Dehydration of Oil-Water Emulsion by Pervaporation Using Porous Hydrophilic Membranes

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Pervaporation of Oil-Water Emulsion

1 ABSTRACT

Porous cellulose and polyvinyl alcohol membranes were tested for dehydration of oil-water emulsion by pervaporation at different temperatures. Membranes having pore sizes that correspond to those of reverse osmosis and ultrafiltration membranes, removed water effectively from oil-water emulsions. The permeation rate decreased with an increase in the oil content in the emulsion, probably due to a gradual change in the emulsion structure from the w/o/w to o/w/o type. The permeation rate increased with an increase in the operating temperature without a significant change in the oil separation.

2 INTRODUCTION

Though pervaporation has only a short history, it has become a versatile industrial process. Many studies have been made, including separations of various liquid mixtures, using a number of different polymers as membrane materials. Particular attention has been focused on the separation of water-ethyl alcohol mixtures, since other membrane separation processes proved less effective for obtaining a high separation factor [1]. To date membranes tested for pervaporation possessed small pore sizes, in order to obtain high separation factors. Though no pore size data are available for the pervaporation membranes recorded in the literature, it is assumed that the pore size was in the range of less than one nanometer which is equal to or less than that of reverse osmosis membranes. There is one notable exception where cellulose ultrafiltration membranes have been used for the pervaporation of ethyl alcohol-heptane mixtures. As expected, the separation factor for this liquid mixture was low [2]. The question may then arise whether there are any separation processes where ultrafiltration membranes can be used for pervaporation. This paper attempts to answer the above question.

Let us now imagine replacing ultrafiltration by pervaporation. We may be able to use the same ultrafiltration membrane but we shall apply vacuum on the downstream side of the membrane instead of applying high pressure on the feed side of the membrane. If the solvent is sufficiently volatile, we are able to collect permeate on the downstream side of the membrane as vapor. If the pore size is so small that the solute permeation through the membrane pore is prevented, we are able to separate solute from the solvent. Though the above concept is easy to accept, it has not been experimentally tested, probably because pervaporation was considered less economical than ultrafiltration. But pervaporation has certain advantages over ultrafiltration. Suppose solutes in the feed solution are nonvolatile, which is usually the case, they will be completely retained on the feed side of the membrane during pervaporation. The membrane pore may be of any size as long as the membrane can hold the solvent liquid on the high pressure side of the membrane. Such a pore size can be calculated by the Cantor equation for a given pressure drop across the membrane [3]. We may expect a sufficiently large flux if pore sizes of the membrane are large. The attractive force working between the solvent and the membrane surface may also enhance the solvent permeation rate. The ultrafiltration membrane, on the other hand, requires a pore size

which is smaller or only slightly larger than the size of the solute depending on the interaction force working between the solute and the membrane surface, which may set a limit to the solvent permeation rate.

The objective of this paper is to demonstrate that both reverse osmosis and ultrafiltration membranes can be used for membrane separation by pervaporation. Dehydration of the kerosine oil-water (o/w) emulsion was chosen for this purpose since it is known that ultrafiltration is also applicable to the above process [4, 5, 6]. Kerosine oil is significantly less volatile (boiling point 150°C -300°C) than water. Besides, we have chosen hydrophilic polymers as membrane materials to enhance the dehydration rate. Therefore, this is an appropriate system to test whether the aforementioned concept is truly workable. An economic comparison of pervaporation and ultrafiltration is beyond the scope of this work since the pore sizes of the membranes tested were not necessarily optimized for pervaporation.

3 EXPERIMENTAL

Materials. Kerosine (Class III A) and sodium lauryl sulfate were supplied by Fisher Scientific Co. Crude oil samples were supplied by the Saskatchewan Oil Co. Samples 1 and 2 having different viscosities were supplied separately. Cellulose was supplied by Baker Chemical Co. in powder form and was of chromatography grade. Paraformaldehyde and dimethyl sulfoxide were supplied by Anachemia Chemicals Ltd. and used without further purification. Polyvinyl alcohol (MW 10,000) was from Fluka AG.

Emulsion preparation. Oil-water (o/w) emulsions were prepared by mixing kerosine, sodium lauryl sulfate and water. The sodium lauryl sulfate content in the emulsion was fixed at 0.5%. The kerosine in the emulsion was from 10 to 90 wt %. The oil-surfactant-water mixture was stirred vigorously for at least two days. Stirring was continued until the emulsion was loaded into the pervaporation cell. In order to express the concentration of kerosine in the feed emulsion, the term oil content will be used hereafter. Oil content is defined as the weight per cent of kerosine plus surfactant in the total emulsion. Since the amount of the surfactant added is so small, the oil content and the kerosine weight per cent are almost equal.

