

Pervaporation of aqueous organic mixture through in situ complex membranes based on polyacrylonitrile*

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Abstract

Modified polyacrylonitrile(PAN) membranes were prepared by emulsion or emulsifier-free emulsion polymerization technique. Separation capacity was determined at several operating temperatures(25, 40, 55 and 70 °C) to dehydrate 56wt% pyridine aqueous solution through modified PAN membranes having different functional groups. All these PAN-based membranes were selective toward water to different degrees depending on the nature of functional groups present in the membranes. Pervaporation characteristics of PAN-based membranes are so different and classified into three categories depending on the type of the functional groups in PAN copolymers. Among PAN-based membranes, the *in-situ* complex membranes show the best separation capacity over the operating temperatures.

Keywords : pervaporation, PAN-based membranes, *in-situ* complex

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Introduction

Pyridine is an important solvent or catalyst and also frequently present in effluents from rubber and plastics, petrochemicals and some other organochemical industries such as pharmaceuticals and agrochemicals[1]. The recovery of pyridine from outflow is an important problem because it is often necessary to reuse relatively expensive chemicals. Pyridine has an azeotropic point with water at 58.7% by weight at 93.6°C[2]. Dehydration of pyridine aqueous solution has been conducted by an extractive distillation, extraction, strong drying agent and azeotropic distillation[3,4]. However, extractions are less efficient for gaining high purity pyridine and the rest of the methods are somewhat expensive or energy intensive separation methods.

Pervaporation, one of the membrane processes, offers an effective recovery from aqueous media, and is an energy efficient separation technique for the separation of liquid mixture, especially azeotropic mixtures, close boiling compounds and isomers such as *m*-xylene and *p*-xylene[5~8].

Studies on the separation of pyridine/water mixture by pervaporation have been reported and evaluated by Eustache and Histi[9], more recently by Drioli et al.[10,11] and Néel et al.[12](see Table 1). In the dehydration process, treated GFT membrane, which has hydrophilic support(polyacrylonitrile) and skin layer(poly(vinyl alcohol)), shows a good selectivity toward water. Ionomer membranes such as acrylic acid grafted polyethylene, the interpenetrating polymer network of polyethylene and sulfonated poly(styrene-co-divinylbenzene), Nafion, poly(tetrafluoro-ethylene-co-styrene sulfonic acid) and so on, all possessing special functional groups in the membranes have high permeate fluxes but low selectivities. In addition to these, Naylor et al. also reported the results of dehydration of aqueous pyridine by using BP poly(acrylic

acid) membrane, which showed high permeate selectivity. The permeates contained only less than 0.2% pyridine over the feed concentration range examined (up to 40% water)[13].

In our previous studies, we proposed *in-situ* complex membrane concept for the dehydration of acetic acid[14] and pyridine aqueous solutions[18]. Particularly for the dehydration of pyridine solution, PAN and poly(acrylonitrile-*co*-acrylic acid) (PAN-*co*-AA) membranes behave differently. The permeate flux of PAN is almost independent of operating temperature while that of PAN-*co*-AA membrane is increased with temperature below 70°C. This behavior prompts to study the effects of functional groups and operating temperature on the pervaporation performances of PAN-based membranes. Among the PAN-based membranes, we have selected several functional groups based on the types of interaction with permeants, water and pyridine. Three categories are as follows ; 1) non-specific interactions between PAN-based membrane and permeants, 2) specific interactions between PAN-based membrane and major permeant, and 3) specific interaction between PAN-based membrane and minor permeant.

PAN-modified membranes (see Table 2) were prepared by emulsion or emulsifier-free emulsion polymerization. Separation capacity was determined at four operating temperatures (25, 40, 55 and 70 °C) to separate 56wt% pyridine aqueous solution through the membranes having different functional groups.

