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MEMBRANE DISTILLATION EMPLOYED FOR SEPARATION OF WATER ISOTOPIC COMPOUNDS

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ABSTRACT

An attempt to apply membrane distillation (MD) for the enrichment of water isotopic compounds was made. The process was conducted as a direct-contact MD with flat-sheet microporous, hydrophobic polytetrafluoroethylene (PTFE) membranes in the temperature range 323-353K. The distillate condensation was carried out directly into a stream of cooling water. The comparison between calculated Rayleigh distillation curves and the results of permeation experiments demonstrated the MD process to be more efficient than simple distillation for enrichment of the heavy isotopes in water.

INTRODUCTION

The heavy isotope components of water used in science and technology are produced by several methods. Distillation is the only method of heavy oxygen enrichment, and it is still used sometimes for deuterium enrichment even though it is not economically competitive with the more recently developed processes (1). Although expensive due to the low separation factor, distillation technology is a simple and well-developed process, safe for staff and the environment.

The membrane process proposed by the authors (2) seems to be promising as a possible new method for separating heavy isotopes in water on a commercial scale. Preliminary engineering calculations based on the cascade theory showed many advantages of membrane permeation. Employing the system of two combined counter-current cascades results in savings in stage number, reflux ratio, and energy demand (3). The process proposed previously was performed applying a low pressure on one side of the membrane. The condensation of the vapor permeate took place outside the permeation cell. The partition used was a polytetrafluoroethylene (PTFE) hydrophobic porous membrane.

The latest experiments conducted in the Institute of Nuclear Chemistry and Technology (INCT) laboratory were performed applying direct-contact membrane distillation. In this arrangement, the liquid on both sides of the polymer partition was in direct contact with the membrane, and the cold liquid was used as the condensing medium.

Membrane distillation (MD) is a membrane process in which two aqueous solutions at different temperatures, T_1 and T_0, where $T_1 > T_0$, are separated by a hydrophobic porous membrane. The driving force of the MD process is the partial vapor pressure difference caused by the temperature gradient between two solutions. The vapor molecules are transported through the membrane pores from the high-vapor-pressure side to the low-pressure side. The component with the higher partial pressure shows a higher permeation rate. The principle of the process is shown in Figure 1. Membrane distillation constitutes a sequence of three steps:

- evaporation of the water at the warm feed-membrane interface,
- transport of vapor molecules through the membrane pores, and
- condensation of the permeate at the membrane-cold permeate interface.

As the transport through the membrane occurs in a sequence of three steps, the selectivity of the process will be determined by the vapor-liquid equilibria, the difference in partial pressures of the separated substances, and their transport rate through the pores of the hydrophobic membrane as well.

Potential applications of MD have been described by a number of authors (4-11). Membrane distillation is being developed for production of high-purity water and wastewater treatment (7), and for the concentration of various kind of solutions near

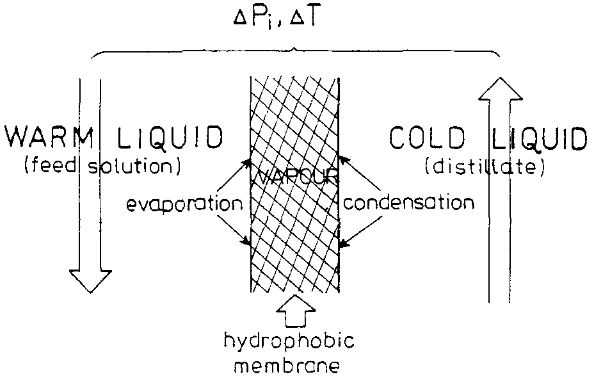

FIGURE 1. Principle of membrane distillation.

saturation conditions (8). The process allows removal of salt from seawater (9,10) and separation of alcohol-water solutions (11).

Different configurations of membrane distillation are considered (Figure 2):

1. Direct-contact MD (12), in which the membrane is in direct contact with liquid phases on both sides;
2. Air gap MD (13), in which air gap is additionally interposed between the membrane and condensation surface;
3. Vacuum-enhanced MD (11), in which vapor is stripped away from the liquid through the membrane and condensation takes place in a separate unit; and
4. Sweeping gas membrane distillation, when a sweeping gas is applied downstream and the permeating vapor condenses outside the module.

