Separation performances of the membranes prepared from Schiff bases of poly(allylamine) for organic solutes

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Permselective separation between water and water-soluble organics was investigated up to high concentration levels through crosslinked and metal complexed membranes of hybrid Schiff-base derivatives of poly(allylamine), which were prepared by the reaction between pyridine-2-carboxaldehyde (P) and salicyl aldehyde (S) with varying ratios of P/S. The complexed membranes had strong hydrophilic character and showed an increased flux and high permselective separation for t-butanol and tetrahydrofuran at high concentrations. Correlations between the performance of the complexed membranes and the physico-chemical parameters, especially the solubility parameters, of alcohols and aprotic solutes were studied and discussed. It was found that a membrane with a higher P/S value tended to reject the aprotic solute with a smaller solubility parameter, while other physical properties of the alcohols also effected the alcohol separation.

(Keywords: poly(allylamine); Schiff base; complexation)

INTRODUCTION

The separation of water and organic solutes from their aqueous solutions is very important industrially, e.g. in the separation of alcohol from biomass products, the concentration of acetic acid in its aqueous solution, etc. A number of reports have been published, mostly concerning the pervaporation of the ethanol–water system. In addition to pervaporation, reverse osmosis (r.o.) has been employed and a close relationship was found to exist between the results obtained by the two methods[1]. However, few publications have so far appeared concerning the separation of organics from their aqueous (mostly dilute) solutions by r.o.[2-4]. The crucial role of the interaction between the organic and the membrane polymer chosen for the selectivity has been demonstrated by Sourirajan, Fang *et al.*[5], Pusch *et al.*[6], Jiang and Jiayan[7] and other workers. We have prepared a range of organics-soluble Schiff-base derivatives from water-soluble poly(allylamine) (PAAm) by reacting the latter with various aldehydes, and have investigated the r.o. performance of the crosslinked Schiff-base membranes, mostly in the separation of inorganic solutes such as sodium chloride (NaCl) and cobalt (II) chloride ($CoCl_2$)[8-10]. The Schiff-base membranes readily formed a complex with $CoCl_2$ during permeation, which made the membranes very hydrophilic, and the cobalt-salt-complexed membranes showed a strong tendency to be more selectively permeable to water than to organic solutes[10]. Therefore, the objective of this work is to investigate the separation performances of the crosslinked membranes of the hybrid Schiff bases prepared from PAAm, pyridine-2-carboxaldehyde (P) and salicylaldehyde (S) with varying values of P/S in relation to various physico-chemical parameters of the organic solutes; in other words, to study how the separation efficiency is influenced by the composition (i.e. the ratio of aldehydes), the complexation with cobalt ions, and the type and concentration of the water-soluble organic solutes.

EXPERIMENTAL

Poly(allylamine) (PAAm) hydrochloride ($\bar{M}_w = 60\,000$) was kindly provided by the Nitto Boseki Co. Ltd (Japan). The PAAm free base was used after removal of hydrogen chloride by using an anion exchanger. All aldehydes and solvents were distilled before use, with the crosslinking agent, ethylene glycol diglycidyl ether (EGE), being used as received.

The hybrid Schiff bases were prepared from P and S using the same procedure as described previously[9,10] (see *Scheme 1*). The composition of the derivatives was determined by ^{1}H n.m.r. spectroscopy.

Composite membranes were prepared by casting 10 wt% solutions in dimethyl sulfoxide (DMSO) with stoichiometric amounts of EGE on a sheet of filter paper (Toyo 4A, thickness 120 μm), followed by drying for 2 h at 80°C. These were again coated with the same solution and then dried for 1.5 h at 80°C. The membranes were immersed overnight in water before use. The thickness was measured with an electromagnetic meter. Reverse osmosis (r.o.) was carried out in the same manner as described in an earlier report[9], using NaCl and $CoCl_2$ feeds prior to introduction of the organics, under a nitrogen pressure of 7.85 MPa at 25°C. The concentration of the inorganic feed solutions was 0.06 M. The NaCl

