# Dehydration of Glycerine–Water Mixtures by Pervaporation

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**ABSTRACT:** Dehydration of glycerine–water mixtures by pervaporation (PV) was studied with Nafion® (NA), cellulose triacetate (CA), polyimide, carboxylated polyvinyl chloride (CPVC), and polyethersulfone (PES) membranes. PES membrane yielded the highest selectivity (6580) and CPVC membrane yielded the lowest selectivity (1552) at 5% by weight of water in the feed and 30°C. The NA membrane yielded the highest permeation flux (0.2–1.45 kg/m$^2$h) of water over the entire water concentration range. Energy of activation of permeation for water was in the range of 7–15 kJ/mol, being highest for CPVC and lowest for CA. Comparison of PV and vapor liquid equilibrium data showed that the former gave better results, particularly for concentrating glycerine above 90 wt%.

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**KEY WORDS:** Dehydration, glycerine, membranes, pervaporation, sorption

Pervaporation (PV) is a membrane-based separation process suitable for separating liquid mixtures comprising azeotropes and close boiling and temperature-sensitive products (1–3). Extensive research has been carried out to separate ethanol–water mixtures by PV. Apart from ethanol–water mixtures, work dealing with various applications was also published to explore the potential of PV (4–6). Because of its high selectivity and low energy requirements, PV is an alternative separation method in the chemicals industry.

Glycerine is used in various products as a solvent, humectant, plasticizer, emollient, sweetener, a fermentation nutrient in the production of antibiotics, antifreeze in automobiles, etc. In the fat-splitting process glycerine is a co-product of soap manufacture and the manufacture of fatty acids (7). Removal of water from crude glycerine is an important step in the production of pure glycerine by the fat-splitting process. Presently, water is removed by evaporation/distillation. The high boiling point of glycerine (290°C), along with its relatively low decomposition temperature (190°C), necessitates the use of vacuum to lower the temperature requirements. For instance, at 10 mm Hg absolute the boiling point of glycerine is 166°C. Even this option cannot prevent the degradation and polymerization of glycerine (7). PV, which can achieve dehydration at much lower temperature, is therefore an attractive alternative.

In the present work, attempts were made to use PV for dehydrating aqueous glycerine as a convenient and energy-efficient technique. Various polymeric membranes were prepared and tested for pervaporation of glycerine–water mixtures. PV performance was evaluated in terms of selectivity and flux. The effects of functional groups of the polymer comprising membrane, feed concentration, and feed temperature on the flux and selectivity were studied. Here, selectivity is defined as follows:

$$\alpha = (Y_A/X_A)/(Y_B/X_B) \qquad [1]$$

where $\alpha$ = selectivity (dimensionless), $X_A$ = concentration in the feed (wt%) with water, and $Y_B$ = concentration in the permeate (wt%) with glycerine. Overall performance of the membrane was evaluated in terms of pervaporation separation index (PSI), defined by Huang (8) as given below:

$$\mathrm{PSI} = J_p[(C_{\mathrm{pwater}}/C_{\mathrm{fwater}}) - 1] \qquad [2]$$

where $C_{\mathrm{pwater}}$ and $C_{\mathrm{fwater}}$ are water concentrations in the permeate and feed, respectively, and $J_p$ is permeation flux (kg/m$^2$h).

## EXPERIMENTAL PROCEDURES

*Materials.* Glycerine was procured from Ranbaxy Laboratories Ltd., Punjab, India. Polyethersulfone (PES) and cellulose triacetate (CA) were supplied by Ion Exchange Ltd. (Mumbai, Maharashtra, India). Nafion (NA) solution was procured from Aldrich Chemicals (Milwaukee, WI). Polyimide (PI) was supplied by ABR Organics (Hyderabad, India) in film form. Carboxylated polyvinyl chloride (CPVC) was procured from Aldrich Chemicals. All chemicals were used without further treatment.

*Membrane preparation.* Membranes used in this work were prepared by solution casting, except for the PI membrane. Solutions of the polymers were prepared by dissolving them in appropriate solvents. These solutions were then cast onto a glass plate with a doctor blade. The solvents were allowed to evaporate at room temperature to obtain membranes in film form. These films were then cured at various temperatures in a controlled temperature oven. Table 1 gives the details of the conditions used to prepare the membranes.