Experimental

Materials

Acrylonitrile(AN, Katayama Chem. Co., Japan) and acrylic acid(AA, Junsei Chem. Co., Japan) were purified through the inhibitor remover column(Aldrich Chem. Co., USA) to remove hydroquinone before use. Acryl amide(AAm, Junsei Chem. Co. Japan) and 4-styrene sulfonic acid sodium salt(SS-Na, Aldrich

Chem. Co., USA) were used as received. Sodium bicarbonate(Duksan Chem. Co., Japan), potassium persulfate (PPS, Wako Pure Chem. Co., Japan) and conc. HCl(Duksan Chem. Co., Japan) were used as received. Reagent grade pyridine(Junsei Chem. Co., Japan), toluene(Junsei Chem. Co., Japan) and dimethylformamide(DMF, Junsei Chem. Co., Japan) were used without further purification. Water was distilled and deionized by Milli-Q ultra-pure water system(Millipore Co., USA). Sodium lauryl sulfate(SLS, Pacific Chem. Co., Korea) was used as a surface active agent.

Synthesis of PAN-based polymers

The preparation method of PAN-based polymers was previously reported in reference 14 and the conditions of polymerizations were listed in Table 3.

Characterization

Elemental analyses were conducted by Carlo Erba Model EA 1108. Inherent viscosities of all polymers were determined by using Cannon-Fenske type viscometer and measured at the concentration of 0.5g/dL in DMF at 25°C.

Degree of swelling

PAN-based membrane samples were dipped into 200ml vials filled with 56wt% pyridine aqueous solution, respectively. The degree of swelling was determined after the vials were placed in an incubator kept at 25, 40, 55 and 70°C for 5 days, respectively. The following equation was used,

$$\text{Degree of swelling (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_w and W_d represent the weights of the membrane in wet and dry states, respectively.

Pervaporation

The equipment and procedures used to conduct the pervaporation experiments were identical to those described previously by Lee et al.[15]. However the feed mixture was continuously supplied into the pervaporation cell. The effective membrane area in contact with liquid was about 25.98cm². The downstream pressure was lower than 1 torr and the operating temperature was 25, 40, 55 and 70°C.

The composition of the permeate was measured by Shimadzu GC-14A equipped with a 3m long glass column packed with GE-SE 30. Separation factor(α) and permeate flux(J) are defined respectively as follows,

$$\alpha = \frac{Y_w / Y_p}{X_w / X_p} \quad (2)$$

$$J = \frac{Q}{A \times t} \quad (3)$$

where Y_i is the weight fraction in permeate and X_i is that in feed. Subscripts w and p denote water and pyridine, respectively. Q , A and t represent the weight of permeant(g), effective membrane area(m²) and operating time(hr), respectively.

Swelling behavior

Swelling degree of a membrane gives a qualitative indication of the membrane affinity for a given water-pyridine mixture. Results of the swelling measurements according to the temperature are illustrated in Fig. 1. An increase of swelling degree with temperature may indicate that a permeation flux will increase at high operating temperature in pervaporation. PAN has no specific functional group with water or pyridine and has the swelling degree of 7.4~12.4% which is less affected by temperature. However, the swelling degrees of PAN-AAm, PAN-AA and PAN-SS membranes, that have functional groups which can interact with solutes(water and pyridine), increase with the operating temperature. It is also a significant observation that the affinity of PAN toward solutes was enhanced by introducing several functional groups in the polymer.

Pervaporation

The separation capacity was determined at several temperatures(25, 40, 55 and 70 °C) for a 56wt% pyridine aqueous solution through PAN membranes having different functional groups. Fig. 2 shows the permeation fluxes of PAN-based membranes as a function of operating temperature. Since the diffusivity of feed components in polymeric membranes is generally dependent upon the operating temperature following an Arrhenius-type equation, permeation fluxes should also depend on the temperatures. As expected, an increase in permeation flux with temperature was observed in the case of type II and III membranes. Especially, PAN-AAm showed 28 times higher flux values than that of PAN. However, in the case of PAN membrane, there is no remarkable increase of permeation flux depending upon temperature and it has relatively low permeation flux of 15.4~48.0g/m²hr. Therefore, the effect of operating temperature on the permeation flux is less with PAN than with PAN modified membranes. We also