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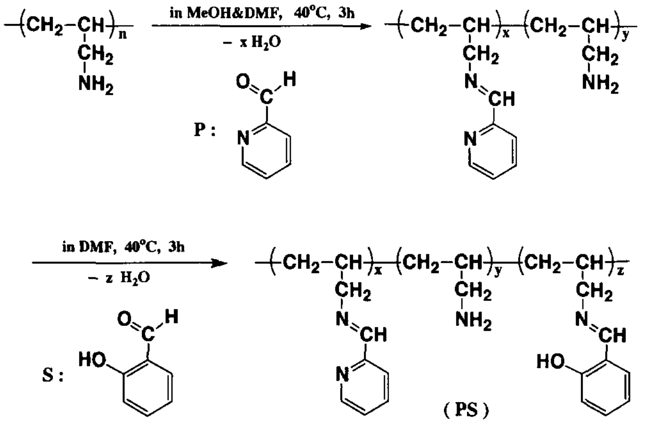

Scheme 1

feed was supplied first and the membrane was washed with water under pressure overnight, and the $CoCl_2$ feed was then supplied. The membrane, after having been in contact with $CoCl_2$ was given the symbol 'Co' at the end of the membrane code, and was referred to as a 'complexed' membrane. After supply of the inorganic feeds and washing with water, an aqueous organic feed was supplied in the following order: ethanol (EtOH), isopropanol (i-PrOH), normal propanol (n-PrOH), tertiary butanol (t-BuOH), acetone, tetrahydrofuran (THF), 1,4-dioxane, *N*,*N*-dimethylformamide (DMF) and DMSO, and the permeation process was conducted under the same conditions. The concentration was estimated conductometrically for inorganic solutes, and by the use of a Shimazu total organic carbon analyzer (TOC-500) for organic solutes. The results obtained from carbon analysis agreed, within a 5% relative error, with those found from the calculated weight concentrations.

The inorganic solute rejection (R) and hydraulic permeability (K_1) were obtained, respectively, from the following equations:

$$R = 100(c - c')/c \qquad (1)$$

$$J_1 = K_1(\Delta P - \Delta\pi)/\Delta x \qquad (2)$$

where c and c' are, respectively, the feed and product concentrations of the solute, J_1 is the volumetric flux, ΔP is the pressure difference, $\Delta\pi$ is the osmotic pressure difference between the feed and product solution, and Δx is the membrane thickness.

The separation factor (α), with respect to water in the separation of organic solutes, was determined from:

$$\alpha = (Y_w/Y_o)/(X_w/X_o) \qquad (3)$$

where X and Y denote the weight fractions of the feed and product, respectively, with the subscripts w and o standing, respectively, for water and organic solute. The swelling degree (Q) of a membrane was estimated in the same manner as reported previously[10]. The solubility parameter δ of the PS polymer was estimated by a calculation according to the group contribution method[11].

RESULTS AND DISCUSSION

Characteristics of the cobalt-salt-complexed membranes

The results obtained for the formation of the PS polymer, i.e. the hybrid Schiff bases, prepared by the reaction of PAAM with P, and then with S, are summarized in *Table 1*. Good yields were obtained in most cases. A composition showing the relative content of P and S may be represented by the ratio of each fraction, namely x/z. The polymer sample number denotes the run number and stands simply for the different composition x/z caused by the different charges of P and S in the reaction mixture. Since the sum of the fraction of the pyridine moiety (x) and the primary amine fraction (y) exceeds the phenolic group fraction (z) by a considerable amount in most cases, these derivatives are substantially basic. The r.o. results for the composite membranes that were prepared on filter paper are summarized, for the inorganic salt feeds, in *Table 2*. The R and J_1 values of $CoCl_2$ are much higher than those of NaCl, and even the low values of R for NaCl are greatly improved when the feed is replaced by $CoCl_2$ (e.g. PS-32Co and -12Co). This was explained in terms of three effects: capture of cobalt ions by complexation with the membrane polymer, Donnan exclusion by the fixed cobalt ions when complexed with the pyridine moieties and azomethine groups, and repair of defects in the membrane, if any, by swelling of the charged membrane with water, giving a swollen but defect-free dense membrane[9]. The hydrophilic features of the complexed membrane are apparent from *Figure 1*, where J_1 increases with an increasing water concentration (i.e. a decreasing feed concentration). Hence, the complexed membranes may be expected to separate water from aqueous solutions of the organics by preferential permeation. The variation in α with feed concentration for some organics

Table 1 Preparation of the hybrid Schiff bases (PS polymers)