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**TABLE 1**
**Experimental Conditions for the Preparation of Various Membranes**

| Membrane | Solvent | Concentration (wt%) | Curing temperature (°C) |
|---|---|---|---|
| CPVC | Dimethyl formamide | 4 | 80 |
| CA | Methanol/chloroform (1:9) | 4 | 40 |
| PES | Dimethyl formamide | 4 | 70 |
| NA[a] | Methanol | 2 | 30 |

[a]Membrane was prepared by the method described by Netke *et al.* (4). CPVC, carboxylated polyvinylchloride; CA, cellulose triacetate; PES, polyethersulfone; NA, Nafion (procured from Aldrich Chemicals, Milwaukee, WI).

*Sorption.* Pieces of membranes of known weight were immersed in aqueous solutions of glycerine at different known concentrations. The membranes were allowed to equilibrate for 72 h at 30, 50, and 70°C. The membranes were then removed and weighed after the superfluous liquid was wiped off with tissue paper. The increase in weight was due to the water and glycerine sorbed by the membrane. The amount of water in the membrane phase was analyzed by Karl Fischer titration. The amount of glycerine sorbed was obtained by material balance.

*Permeation studies.* The setup used for PV experiments was the same as described by Netke *et al.* (4). The membrane was allowed to equilibrate for 1 h with the feed solution before beginning the PV experiment. After steady state was attained, the permeate was collected in traps immersed in liquid nitrogen. The permeate composition was determined by using a refractometer and preparing a standard chart of refractive index (RI) vs. concentration. Permeation studies were carried out at 30, 50, and 70°C. The downstream pressure was varied from 1 to 20 mm Hg. Reproducibility of the experimental data was ±2%.

## RESULTS AND DISCUSSION

*Sorption.* Figure 1 gives the variation of sorption of water and glycerine in various membranes at 30°C. Substantially large quantities of water were sorbed by these membranes compared to glycerine. Thus, all membranes tested exhibited high sorption selectivity with respect to water. Among the membranes tested, the NA membrane absorbed more water. NA is a copolymer of sulfonylfluoride vinyl ether and tetrafluroethylene monomers. Due to the bulky and dissimilar structures of the monomer units, the free volume available in this copolymer matrix is also maximum, and thus allows greater sorption of water as well as glycerine compared to the other membranes. The PI membrane had the lowest water sorption and the highest water sorption selectivity. The PI membrane (highly compact and rigid structure with highest glass transition temperature, Tg) has only carbonyl groups as hydrophilic parts in its structure. Thus, water–polymer pair formation as well as plasticization due to water were less and, therefore, its water sorption capacity was less. The CPVC (2% carboxylated) membrane has carboxyl functional groups as hydrophilic parts with a vinyl backbone. Although the carboxyl content in CPVC is low, these groups interact strongly with water through hydrogen bonding. The PES and CA membranes yielded intermediate sorption values. The sorption isotherm of water for PES membrane was similar to that of the type IV isotherm of Roger (9), which is a combination of type II at low concentration and type III at high concentration. Sorption isotherms for the other membranes cannot be described by Roger's isotherms.

*Effect of feed temperature.* Figure 2 gives the variation of sorption coefficient of water with its feed concentration at 30, 50, and 70°C for the NA membrane. Increased feed temperature decreased the sorption of water. This implies a negative heat of sorption. Similar trends were observed for the other membranes. Heats of sorption ($\Delta H_s$) for water for various membranes at 10% by weight of water in the feed are given in Table 2. These values can be used to predict the sorption at elevated temperatures.

