concentration polarization does not necessarily affect components present at low concentrations more than components present at higher concentrations. The primary requirement for significant concentration polarization effects is a high value for the enrichment factor, E. However, because E has an upper bound equal to $1/w_b$, a low feed concentration is a secondary requirement for severe concentration polarization effects. This confirms an empirical rule long held by membrane separation practitioners.

Transport Equations Incorporating Concentration Polarization

As pointed out in the previous sections, concentration polarization primarily affects membrane permeation by the change in composition at the membrane interface relative to the bulk of the feed mixture. To calculate the effect of concentration polarization on flux and separation, the transport equation for the membrane can be combined with eqn [5] or eqn [11] to arrive at a set of equations that predict the permeate flux and composition.

Ultrafiltration, nanofiltration and reverse osmosis are membrane processes in which a solute is separated from a solvent using a solute-rejecting membrane. Typically the permeate is essentially pure solvent, free of the solute. A simple but very effective transport equation developed for this situation is given below.

The pure solvent flux $J^w_{solvent}$ (g cm^{-2} s^{-1}) of the membrane is given by:

$$J^w_{solvent} = \Delta P / R_m \qquad [13]$$

where ΔP (bar) is the pressure difference applied across the membrane and R_m (bar cm^2 s g^{-1}) is the membrane resistance to the solvent. When a solute is present, the driving force for permeation is reduced by the osmotic pressure difference between the feed at the membrane interface and the permeate, $\Delta\pi_m$ (bar), therefore:

$$J^w_{solvent} = (\Delta P - \Delta\pi_m)/R_m \qquad [14]$$

Eqn [14] is called the 'osmotic pressure model', in which the osmotic pressure is a measure of the thermodynamic work required to produce solvent from a solvent–solute mixture. Assuming that the permeate solute concentration is neglible:

$$\Delta\pi_m = a \cdot w^n_m \qquad [15]$$

where a is a constant and n is an exponent equal to approximately 1 for low-molecular-weight solutes,

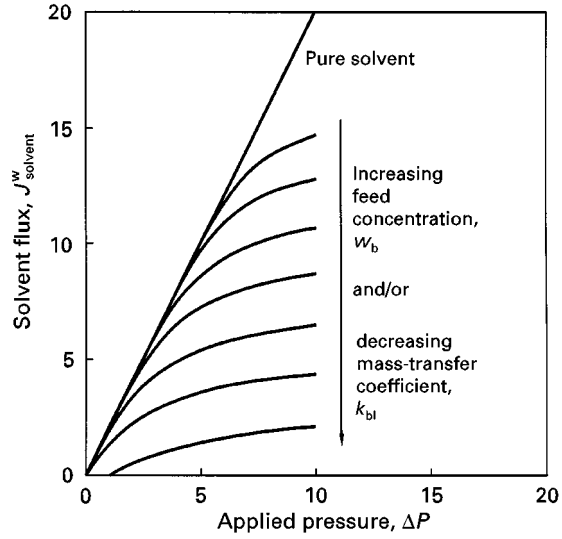

Figure 4 Solvent flux as a function of applied pressure as calculated from eqn [17]. The flux observed with solvent–solute mixtures is always less than the pure solvent flux. The deviation increases with increasing applied pressure, increasing solute concentration, and decreasing mass-transfer coefficient in the boundary layer.

but equal to 2 or higher for macromolecular solutes. Combining eqn [15] with eqn [5] and assuming $w_p = 0$ gives:

$$\Delta\pi_m = a \cdot w_b^n \cdot \exp(n \cdot J^w_{solvent}/\rho k_{bl}) \qquad [16]$$

and:

$$J^w_{solvent} = (\Delta p - a \cdot w_b^n \cdot \exp(n \cdot J^w_{solvent}/\rho k_{bl}))/R_m \qquad [17]$$

From eqn [17] it is clear that an increase in the flux $J^w_{solvent}$ leads to an exponential increase in the osmotic pressure and that the flux will increase less than linearly with the applied pressure. This means that any increase in driving force ΔP will be negated at least in part by the increase in osmotic pressure. The general effect of pressure on flux predicted by eqn [17] is illustrated in **Figure 4** and is in agreement with the vast majority of experimental data. As can be seen from Figure 4, the flux observed with solvent–solute mixtures is always less than the pure solvent flux, and the deviation increases with increasing applied pressure, increasing solute concentration and decreasing mass transfer coefficient in the boundary layer. Figure 4 also shows that at higher applied pressures the flux becomes essentially independent of the applied pressure. This is often observed in ultrafiltration applications and is referred to as the limiting flux. Eqn [17] predicts that under 'limiting flux' conditions the flux is independent of the membrane resistance, which also has been confirmed experimentally.