Polymer sample	Yield (%)	Composition (mol%)[a] x	y	z	x/z
PS-29	87.2	83.4	10.2	6.4	13.10
PS-32	80.7	78.4	14.3	7.3	10.80
PS-12	81.1	60.6	24.3	15.1	4.01
PS-26	99.0	58.4	22.8	18.8	3.11
PS-28	98.7	43.8	19.2	37.0	1.19
PS-18	87.2	37.8	20.1	42.1	0.90
PS-16	54.8	39.8	12.9	47.3	0.84
PS-22[b]	36.7	59.1	4.7	36.2	1.63

[a] Determined by ^1H n.m.r. spectroscopy: x, pyridine moiety; y, primary amine; z, phenolic group

[b] Used in calculation of the degree of swelling Q

Table 2 Reverse osmosis results obtained for the composite membranes with inorganic solutes[a]

Membrane code	x/z[b]	Δx[c] (μm)	NaCl R (%)	NaCl $J_1 \times 10^2$ (g cm^{-2} h^{-1})	$CoCl_2$ R (%)	$CoCl_2$ $J_1 \times 10^2$ (g cm^{-2} h^{-1})
PS-29	13.10	62	65.6	1.07	–	–
PS-32Co	10.80	80	78.3	0.74	99.0	2.33
PS-12Co	4.01	56	59.3	1.22	100.0	3.29
PS-261	3.11	96	66.9	2.07	–	–
PS-262Co	3.11	98	73.6	1.99	98.5	6.43
PS-28Co	1.19	149	82.9	0.01	93.9[d]	0.33[d]
PS-18	0.90	69	98.1	0.24	–	–
PS-18Co	0.90	79	98.9	0.42	99.8	0.98
PS-16Co	0.84	97	95.7	0.10	99.0	0.56

[a] Feed solution concentration of 0.06 M, at 7.85 MPa and 25°C

[b] Determined by ^1H n.m.r. spectroscopy: x, pyridine moiety; z, phenolic group

[c] Net thickness of the coated PS

[d] Measured after r.o. of THF and t-BuOH

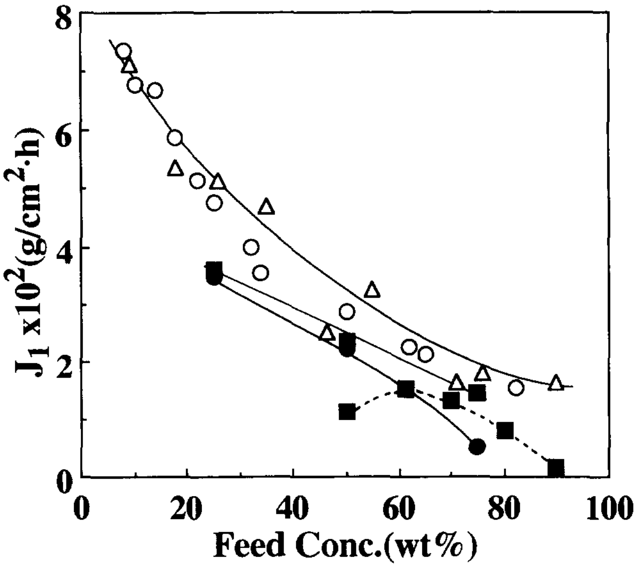

Figure 1 Volumetric flux J_1 vs. feed concentration of various organics for the PS-12Co membrane: (■) THF (dotted line shows results for PS-18Co membrane); (●) t-BuOH; (△) acetone; (○) EtOH