Membrane preparation. Cellulose membranes were prepared according to the method of Farnand [7] and Johnson et al. [8]. Briefly, cellulose poly-

mer (8.89 wt %), paraformaldehyde (8.75 wt %) and potassium hydroxide (0.05 wt %) were mixed in dimethyl sulfoxide solvent (82.31 wt %) and the mixture was heated to form methylol cellulose, which could be dissolved in dimethyl sulfoxide solvent. The polymer solution was cast on a glass plate after the solution was cooled to room temperature and the cast film was placed in a gelation medium (ice cold water). Cellulose was regenerated in water by hydrolysis, while an asymmetric cellulose membrane was being formed. Polyvinyl alcohol membranes were produced by the method of Korsmeyer and Peppas [9] and Higuchi and Iijima [10]. Polyvinyl alcohol polymer (15 wt %) was dissolved in a water - dimethyl sulfoxide mixture by heating. The polymer solution was cast on a glass plate and the cast film was gelled and cross-linked simultaneously in a mixture of water, sodium sulfate, sulfuric acid and glutaraldehyde. Sometimes the membranes were cast on a backing material.

Both cellulose and polyvinyl alcohol membranes showed sodium chloride separation of less than 30% at a pressure of 250 psig and the feed sodium chloride concentration of 3500 ppm. Cellulose membranes showed polyethylene glycol (MW 6000) separation of 80%, when the operating pressure was 50 psig and the feed polyethylene glycol concentration was 100 ppm. Therefore, both cellulose and polyvinyl alcohol membranes were regarded as ultrafiltration membranes.

Pervaporation. The equipment and the method used for the pervaporation experiment were described in detail previously [2]. As for the operating conditions, the downstream pressure was changed in the range 2-12 mmHg (267- 1600 Pa) and the operating temperature was between 25°C- 75 °C.

Analytical method. The total carbon content in the feed and in the permeate was determined by a total carbon analyser (Beckman Model 915B). Each sample had to be diluted to a total carbon content below 100 ppm. The separation based on the total carbon content was calculated by

Separation =(total carbon content in the feed - total carbon content in the permeate) / (total carbon content in the feed) × 100

When sodium chloride was used as the reference solute in the reverse osmosis experiment, the sodium chloride concentration in the feed and in the permeate was measured by a conductivity bridge. The separation of sodium chloride was calculated by an equation similar to the above equation, but

sodium chloride concentration was used instead of the total carbon content in the equation. The conductivity was measured also for feed oil emulsions, in order to determine whether oil or water constitutes the continuous phase of the emulsion.

4   RESULTS AND DISCUSSION

Figure 1 shows results of long duration experiments using cellulose membranes. The total carbon separation was maintained above 99% at each temperature throughout the experiment. The permeation rate increased with an increase in the operating temperature but decreased with the operation time since the oil concentration in the feed emulsion increased with time. The fractional water recovery and the oil content in the feed emulsion were calculated from the separation and the permeation rate data and plotted also in Fig. 1 as a function of operation time. As water recovery in the permeate approaches 100%, the oil content in the emulsion also increases. Permeation rate versus oil content was replotted in Fig. 2. At each operating temperature the permeation rate decreases when the oil content increases from 10 to 15%, remains constant from 15 to 30%, then gradually decreases from 30 to 70%. Above 70% of the oil content the permeation rate is very low. The permeation data shown in Fig. 2 seem to reflect the structure of the feed emulsion. In order to obtain structural information of the kerosine-water emulsion, microscopic observations of the emulsion were made. Many oil globules (diameter 10-100 μm) dispersed in a continuous water phase were observed when the oil content was lower than 70%, corresponding to w/o/w emulsion (Fig. 3a). On the other hand, few small water particles were observed in a continuous oil phase (small white points are seen in the dark background, large white circles are air bubbles.) when the oil concentration was higher than 90%, corresponding to o/w/o emulsion (Fig. 3b). The oil content from 70 to 90% was a transition region. It was difficult to determine whether water or oil was the continuous phase in this region. No abrupt change from w/o/w to o/w/o emulsion occurred. The gradual transition from w/o/w to o/w/o emulsion was also reflected in the conductivity data shown in Fig. 4. The conductivity of kerosine/surfactant/water mixtures decreased gradually with an increase in the kerosine content in the emulsion. There was no indication of an abrupt drop in the conductivity data which was supposed to occur when a sudden

change from w/o/w to o/w/o emulsion would occur. Above 90% oil content it was difficult to measure the conductivity because of high viscosities. Kerosine with 0.5% surfactant showed a conductivity between 40- 90 μS/cm.