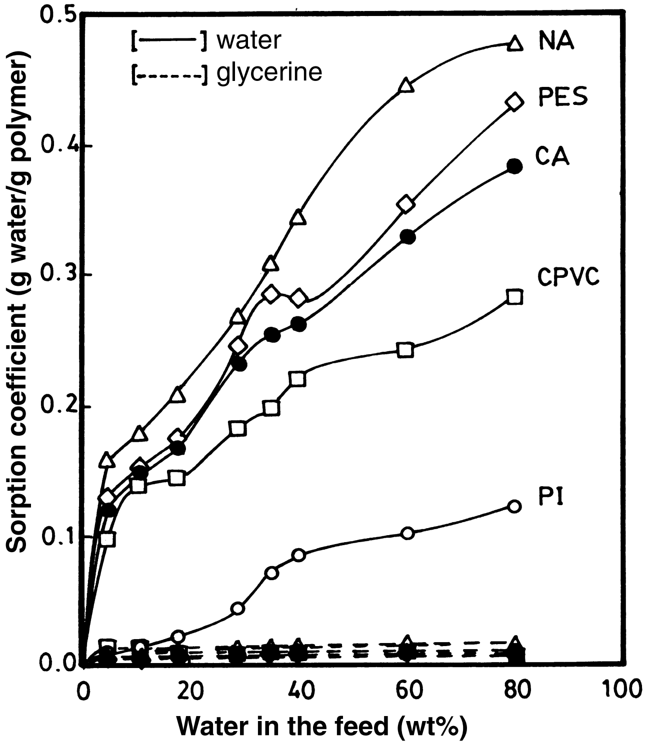

**FIG. 1.** Sorption isotherms of glycerine and water for various membranes at 30°C. NA, Nafion (procured from Aldrich Chemicals, Milwaukee, WI); PES, polyethersulfone; CA, cellulose triacetate; CPVC, carboxylated polyvinylchloride; PI, polyimide.

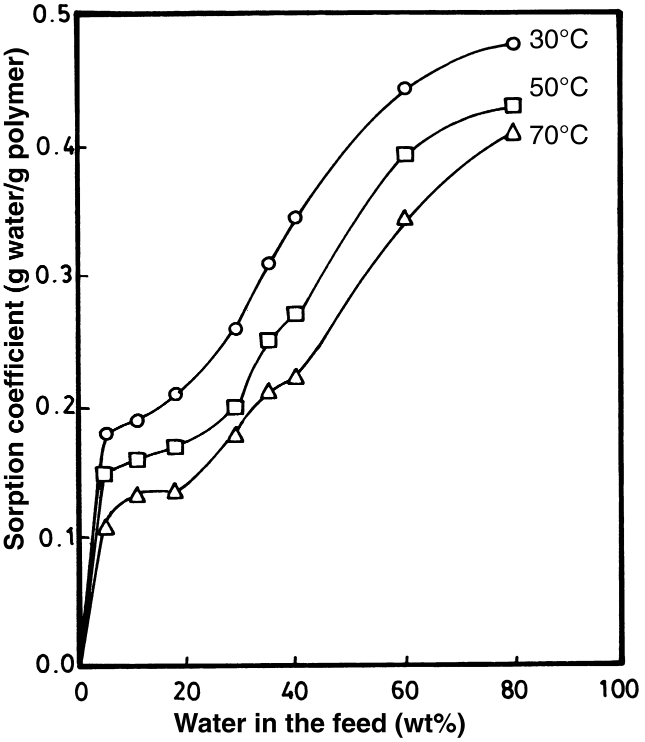

**FIG. 2.** Sorption isotheris of water at 30, 50, and 70°C for Nafion membrane.

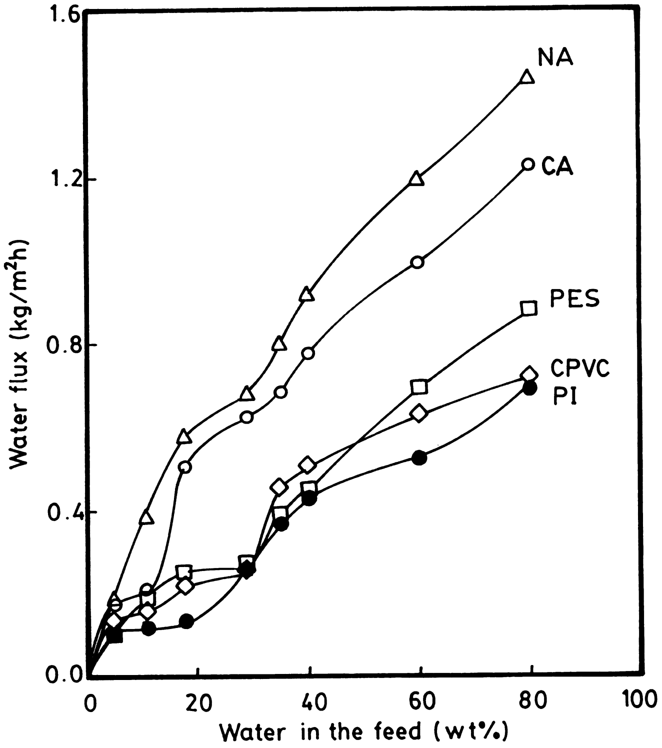

**FIG. 3.** Variation of water flux with concentration of water in the feed for various membranes at 30°C. For abbreviations, see Figure 1.