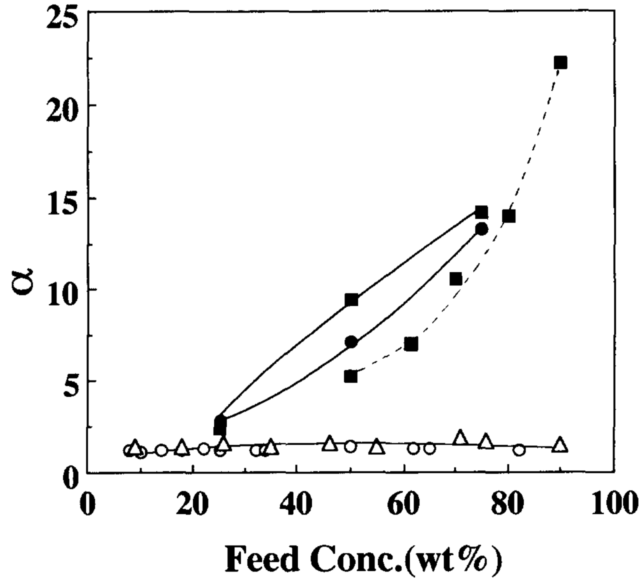

Figure 2 Separation factor α vs. feed concentration of various organics for the PS-12Co membrane: (■) THF; (●) t-BuOH; (△) acetone; (○) EtOH

is shown in *Figure 2*, using the same membrane as in *Figure 1*. This membrane is very characteristic with respect to the fact that the values of α for THF and t-BuOH are very high (i.e. $\alpha = 14.2$ at 75% THF, 22.2 at 90% THF and 13.2 at 75% t-BuOH, which correspond to $R = 73.0\%$, 79.4% and 69.6%, respectively, when calculated according to equation (1)); the product was obtained even with high feed concentrations up to 90%, which implies that the osmotic pressure difference, $\Delta\pi$, is smaller than the applied pressure of 7.85 MPa, at least up to 90%, since if $\Delta P < \Delta\pi$, no product would be obtained.

Dependence of the membrane performance on the properties of the organics

The interaction between the membrane and the organics, which is responsible for their separation, comprises electrostatic or polar interactions, hydrogen bonding, and dispersion forces, including other secondary interactions[12]. Since all of the organics used in this study contain either oxygen, nitrogen or sulfur, it is likely that hydrogen bonding comprises the major part of the interaction in an aqueous solution of the organics. The solubility parameter δ, commonly used as a measure of the affinity or compatibility between two substances, represents the sum of the interactions described above and therefore can be considered to be an appropriate parameter to realistically represent the properties of the organics. The dielectric constant ε, and the viscosity η are also suitable candidates as parameters of the organics, as Glueckauf considered ε in his theory for the separation of inorganic solutes through a charged matrix[13], and the difference in η of the solutes possibly influences J_1 as well as α. *Figure 3* depicts the dependence of α on ε, and η, while *Figures 4, 5* and *6* show the dependence of α and J_1 on δ for various membranes. The values of ε and η were obtained from a standard reference text[14]. In *Figure 3*, while the proton-releasing alcohols show a certain correlation, the aprotic organics do not show any relationship to each other. These organics behaved very similarly towards the other PS membranes. On the other hand, some correlations are observed between α and δ in *Figures 4–6* if the organics are classified into two groups, namely alcohols and aprotic solutes. These figures indicate that α increases with decreasing values of δ. The δ-values of the polymers vary over a small range, i.e. from 12.1 for PS-29 to 12.5 for PS-16, according to the group contribution method[11]. These values are very close to those of DMF, DMSO, and also EtOH. In other words, these organics have a stronger affinity for the membrane polymer, leading to higher concentrations in the membrane and lower values of α. In contrast, organics such as THF and t-BuOH, where the difference between their δ-values and that of the polymer is much greater, i.e. a smaller affinity for the polymer, tend to be rejected and show higher α-values. The order of the α-values shown in *Figures 4–6* almost parallels the reverse order of the degree of swelling of the organics (see *Table 3*), except in the case of 1,4-dioxane. The reason for this exception is not clear at present.

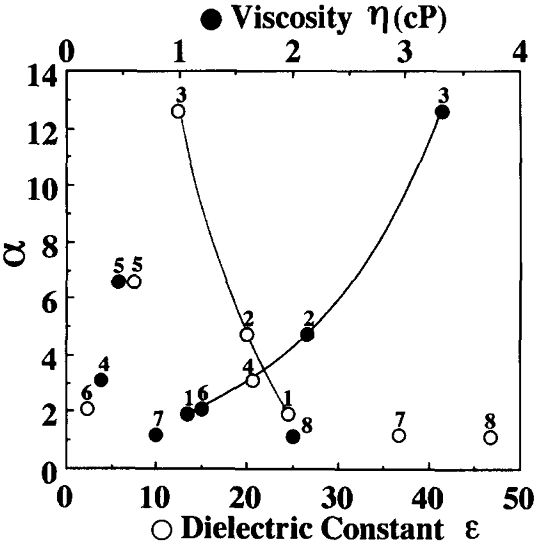

Figure 3 Separation factor α vs. viscosity (●) and dielectric constant (○) of various organics for the PS-18Co membrane, with a feed concentration of 28.1 mol%: (1) EtOH; (2) i-PrOH; (3) t-BuOH; (4) acetone; (5) THF; (6) 1,4-dioxane; (7) DMF; (8) DMSO