It is conjectured that water transport from the feed emulsion to the membrane surface undergoes only little resistance when w/o/w emulsion is formed. On the other hand, when water droplets are trapped in a continuous oil phase, as happens for the o/w/o emulsion, the transport of water to the membrane surface is hindered strongly by the continuous oil phase. Therefore, the water flux decrease occurring in the transition region from w/o/w to o/w/o emulsion seems natural. Since the phase change occurs only gradually with a change in the oil content in the emulsion, the change in the permeation rate is also gradual.

Figure 5 shows experimental results using cellulose and polyvinyl alcohol membranes cast on a backing material. Note that the permeation rate decreased continuously with an increase in the feed oil content when pervaporation was performed with a cellulose membrane, whereas it remained constant in the 10 to 50 % oil content with a polyvinyl alcohol membrane. But the permeation rate decreased drastically when the oil content was increased from 50 to 70%. The difference in the pattern of the permeation rate can presumably be ascribed to the difference in the interaction between oil particles and the membrane material and in the pore size and the pore size distribution of the membranes being compared. It is interesting to note that the permeation rate can be improved significantly by changing the pore size and the pore size distribution of the membrane.

The dehydration of crude oil samples was attempted using both cellulose and polyvinyl alcohol membranes. Figure 6 shows results of dehydration of the first crude oil sample by a cellulose membrane. The figure shows that the pervaporation rate was extremely low and decreased gradually with the operation time, whereas the carbon content in the permeate steadily increased. Table I shows the results of pervaporation for the second crude oil sample at various temperatures. The data show that a higher permeation rate and a higher carbon content in the permeate were obtained at a higher operating temperature.

Finally, Table II shows the results of two experiments of pervaporation with 50% kerosine concentration. In one the emulsion underwent pervaporation without salt. In the other 0.5% of NaCl was added into the emulsion. The presence of NaCl in the emulsion is reflected in a high conductivity value

of the second feed emulsion. The permeate conductivities from both feed samples were between 12 and 20 μS/cm. These values were far lower than feed conductivities, but an order of magnitude higher than that of distilled water (ca. 1 μS/cm). This indicates that a small quantity of electrolytes passed through the membrane. The nearly identical values of the permeate conductivity in the two experiments indicate that the electrolyte passage is not that of NaCl but that of the surfactant.

5   CONCLUSION

1. The dehydration of oil-water emulsion is possible by pervaporation.
2. Membranes prepared from hydrophilic polymers are suitable for pervaporation of oil-water emulsion.
3. Membranes of different pore sizes can be used for the above separation process. Membranes that have pore sizes corresponding to those of ultrafiltration membranes are especially effective.
4. The retention of the oil component in the emulsion is almost complete. The permeation rate decreases as the emulsion changes from w/o/w to o/w/o type.
5. Electrolytes such as NaCl are retained in the feed emulsion. However, it is likely that a small quantity of surfactant added to form emulsions passes through the membrane.

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Table I Results of Dehydration of Second Crude Oil
by Pervaporation

Temperature °C	Operation time h	Permeate collected g	Average flux g/h	Permeate carbon content ppm
24	10.5	0.1695	0.0226	1581
40	12.5	0.4022	0.0322	2565
60	18.0	0.6427	0.0357	4158

Membrane material, polyvinyl alcohol; membrane area, 9.6 cm^2; downstream pressure, 12 - 15 mmHg

Table II Results of Conductivity Measurement

	Feed conductivity $\mu S/cm$	Permeate conductivity $\mu S/cm$
50% emulsion without salt	810 – 840	12 – 19.2
50% emulsion with 0.5 % NaCl	5840	12 – 20.4

Figure Captions

1. Results of Long-Run Pervaporation Experiments

Initial feed, kerosine (10 wt %) - sodium lauryl sulfate (0.5 wt %) - water (89.5 wt %); membrane, cellulose; membrane area, 9.6 cm^2; downstream pressure, 10-12 mmHg at 25 °C, 12- 15 mmHg at 45 °C, 25-35 mmHg at 78 °C