The expected advantages of membrane distillation are moderate temperatures and a relatively small temperature difference across the membrane which produces relatively high fluxes of the permeate. The low operation temperatures enable the utilization of waste heat as the preferable energy source, so the energy cost can be significantly reduced. In such a process, various cheap energy sources can be used (10). The reduction of energy demand is a very important factor in its application to expensive processes like isotope enrichment. Direct-contact MD involves two streams at different temperatures, and can be performed as a countercurrent flow system, an effective and economical arrangement.

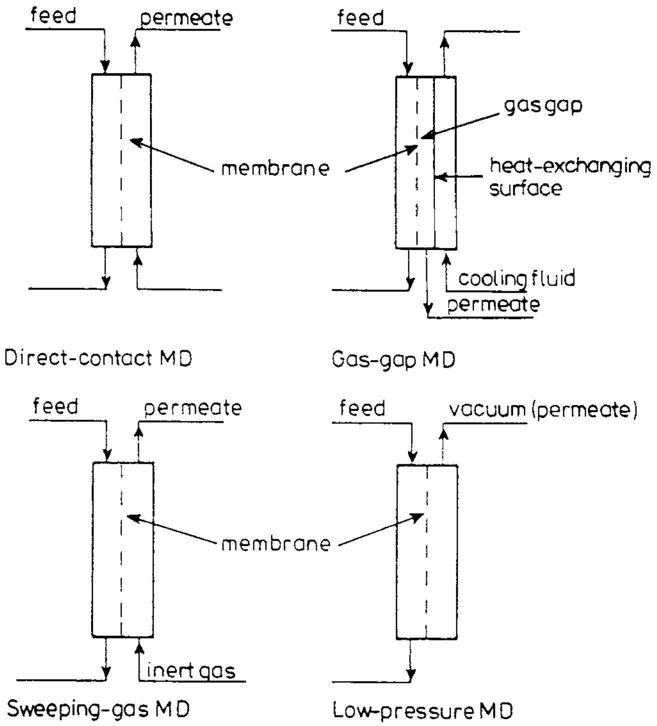

FIGURE 2. Membrane distillation configurations.

EXPERIMENTAL

Membranes

The experiments were conducted with flat-sheet Tarflen-2 membranes made of polytetrafluoroethylene as described by Tomaszewska (14), and commercial Millipore FGLP polytetrafluroethylene filters. Characteristics of the membranes are given in Table 1. Both kinds were hydrophobic and maintained hydrophobicity even after an 80-h operating time.

Experimental Procedure

The experimental setup for membrane distillation studies is schematically shown in Figure 3. The main component of the system is the permeation cell - 1, which is

TABLE 1. CHARACTERISTICS OF THE MEMBRANES.

Membrane	Thickness (μm)	Maximum pore size (μm)	Empty volume fraction (%)	Distillate flux T_h=323K T_c=293K (dm^3/m^{2*}d)
PTFE-Tarflen-2	60	0.84	20	108
Millipore FGLP	175	0.20	70	156

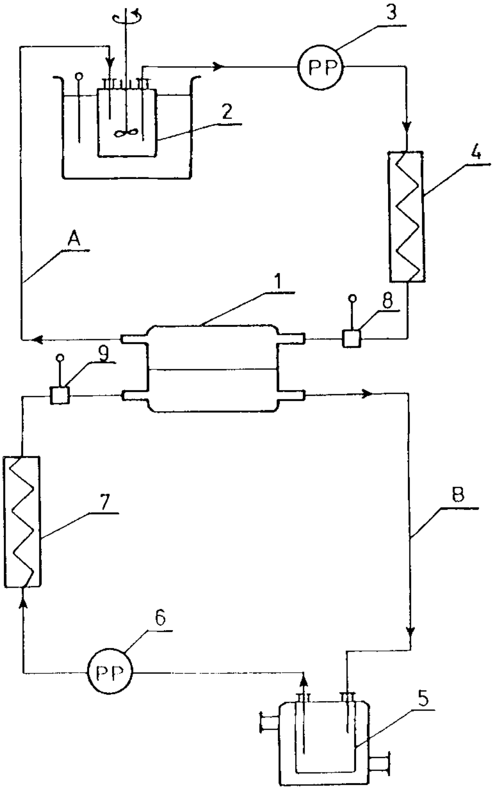

FIGURE 3. Experimental setup: A– hot system; B– cold system; 1–permeation cell; 2–hot liquid reservoir; 3,6–peristaltic pumps; 4,7–heat exchangers; 5–cold liquid reservoir; 8,9–temperature control.