*Permeation. Effect of feed concentration.* Effect of feed concentration of water on the water flux is shown in Figure 3 for various membranes at 30°C. The NA membrane yielded the highest flux of water over the entire range of water concentration among the various membranes tested. This was attributed to plasticization of NA membrane due to increased water concentration in the membrane phase, which increases the free volume, consequently increasing sorption. Similar trends were observed at 50 and 70°C. Figure 4 shows the effects of feed concentration of water on the water selectivity of various membranes at 30°C. The permeation selectivities of various membranes for water follows the order: PES > PI > NA > CA > CPVC. Figure 5 shows the variation of PSI with water concentration in the feed for various membranes at 30°C. NA membrane yielded the highest PSI compared to the other membranes.

*Effect of feed temperature.* Figure 6 shows the variation of water flux with water concentration in the feed at various feed temperatures for the NA membrane. In general, the effect of temperature on flux was positive. Although the amount sorbed by the polymer decreased with an increase in temper-

**TABLE 2**
**Energy of Activation for Permeation ($\Delta E_p$), Diffusion, ($\Delta E_d$), and Heat of Sorption ($\Delta H_s$), for Water for Various Membranes (10% by wt of water in the feed)**

| Membrane[a] | $\Delta E_p$ (kJ/mol) | $\Delta E_d$ (kJ/mol) | $\Delta H_s$ (kJ/mol) |
|---|---|---|---|
| CPVC | 15.02 | 17.48 | −2.46 |
| NA | 7.90 | 11.32 | −3.42 |
| PI | 10.06 | 14.54 | −4.48 |
| CA | 6.96 | 15.12 | −8.16 |
| PES | 11.35 | 13.39 | −2.04 |

[a] PI, polyimide. For other abbreviations, see Table 1.

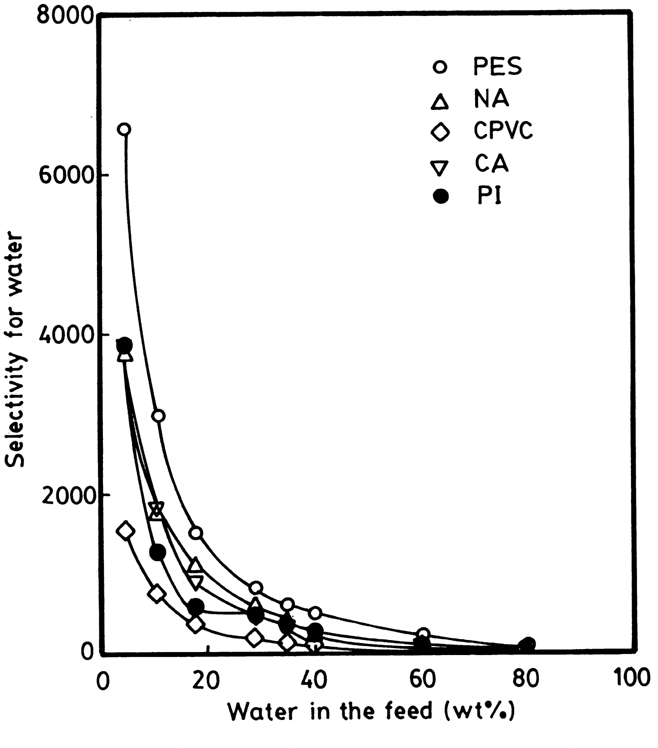

**FIG. 4.** Variation of selectivity for water with concentration of water in the feed for various membranes at 30°C. For abbreviations, see Figure 1.