knew from Fig. 1 that the swelling behavior of PAN is less affected by emperature below its T_g (minimum value of T_g of PAN reported is 80°C). We had reported the similar result in the separation of water and ethanol mixture through PAN membrane and it can be seen that flux is only increased about 10% when the operating temperature increased from room temperature to 75°C[16]. If the polymer is glassy, the solutes that interact with the polymer lower the T_g by a plasticizing action[17]. The formation of hydrogen bonding or *in-situ* complex increase the plasticizing action and thus the free volume or chain flexibility, resulting in an increase in permeation flux at higher operating temperature for type II and III membranes compared with type I PAN membrane.

When the temperature of the feed increases, the permeation flux generally follows an Arrhenius-type equation[18].

$$J_i = J_{o,i} \exp(E_i / RT) \quad (4)$$

E_w and E_p are activation energies for J_w and J_p respectively. Fig. 3 shows Arrhenius plots of PAN-based membranes. From these plots, E_w and E_p were calculated and listed in Table 5. In general E_p is greater than E_w . Thus the permeation of pyridine through PAN-based membranes is more temperature-sensitive than that of water. In the case of PAN-AAm, its high E_w and E_p and relatively large difference between them contributed to the large increase of permeation flux at high temperature (see Fig. 2) and a little decrease of the weight % of water in the permeate (see Fig. 4). Comparatively through PAN-based membranes, as can be seen in Table 5, PAN has relatively small E_w and E_p values.

Fig. 4 illustrates the concentration of water in the permeate, C_p^w , with temperature. All PAN-based membranes exhibit high selectivity toward water.

PAN, PAN-AA and PAN-SS membranes show C_p^w of above 99%. In type III membranes(PAN-AA and PAN-SS), E_w and E_p range between 8.3~10.5 kcal/mol and a relatively small reduction in C_p^w can be found as temperature increases. It is probably related to the effect of hindered permeation of pyridine through *in-situ* complex membrane although the chain mobility is affected by temperature. That is, the formation of *in-situ* complex between pyridine in the feed and an acidic functional group in the membrane holds pyridine and hinders the pyridine permeation, while the permeation of water is accelerated through the complex[19]. In this case, pervaporation can be advantageous when operating at high temperature. PAN membrane has no reduction in C_p^w operated at below 70°C. It is mainly due to the low activation energy and less temperature dependence below T_g . However, a marked decrease of C_p^w is found in PAN-AAm membrane. PAN-AAm has a functional group which can interact with solutes through hydrogen bonding. The hydrogen bonding cannot selectively hinder the permeation of pyridine as in the case of type III, *in-situ* complex membrane. A similar behavior such as in type II membrane can be found in reference 20 which describes the effect of the operating temperature on the separation factor and the weight fraction of water in permeate through poly(acrylonitrile-co-maleimide) membrane that can also interact with solutes(water and ethanol) by hydrogen bonding. They reported that the weight % of water in permeate decreased from 99.9 to 88.7 with increasing operating temperature ranging from -10 to 40°C and that this temperature dependence was due to the hydrogen bonding interaction between water and maleimide units in the membrane.

From Figs. 2-4, we know that *in-situ* complex membranes show only a few decrease in the water concentration in permeate with temperature although the permeation flux moderately increases. With these separation results, the *in-situ*

complex concept is believed to be a useful system for the dehydration of aqueous pyridine.

Conclusions

PAN-based membranes were prepared by using emulsion and emulsifier-free polymerization. All these PAN-based membranes were selective toward water to different degrees depending on the nature of the functional groups in the membranes. Pervaporation characteristics of PAN-based membranes depend on the functional groups in the polymer. It was thought that the different separation behaviors of PAN-modified membranes were attributed to the difference in the interaction between solutes and membranes. According to these interaction, three types of PAN-based membranes were classified. In the case of type I membrane(PAN), there is no remarkable interaction with permeants because it does not have any specific functional groups in the membrane which can interact with permeants. The separation capacity of PAN-AAm membrane(type II membrane) was decreased with an increase in temperature due to the hydrogen bonding interaction between solutes and the membrane. The *in-situ* complex membranes (type III) show the best separation capacity over the operating temperatures(25~ 70°C) among the membranes tested in this study.