connected to two temperature-controlled reservoirs - 2 and 5, heat exchangers - 4 and 7, peristaltic pumps - 3 and 6, and thermometers - 8 and 9. The permeation cell (Figure 4) consists of two stainless steel sections - 1 and 6, sealed by two rubber O-ring gaskets - 4. The flat-sheet membrane - 3, effective area 15.2 x $10^{-4}m^2$, is supported on the plastic grid - 2. A magnetic stirrer is placed in the cold compartment in order to decrease the temperature polarization effect. The thermostated warm feed (natural water) circulates in the hot compartment (top). During the experiment, the hot stream is enriched in heavy isotopomers of water. The cold compartment is initially filled with natural water. The vapor passing through the porous membrane condenses directly in the cold stream. The isotope concentration of water used on both sides of the membrane was 180 ppm D and 1800 ppm O-18. The experiments were carried out with the feed temperature from 323 to 353 K. The temperature of cold distillate was kept constant at either 287 or 293 K.

The investigations were performed over 30- to 80-h runs at steady state, a flow rate of 4 x $10^{-3}m^3/h$, and stable temperatures of hot (T_1) and cold (T_0) water. Isotopic analyses of water samples extracted from both streams many times during each run were performed by mass spectrometry (SIRA 12 V6 Isogas mass spectrometer). The concentration of deuterium was determined in hydrogen generated by reduction of the water samples with metallic zinc (15); O-18 analyses were performed by isotopic equilibration of water samples with CO_2 (16,17). All analyses were referenced to the V-SMOW standard.

RESULTS AND DISCUSSION

In the temperature range 323-353 K, permeate flow rate varied from 0.20 x 10^{-2} $m^3m^{-2}*h^{-1}$ to 0.60 x 10^{-2} $m^3m^{-2}*h^{-1}$ for PTFE-Tarflen-2 membranes and from 0.316 x 10^{-2} $m^3m^{-2}*h^{-1}$ to 1.046 x 10^{-2} $m^3m^{-2}*h^{-1}$ for Millipore FGLP. Mass flux through the membrane, via MD, proceeds by convective and/or diffusive transport of vapor. If the mean free path of vapor molecules is much less than the pore size, the dominant flux mechanism is viscous, and Poiseuille flow describes the process. If the mean free path of molecules is greater than the pore size, the dominant flux is via Knudsen diffusion. When the flow takes place in the presence of air trapped within the membrane, the mass flux can be described by the molecular diffusion. As the mean free molecular path of saturated water vapor (about 0.3 μm at 60°C) is greater than the Millipore membrane

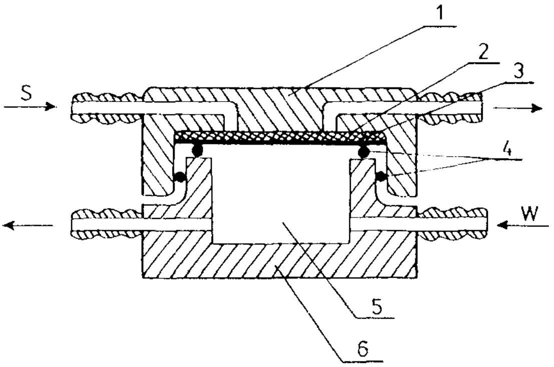

FIGURE 4. Permeation cell:
1– top part of the steel frame,
2–supporting grid, 3–membrane,
4–o–ring gaskets, 5–permeate chamber, 6–bottom part of the steelframe, S–hot–water stream, W–cold–water stream.

pore size (0.2 μm), Knudsen diffusion flow is expected. The Knudsen model may not be useful for predicting mass fluxes through the PTFE-Tarflen-2 membranes, pore size 0.84 μm. Calculations showed a transport mechanism based largely on Knudsen diffusion for Millipore FGLP filters, and on molecular diffusion for PTFT-Tarflen-2 (18).