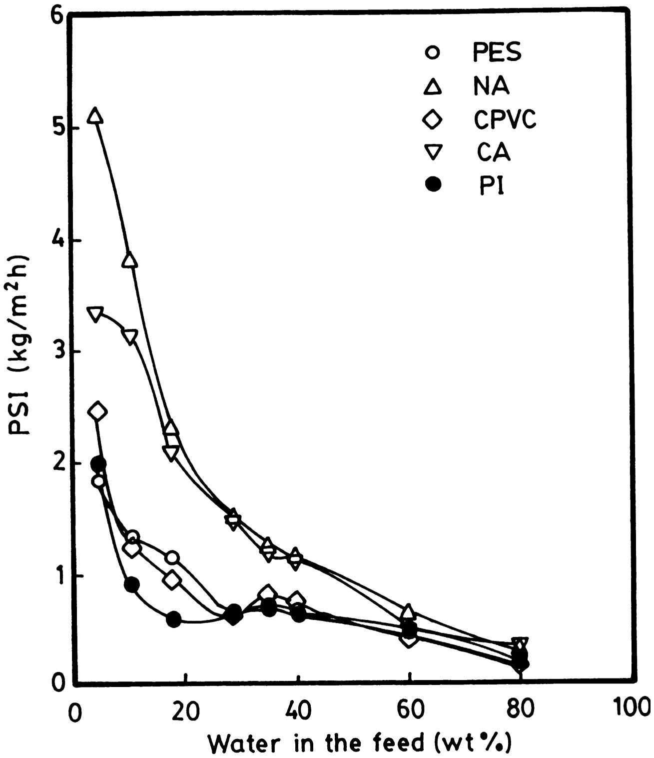

**FIG. 5.** Variation of pervaporation separation index (PSI) with concentration of water in the feed at 30°C. For abbreviations see Figure 1.

ature, this was more than offset by the increase in diffusion coefficient of the solute due to increased temperature. The sorption and diffusion steps involved in permeation are activated processes, and the temperature effect can be described by an Arrhenius-type relationship. The energy of activation for diffusion is given by Equation 3 (10),

$$\Delta E_d = \Delta E_p - \Delta H_s \qquad [3]$$

where $\Delta E_d$ = energy of activation for diffusion (kJ/mol), $\Delta E_p$ = energy of activation for pervaporation (kJ/mol), and $\Delta H_s$ = heat of sorption (kJ/mol). The values of $\Delta E_d$ and $\Delta E_p$ in various membranes are given in Table 2. The activation energy for diffusion for water in NA membrane was low compared to the other membranes, indicating easy water transport through it. These values indicate the overall effect of temperature on the permeation process for a given membrane.

With increased permeation, the permeation selectivity of the membrane for water decreased. According to Fujita's free volume theory of diffusion (11), the thermal motion of polymer chains randomly produces free volumes through which permeating molecules can diffuse. As temperature increased, the thermal agitation increased, and the diffusive free volume became larger. Therefore, more solute can diffuse through the membrane. Figure 7 shows the variation of permeation selectivity for water with its concentration in the feed at 30, 50, and 70°C for the PES membrane. For all the membranes at glycerine concentrations >60 wt%, the difference in selectivity at higher temperatures was not large. This was attributed to the fact that the diffusive cross section of glycerine is larger than that of water. At high concentrations of glycerine (>70 wt%), the hydration number (the number of water molecules attached to the glycerine molecules as a result of attraction