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Table 1. Pervaporation performances of water-pyridine mixture from recent literature

Membrane	Feed	Selectivity	Flux (g/m ² hr)	Temperature (°C)	Reference
LDPE	10 ppm	18*	-	35	9
TS 605	1000 ppm	70*	-	35	9
PERVAP 1160	1.9 mol%	23*	1440	50	10
PERVAP 1000	20 mol%	13.1	328	40	11
NAN-ARC-90-1	19 mol%	38.9	1180	40	11
GFT	59wt%	27.3	330	40	12
Treated GFT	59wt%	1438	140	40	12
RAI 1010	59wt%	8.8	3850	40	12
PEA	59wt%	2.2	1500	40	12
PESS	59wt%	6.1	930	40	12
Nafion	59wt%	3.7	680	40	12

* Selectivity toward pyridine

LDPE = low density(0.92g/ml) polyethylene, Covitep, obtained by blow extrusion;

TS 605 = crosslinked polydimethylsiloxane on a polyester support from Rhône-Poulenc;

PERVAP 1160 = composite membrane with a selective layer of modified PDMS from GFT;

GFT = PVA composite membrane from GFT; Treated GFT = crosslinked GFT;

RAI 1010 = poly(tetrafluoroethylene-co-styrene sulfonic acid);

PEA = polyethylene grafted with acrylic acid;

PESS = IPN of polyethylene and sulfonated poly-styrene-co-divinylbenzene

Table 2. Classification of types of interactions between functional groups in the membrane and permeants

Category	Functional group in membrane	Type of interaction	Membrane used in this study
I	-CN, -COOR, -Cl	-	PAN
II	-OH, -CONH ₂	hydrogen bonding with water	PAN-AAm
III	-COOH, -SO ₃ H	<i>in-situ</i> complexation between functional group and pyridine	PAN-AA PAN-SS

PAN : polyacrylonitrile

PAN-AAm : poly(acrylonitrile-co-acryl amide)

PAN-AA : poly(acrylonitrile-co-acrylic acid)

PAN-SS : poly(acrylonitrile-co-4-styrene sulfonic acid)

Table 3. Conditions for preparing PAN-based polymers

Sample	Water [ml]	SLS [mole]	AN [mole]	MFG* [mole]	PPS [mole]	Temp. [°C]
PAN	200	4.68×10^{-4}	0.57	-	2.24×10^{-3}	70
PAN-AAm	300	-	0.64	0.16	3.40×10^{-3}	60
PAN-AA	300	-	0.57	0.13	3.02×10^{-3}	70
PAN-SS	300	-	0.47	0.012	1.99×10^{-3}	70

* MFG : a monomer which gives a functional group in a polymer.

Table 4. Specification of PAN-based membranes

Sample	Mole fraction of functional group*	Yield [%]	h_{inh}^* [dl/g]
PAN	-	96	3.05
PAN-AAm	0.108	94	2.80
PAN-AA	0.105	93	3.00
PAN-SS	0.038	87	4.85

* Determined by elemental analysis of polymers.