The three models all showed a linear dependence of volume flux per unit surface area N, on vapor pressure difference between both sides of the membrane:

$$N = C{*}\Delta P \ ,$$

where C is a membrane mass transfer coefficient for the system. The calculated mass transfer coefficients were 8.293 x 10^{-7} kg $m^{-2}s^{-1}Pa^{-1}$ for Millipore FGLP membranes, and 3.781 x 10^{-7} kg $m^{-2}s^{-1}Pa^{-1}$ for PTFE-Tarflen-2. Figure 5 shows permeate flow dependence on temperature difference, $T = T_h\text{-}T_c$, where T_h is the hot-stream temperature and T_c is the cold-stream temperature. Due to temperature polarization, the interfacial temperatures, T_1 and T_0 (Fig. 6), may vary markedly from the measurable bulk

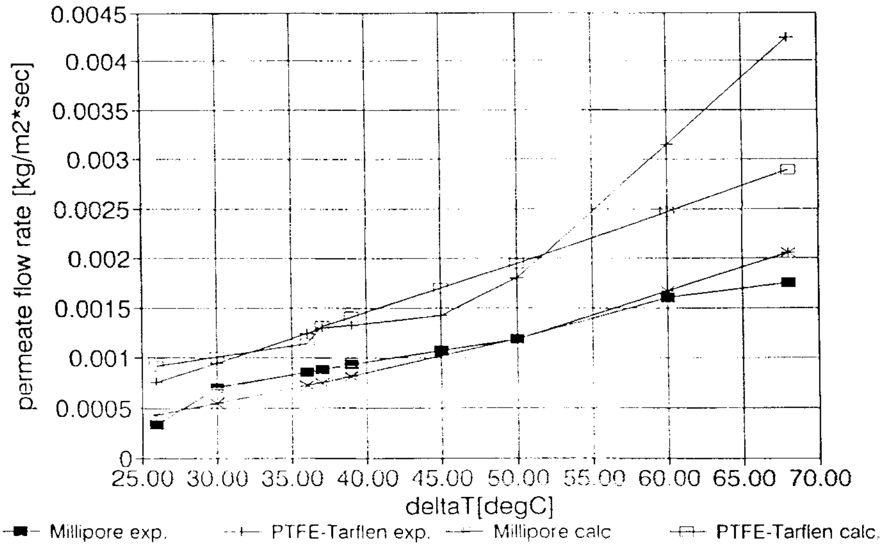

FIGURE 5. Measured and predicted mass fluxes across PTFE membranes.

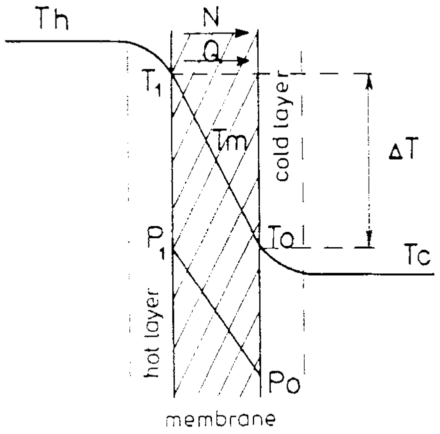

FIGURE 6. Temperature profile through the membrane and boundary–layers.

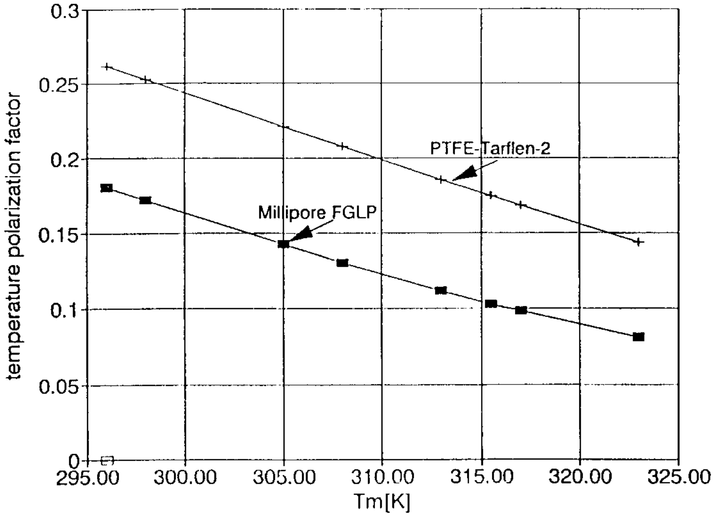

FIGURE 7. Temperature dependence of temperature polarization coefficient for PTFE membranes.