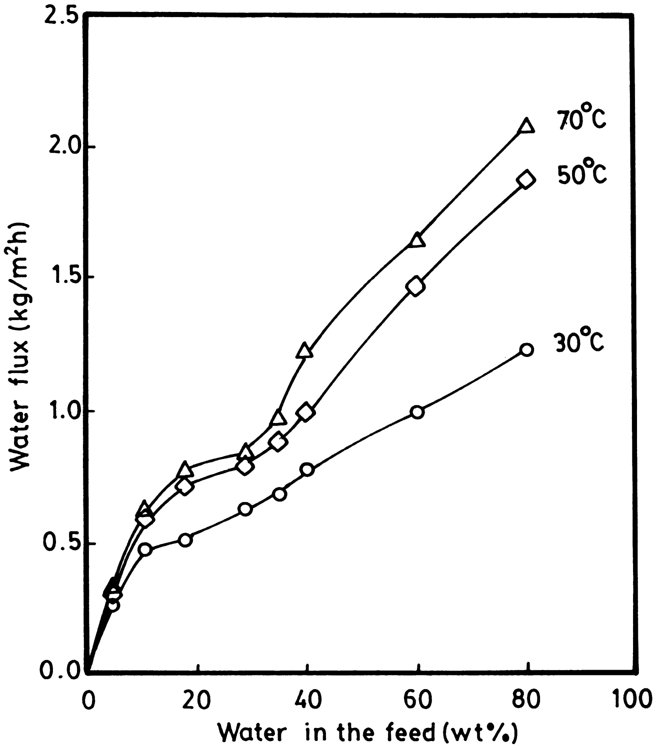

**FIG. 6.** Effect of feed temperature on the flux of water for NA membrane. For abbreviation, see Figure 1.

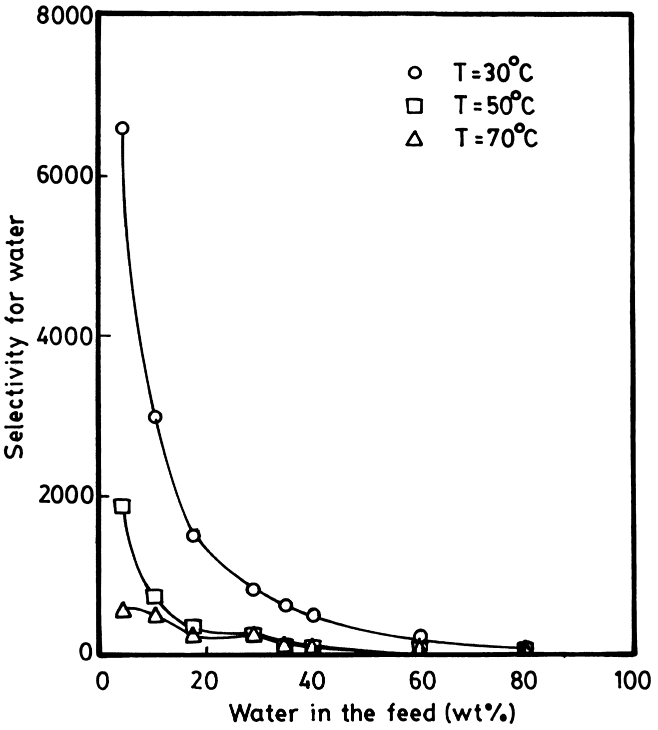

**FIG. 7.** Effect of feed temperature on the selectivity of water for PES membrane. For abbreviation, see Figure 1.

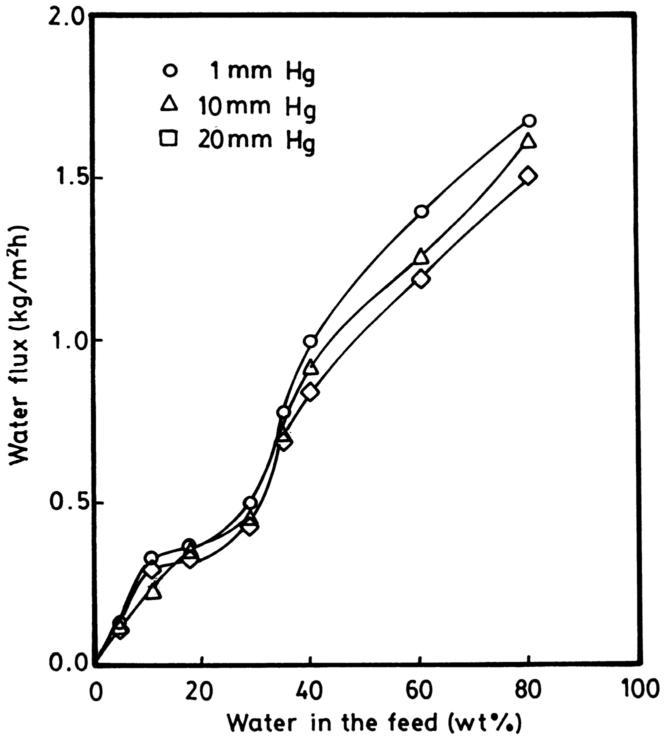

**FIG. 8.** Effect of downstream pressure on the flux of water for PES membrane at feed temperature 70°C. For abbreviation, see Figure 1.