Table 5. Activation energies(E) for water and pyridine through PAN-based membranes for dehydration of 56wt% pyridine aqueous solution

Sample	E_w	E_p
PAN	4.55	6.91
PAN-AAm	18.07	22.10
PAN-AA	8.32	10.53
PAN-SS	8.87	9.41

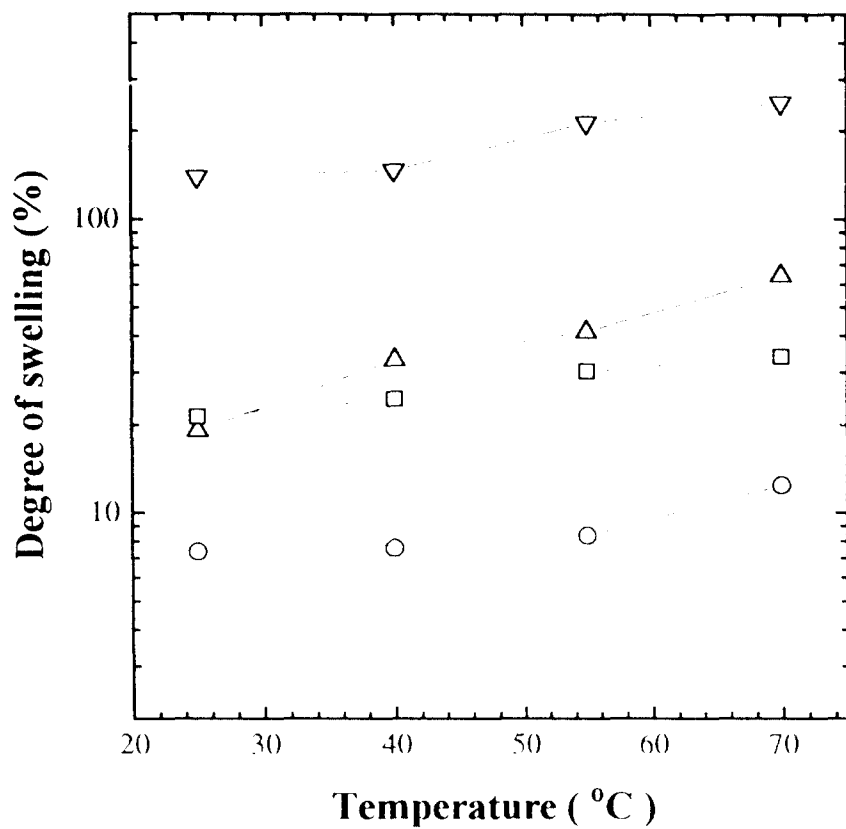


Fig. 1. Effect of the temperature on the swellings of PAN(O), PAN-AAm(Δ), PAN-AA(∇) and PAN-SS(\square) in 56wt% aqueous pyridine.