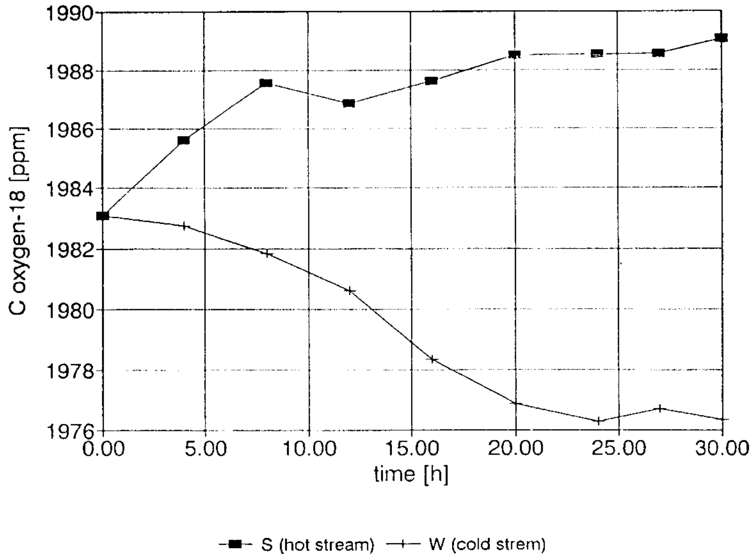

FIGURE 8. Variation of concentration of hot and cold streams in lengthy experiment–experimental data for oxygen–18.

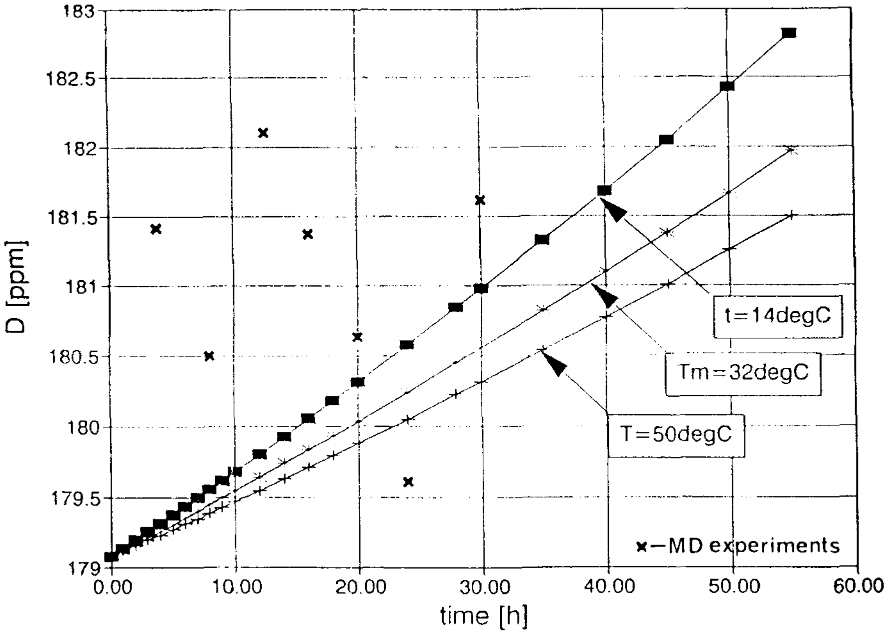

FIGURE 9. Membrane permeation results compared with Rayleigh distillation. Deuterium enrichment.