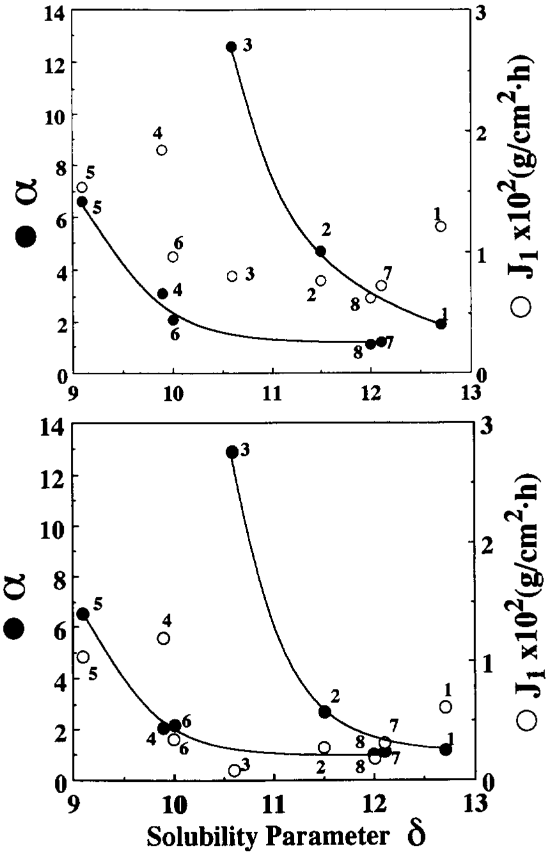

Figure 4 Separation factor α (●) and volumetric flux J_1 (○) vs. the solubility parameter of various organics for the PS-18Co (upper figure) and PS-18 (lower figure) membranes, using a feed concentration of 28.1 mol%: (1) EtOH; (2) i-PrOH; (3) t-BuOH; (4) acetone; (5) THF; (6) 1,4-dioxane; (7) DMF; (8) DMSO

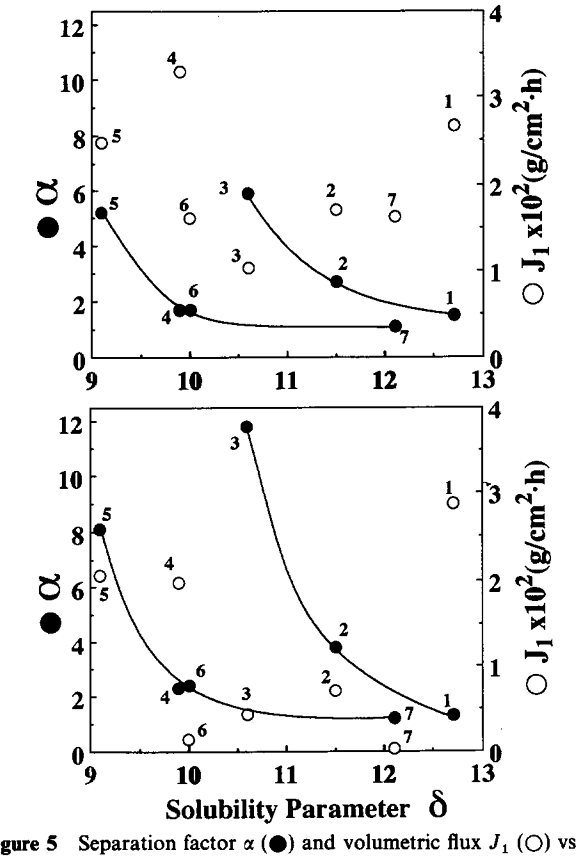

Figure 5 Separation factor α (●) and volumetric flux J_1 (○) vs. the solubility parameter of various organics for the PS-262Co (upper figure) and PS-261 (lower figure) membranes, using a feed concentration of 28.1 mol%: (1) EtOH; (2) i-PrOH; (3) t-BuOH; (4) acetone; (5) THF; (6), 1,4-dioxane; (7) DMF; (8) DMSO