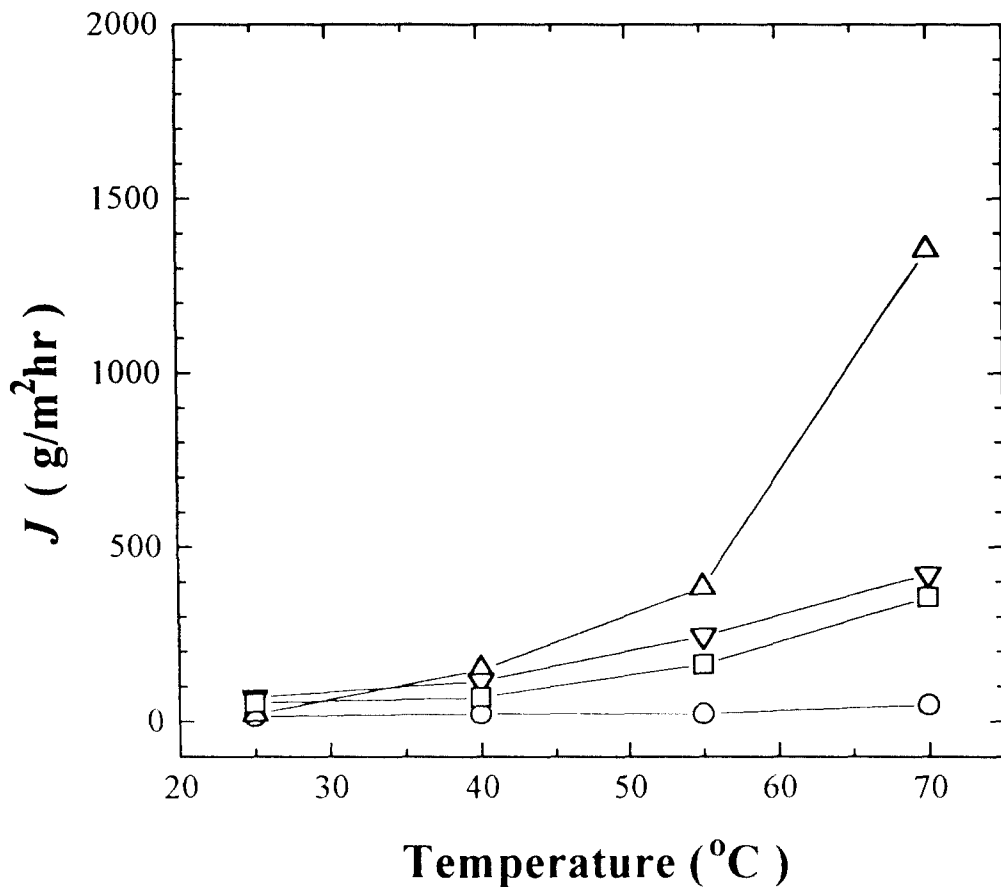


Fig. 2. Effect of the operating temperature on the total permeation flux, J , of PAN(O), PAN-AAm(Δ), PAN-AA(∇) and PAN-SS(\square). The pyridine concentration in the feed was 56wt%.