temperatures, T_h and T_c. The relationship between temperatures can be expressed by the equation

$$\Delta T = T_1 - T_0 = \tau(T_h - T_c) ,$$

where is the "temperature polarization coefficient" (TPC). The coefficient represents the fraction of the total driving force (T_h-T_c) that contributes to the mass transfer driving force (T_1-T_0). The temperature polarization coefficient depends on the mean temperature of the system (Figure 7). In order to improve the efficiency of the MD process, the temperature polarization coefficient should be as close to unity as possible, but many systems have TPC values close to zero (19). In our experiments, the mean polarization coefficient for Millipore FGLP equaled 0.1109 and for PTFE-Tarflen-2- 0.2176; thus, the real temperature gradient generating the permeate flow across the membrane equaled

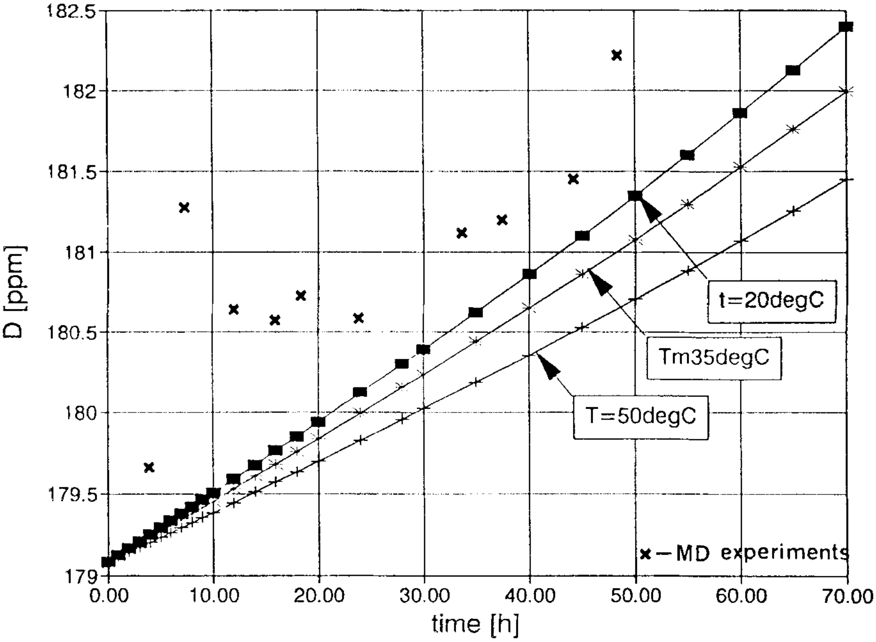

FIGURE 10. Membrane permeation results compared with Rayleigh distillation. Deuterium enrichment.

3 to 5 degrees for Millipore and 6 to 11 degrees for Tarflen membranes. An example of the results of spectrometric analyses of the samples taken during the experiments from the streams is shown in Figure 8. The isotopic concentration of both hot (S) and cold (W) streams varied with time. The upper curve shows the process of heavy isotope enrichment which takes place in the hot stream. The permeate depleted in deuterium and O-18 mixes with condensing medium causing depletion of the cold stream in these isotopes.

For a better presentation of experimental data, the Rayleigh distillation curves were calculated using simplified form of Rayleigh-equation