Gel Layer Formation

When the solute is a macromolecular compound such as a protein or a polymer, there is the possibility that the solute concentration at the membrane interface exceeds the gel concentration, w_g, at which concentration the solution is no longer a fluid. A gel layer thus forms at the membrane interface which creates an additional resistance to the permeation flux which consequently decreases. The flux continues to decrease until the solute concentration at the membrane interface equals the gel concentration, at which point steady state is reached. The flux at that point can be obtained from eqn [5]:

$$J^w_{limit} = \rho \cdot k_{bl} \cdot \ln\frac{(w_g - w_p)}{(w_b - w_p)} \qquad [18]$$

and because w_p is typically close to zero:

$$J^w_{limit} = \rho \cdot k_{bl} \cdot \ln(w_g/w_b) \qquad [19]$$

The steady-state flux J^w_{limit} is called the 'limiting flux' because any increase in applied pressure will just result in a thicker gel layer and not in a higher flux. From eqn [19] it can be seen that the limiting flux as predicted by the gel layer model is independent of the applied pressure as well as the membrane resistance. Additionally, eqn [19] predicts a straight-line plot of J^w_{limit} versus $\ln(w_b)$ with a slope equal to $-\rho \cdot k_{bl}$. All these predictions have been confirmed in a vast number of ultrafiltration experiments. Interestingly, the osmotic pressure model also predicts a limiting flux with the same attributes.

Approaches to Minimize Concentration Polarization

The primary method of reducing the negative influence of concentration polarization is to maximize the mass-transfer coefficient in the boundary layer. Usually the first method used is to increase the feed velocity. This has the drawbacks of a high feed-to-residue pressure drop and the requirement of long, thin modules, which have higher capital costs than shorter, larger-diameter modules. A more efficient approach is to choose optimized feed-spacer materials and/or to create non-linear feed channels which induce mass-transfer-enhancing vortices. More complicated methods used for a feed mixture with a high viscosity and/or a high membrane fouling

potential employ spinning membranes or vibrating modules.

Further Reading

Belfort G, Davis RH and Zydney AL (1994) The behavior of suspensions and macromolecular solutions in cross flow microfiltration. *Journal of Membrane Science* 1: 96.

Brian PLT (1966) Mass transport in reverse osmosis. In: Merten U (ed.) *Desalination by Reverse Osmosis*, p. 181. Cambridge, MA: MIT Press.

Cheryan M (1998) *Ultrafiltration and Microfiltration Handbook*. Lancaster: Technomic Publishing.

Zeman LJ and Zydney AL (1996) *Microfiltration and Ultrafiltration*. New York: Marcel Dekker.

Dialysis in Medical Separations

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Introduction

Although haemodialysis (HD) as a therapy for uraemia (kidney failure) was first described early in the 1900s, its widespread use did not occur until the 1950s. At this time, Travenol Laboratories (now Baxter International) unveiled the 'coil' dialyser ('artificial kidney') in which tubes composed of cellophane membranes were wound around a support structure and immersed in a recirculated dialysis solution. Relative to contemporary models, the mass transfer efficiency of this type of dialyser was extremely poor, due to high mass transfer resistances in all three compartments (blood compartment, membrane, and dialysate compartment). In the early 1960s, solution mass transfer resistances were decreased with the introduction of parallel flow dialysers, in which sheet membranes were formed in a stacked configuration. The improvement in dialysate-side mass transfer with these dialysers was particularly large because the dialysis solution contacted the membrane under flow conditions as opposed to the semi-batch operation of the coil dialyser. In addition, the membranes used in these devices were thinner in structure, providing less diffusive resistance than earlier versions. Although the earliest manufactured parallel flow dialysers were not disposable, design improvements permitted the production of disposable units by the late 1960s.

The last truly major development in haemodialysers occurred more than 30 years ago when the hollow fibre artificial kidney was developed. Blood compartment mass transfer was reduced further with this design due to the high shear rate that could be achieved in the annular space of the hollow fibre. Additional benefits of the hollow fibre artificial kidney included an enhanced ability to control transmembrane pressure (see below) and a lower extracorporeal blood volume. This type of dialyser is now used in virtually all HD treatments.

On a global basis, approximately 800 000 patients receive chronic haemodialysis therapy for the treatment of end-stage renal disease (ESRD) and this population is growing at a rate of 8–10% per annum. This figure represents approximately 85% of the ESRD population, with the remaining patients receiving peritoneal dialysis. Numerous dialysis membrane and haemodialyser manufacturers are situated around the world, with the vast majority based in the three largest markets: United States, Western Europe and Japan.

The Haemodialysis Procedure

In addition to the dialyser, the other fundamental component of a HD system is a dialysis machine, which serves a number of purposes. First, it is equipped with a roller pump that delivers blood, usually at a rate of 200–500 mL min^{-1}, from the patient to the dialyser and back to the patient. Second, the dialysis machine prepares dialysate by mixing ('proportioning') water and a concentrated bicarbonate solution in such a ratio that the dialysis fluid produced is the same as that prescribed by a physician to meet the needs of an individual patient. The typical dialysate flow rate is 500–800 mL min^{-1} and its major constituents are sodium, potassium, calcium and bicarbonate. The pathophysiology of uraemia is such that during the period between dialysis treatments, potassium levels in the plasma rise while calcium and bicarbonate levels fall. Consequently, the concentration of potassium in the dialysate is typically lower than that in the plasma at the beginning of the procedure while dialysate calcium and bicarbonate concentrations are typically higher. The third major function of the dialysis machine is to provide an accurate measurement of transmembrane pressure (TMP) in the dialyser, which is defined as the difference between the average pressure in the blood and