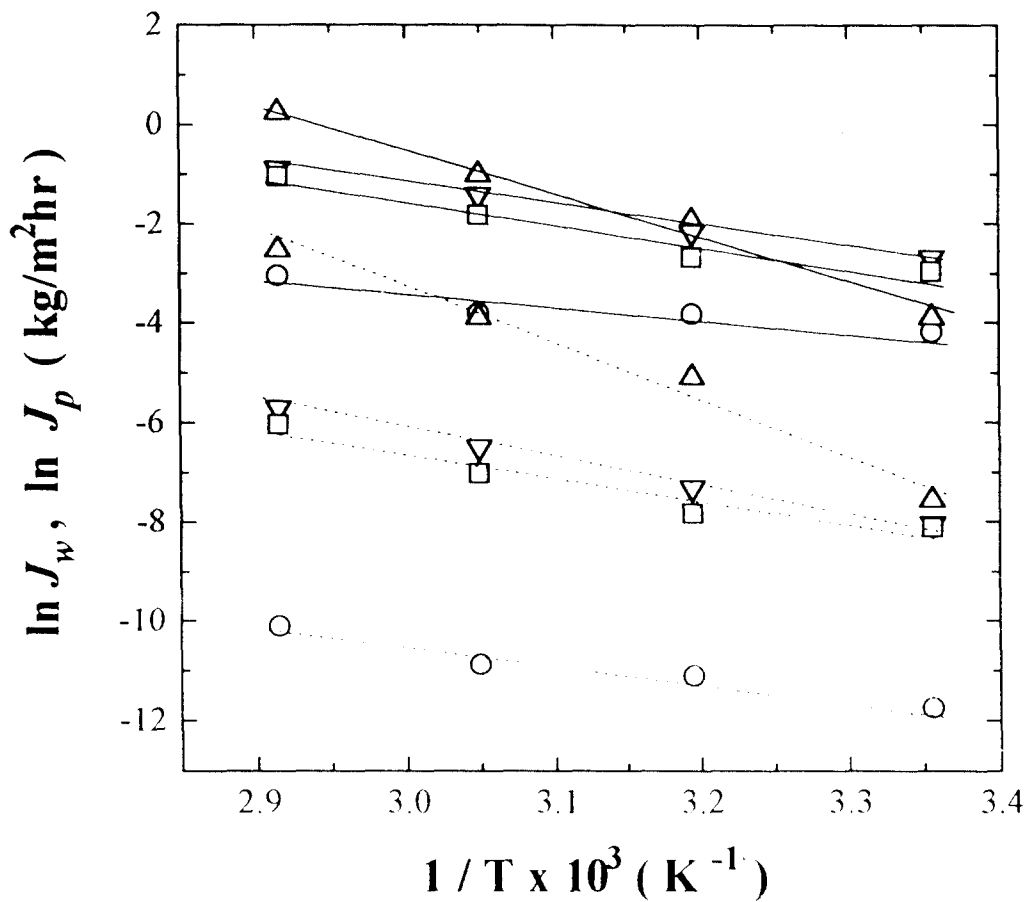


Fig. 3. Arrhenius plots of PAN(O), PAN-AAm(Δ), PAN-AA(∇) and PAN-SS(\square). Straight and dot lines depict $\ln J_w$ and $\ln J_p$, respectively.

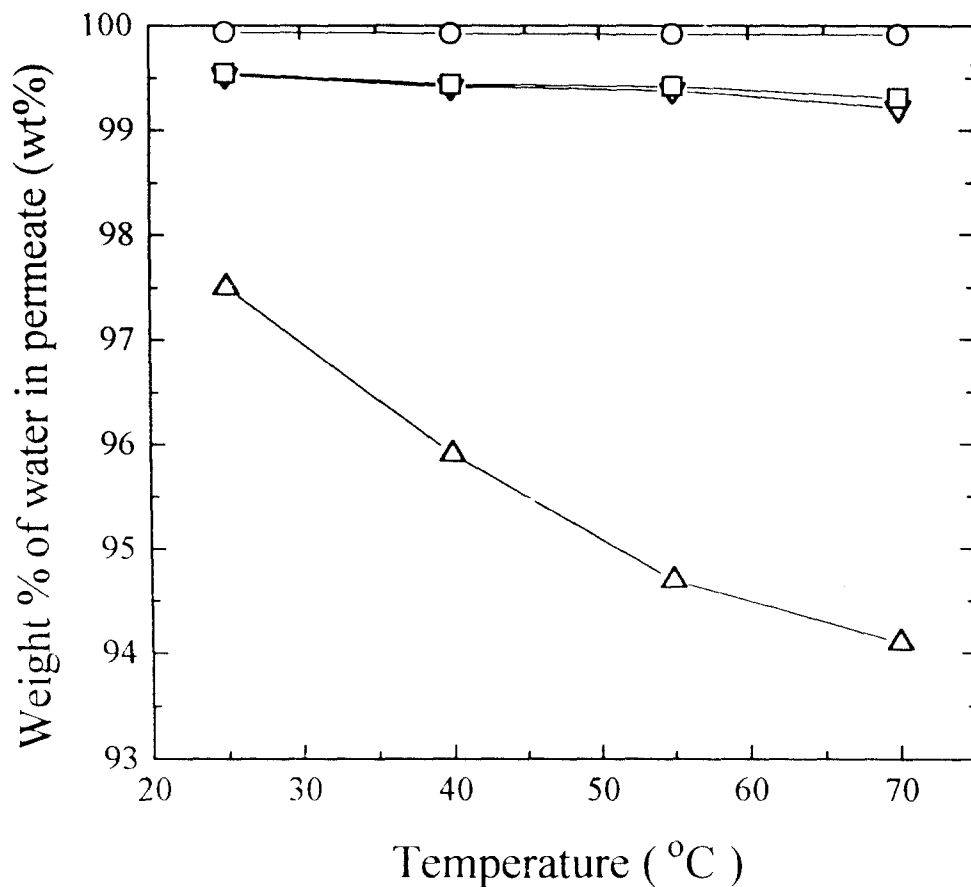


Fig. 4. Effect of the operating temperature on the concentration of water in permeate of PAN(O), PAN-AAm(Δ), PAN-AA(∇) and PAN-SS(\square). The pyridine concentration in the feed was 56wt%.