$$x_p = x_s \left(\frac{V}{V_p}\right)^{\frac{(\alpha-1)}{\alpha}},$$

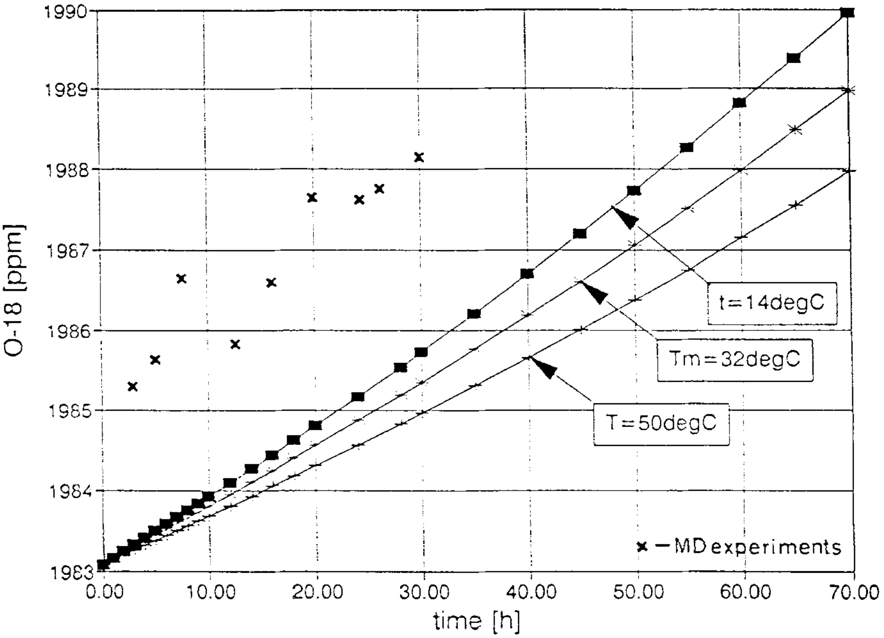

FIGURE 11. Membrane permeation results compared with Rayleigh distillation. Oxygen–18 enrichment.

where x_p is the current concentration of heavy isotope in the hot stream; x_s-initial concentration of heavy isotope in the hot stream; V-initial volume of water; V_p-current volume of water, time dependent function; and a–separation factor. Three curves determined for hot–stream temperature, T_h; cold–stream temperature, T_c; and for the mean temperature of the process, T_m, are compared with experimental data for the permeation process (Figures 9–12). If one considers MD to be a process of evaporation through the polymer partition, the Rayleigh curves calculated for hot–stream temperature or for the mean temperature should be the reference curves. The MD process can be compared with distillation at temperature T_h. However, for membrane distillation the mean temperature, $T_m=(T_h+T_c)/2$, best approximates the real temperature of the membrane. The results of membrane enrichment

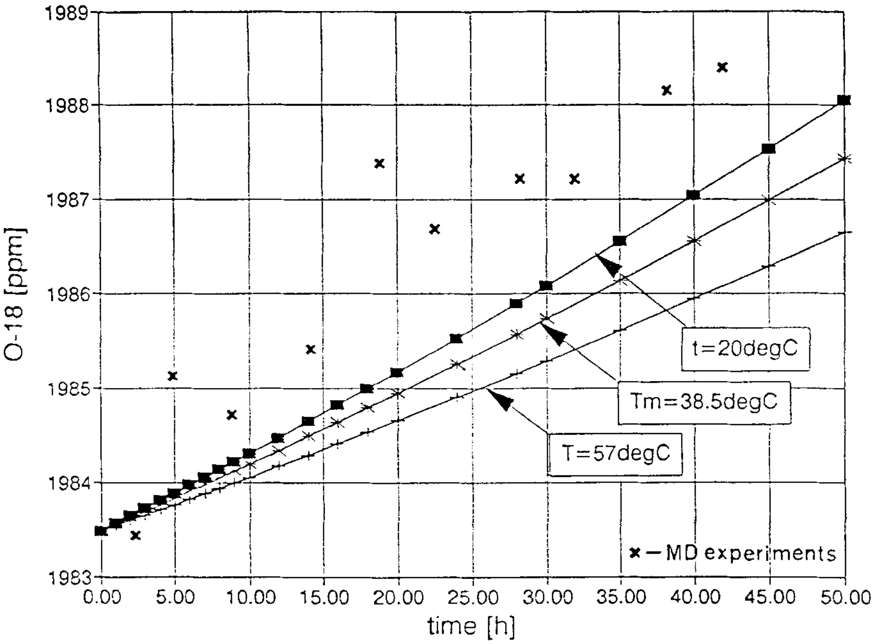

FIGURE 12. Membrane permeation results compared with Rayleigh distillation. Oxygen–18 enrichment.

presented in Figures 9–12 show some advantage over the distillation process. The experimental points that represent the concentration of isotope in the stream being enriched in each case fall above the Rayleigh curves. For both isotopes, D and O–18, MD enrichment seems to be more effective than distillation. In the view of these results, it seems promising to explore MD as a possible method for separating heavy isotopes in water. The use of this technology on a larger scale provided one employs multiple enrichment cascades will make membrane permeation competitive with other technologies for deuterium and heavy oxygen enrichment.

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