2. Permeation Rate versus Oil Concentration

Membranes and operating conditions, same as Figure 1

3. Microscopic Pictures of Oil Emulsions

a. Oil concentration, 70% b. Oil concentration, 90%

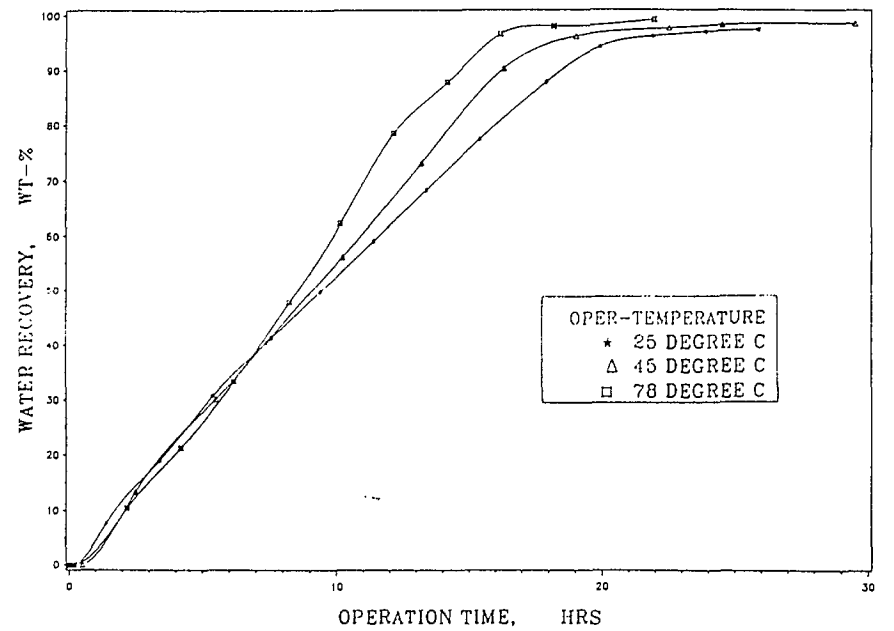