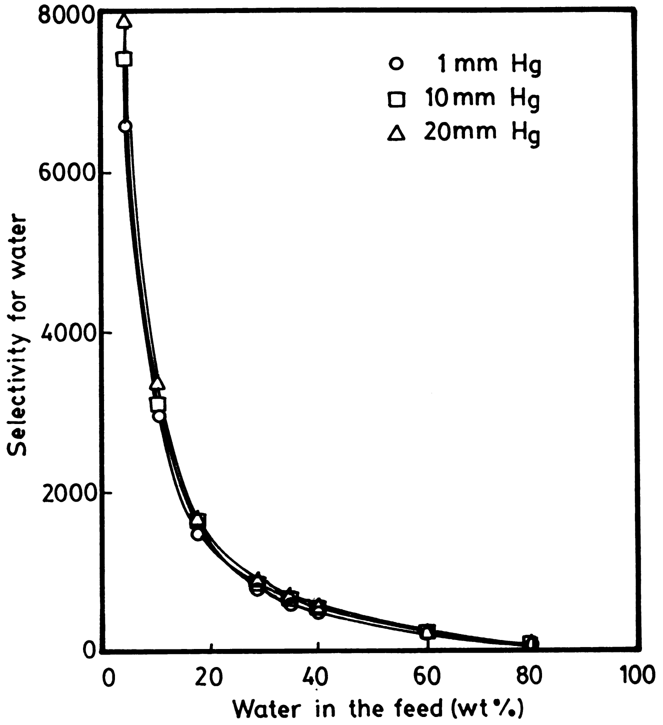

**FIG. 9.** Effect of downstream pressure on the selectivity for water for PES membrane at feed temperature 70°C. For abbreviation, see Figure 1.

between glycerine and water) of glycerine decreases in glycerine–water mixture (12). Therefore, above 70 wt% glycerine, water molecules associated with glycerine are less in number, and thus are available for polymer–water interactions. This also explains the high sorption values of water in glycerine-rich concentrations.

*Effect of downstream pressure.* The evaporation of permeants from the downstream face of the membrane is the final step in the permeation process. The effect of downstream pressure on the membrane performance was discussed by Neel *et al.* (13) for dehydration of water–tetrahydrofuran mixtures. Figure 8 shows the effect of variation of downstream pressure on the flux of water at 70°C for PES membrane. At higher downstream pressure (20 mm Hg), water flux decreased 10% compared to that at 1 mm Hg downstream pressure at 70°C. However, the condenser temperature in the case of 20 mm Hg downstream will be much higher, reducing the load on the refrigeration unit supplying the cooling medium for condensing the water issuing from the equipment. Effect of downstream pressure on the selectivity is shown in Figure 9. It is evident that between 1 and 20 mm Hg downstream pressure, the effect on the selectivity for water is negligible. It will therefore be preferable to use the highest (20 mm) downstream pressure without affecting the selectivity.

*Comparison of PV with vapor liquid equilibrium (VLE) data for evaporation/distillation.* Figure 10 gives the variation of concentration of water (wt%) in the feed with the concentration of water (wt%) in the feed for various membranes at 30°C. These data are compared with VLE data (14). The PV of glycerine–water mixture yielded superior separation to that of distillation, particularly for glycerine concentration >90 wt%.

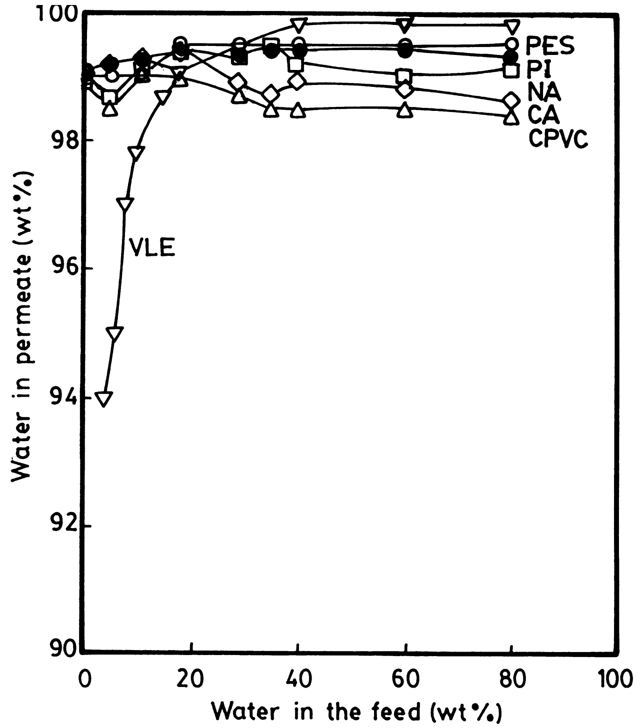

**FIG. 10.** Comparison of pervaporation data with vapor liquid equilibrium (VLE) data for various membranes at 30°C. For other abbreviations, see Figure 1.

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