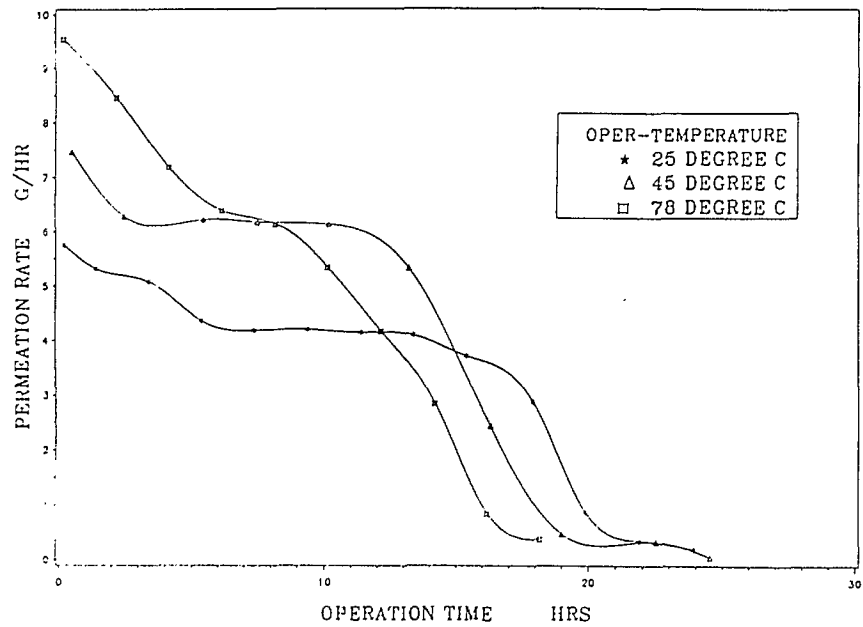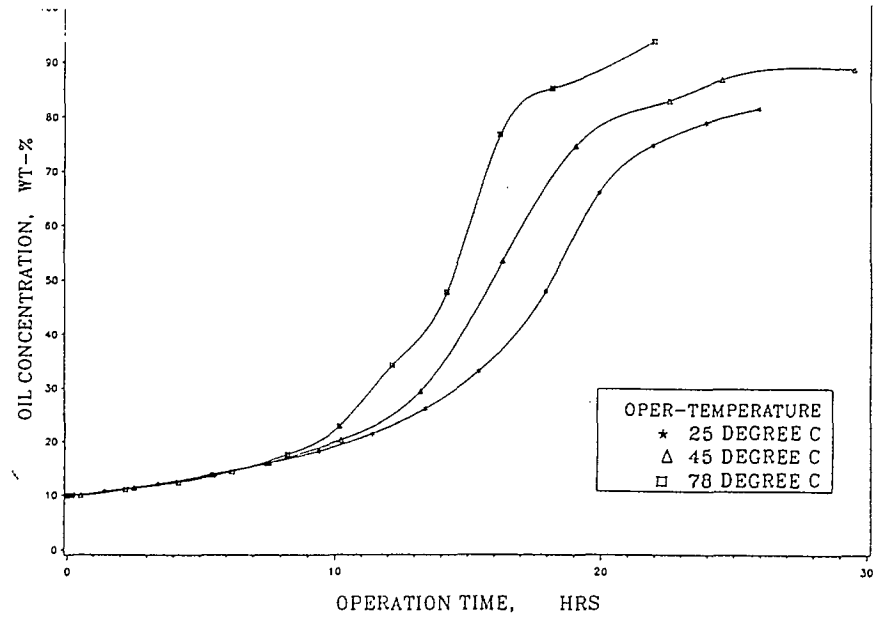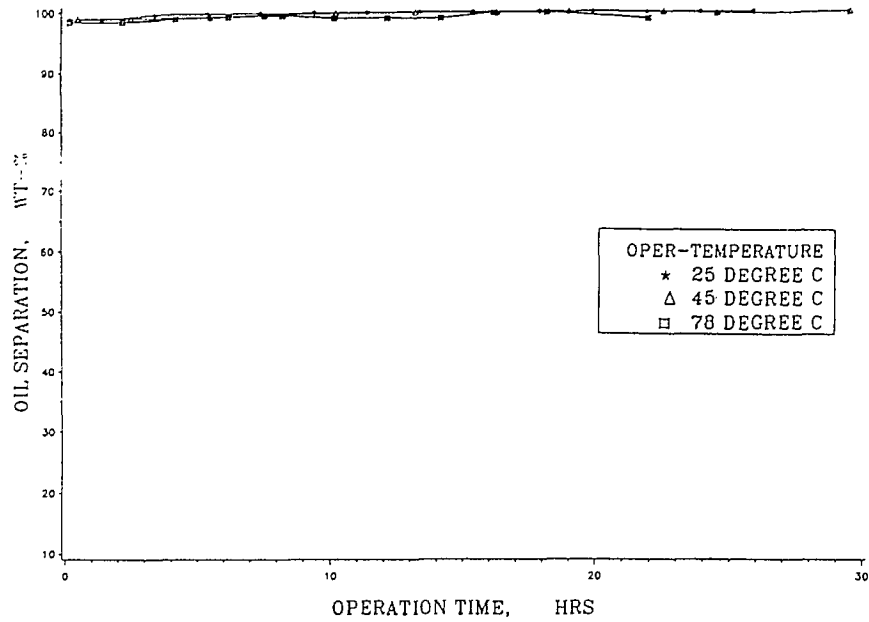4. Conductivity Data at Different Oil Concentrations in the Feed Emulsion
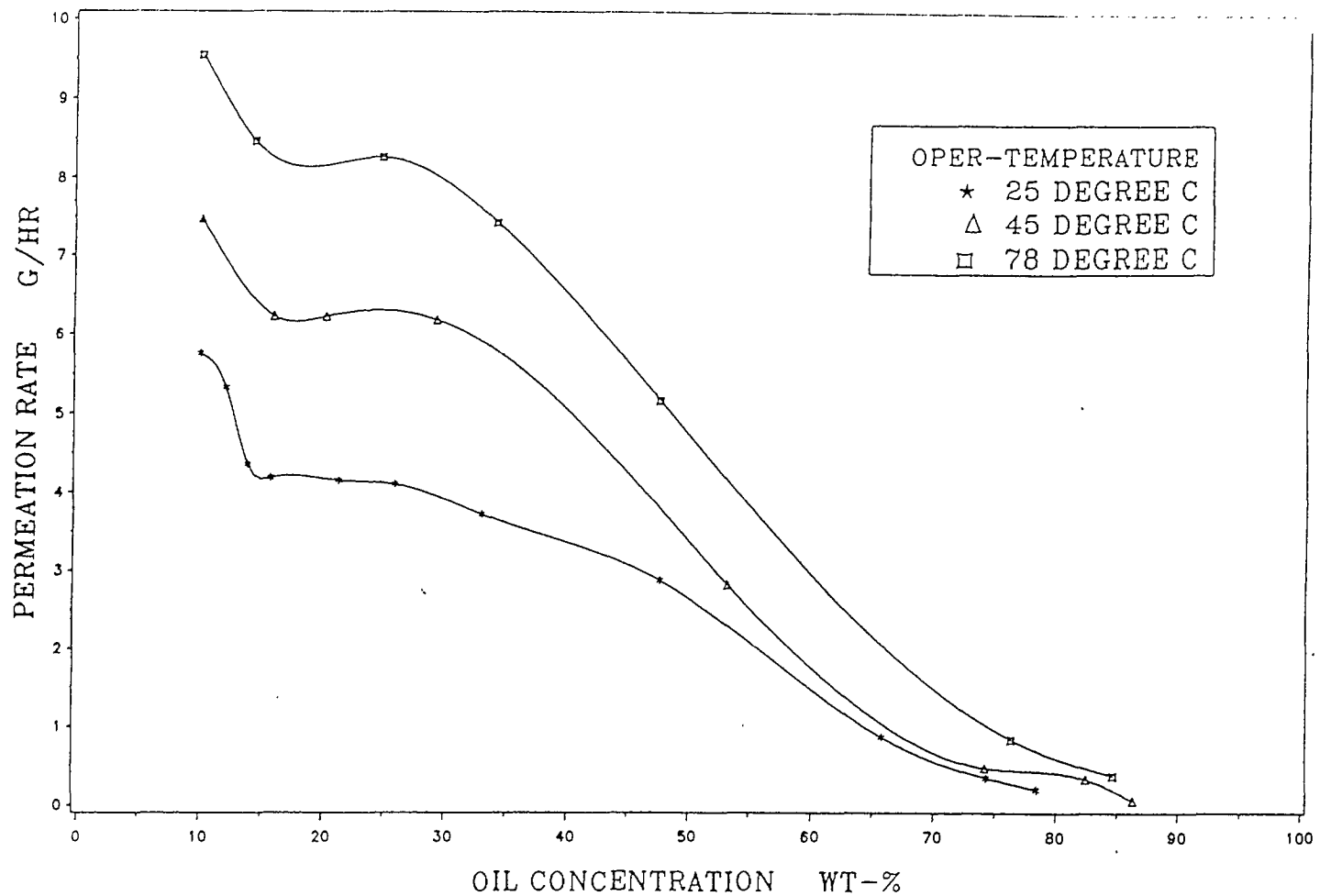
Temperature, 25 °C

5. Permeation Rate versus Oil Concentration Curves for Different Membrane Materials

Initial feed, kerosine (10 wt %) - sodium lauryl sulfate (0.5 wt %) - water (89.5 wt %); membranes, cellulose and polyvinyl alcohol cast on a backing material; membrane area, 9.6 cm^2; downstream pressure, 10-12 mmHg

6. Results of Pervaporation for the First Crude Oil Sample

Feed, the first crude oil sample; membrane, cellulose membrane cast on a backing material; membrane area, 9.6 cm^2; operating temperature, 60-65 °C; downstream pressure, 12-15 mmHg

Top-left chart:

OIL SEPARATION, WT-%

OPER-TEMPERATURE
★ 25 DEGREE C
△ 45 DEGREE C
□ 78 DEGREE C

100 90 80 70 60 50 40 30 20 10

0 10 20 30

OPERATION TIME,   HRS

Top-right chart:

OIL CONCENTRATION, WT-%

OPER-TEMPERATURE
★ 25 DEGREE C
△ 45 DEGREE C
□ 78 DEGREE C

90 80 70 60 50 40 30 20 10 0

0 10 20 30

OPERATION TIME,   HRS

Bottom-left chart:

PERMEATION RATE   G/HR

OPER-TEMPERATURE
★ 25 DEGREE C
△ 45 DEGREE C
□ 78 DEGREE C

10 9 8 7 6 5 4 3 2

0 10 20 30

OPERATION TIME   HRS

Bottom-right chart:

WATER RECOVERY,   WT-%

OPER-TEMPERATURE
★ 25 DEGREE C
△ 45 DEGREE C
□ 78 DEGREE C

100 90 80 70 60 50 40 30 20 10 0

0 10 20 30

OPERATION TIME,   HRS

A

B