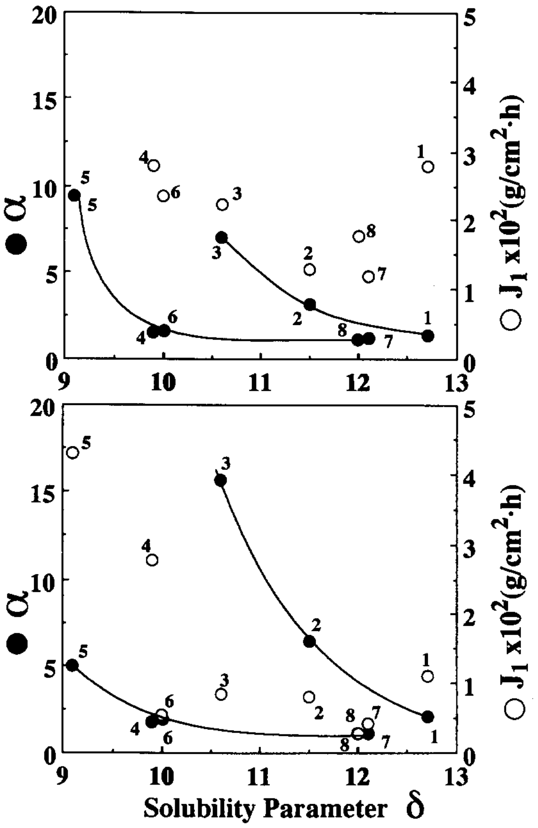

Figure 6 Separation factor α (●) and volumetric flux J_1 (○) vs. the solubility parameter of various organics for the PS-12Co (upper figure) and PS-16Co (lower figure) membranes, using a feed concentration of 50 wt%: (1) EtOH; (2) i-PrOH; (3) t-BuOH; (4) acetone; (5) THF; (6) 1,4-dioxane; (7) DMF; (8) DMSO

Other water-miscible organics with lower values of δ than THF include amines such as piperidine ($\delta = 8.7$) and diethylamine ($\delta = 8.0$). These amines, however, are fairly strong bases and proved unsuitable as they led to deterioration of the complexed membrane, giving a brown-coloured permeate.

J_1, in contrast, did not show any relationship with δ (as can be seen in *Figures 4–6*) nor with ε. However, the viscosity of the organics was found to have considerable effect on J_1, as shown in *Figure 7*. It is also quite obvious from this figure that the complexation of the membranes enhances the flux due to the improved hydrophilicity. The tendency for J_1 to increase with an increase in swelling degree has been shown in our previous report[10].

The plotting of log α *versus* δ for the alcohols gave nearly straight lines (see *Figure 8*). This is the only case that showed a 'straight-lines' relationship in this study. However, if the results for n-PrOH ($\delta = 11.9$, $\alpha = 3.6$) are included in the data for the PS-262Co membrane this relationship does not hold. In the PS-261 membrane also, the order of α was the same (i.e. 11.8 for t-BuOH, 5.1 for n-PrOH, 3.8 for i-PrOH and 1.3 for EtOH). According to Matsuura *et al.*, the logarithmic transport parameter through the membrane of the organics increased proportionally with the polar effect (a value essentially corresponding to δ) and the steric contribution[15]. The steric factor includes a number of geometric parameters of the solute, some of which are presented in *Table 4*. Most of those values favour an order of α in which t-BuOH > i-PrOH > n-PrOH > EtOH, but our results gave t-BuOH > n-PrOH > i-PrOH > EtOH. This latter order is followed only by the molecular length (see

Table 3 Relative degree of swelling Q of the PS-22 membrane for various organics

Organic	DMSO >	(Water) >	DMF >	EtOH >	i-PrOH = Acetone >	t-BuOH >	THF >	1,4-Dioxane
Q	1.88	1.71	1.58	1.16	1.06	1.03	1.01	1.00

[a] Using a single membrane which was soaked in 0.06 M $CoCl_2$ solution for a week, washed with water and then dried under reduced pressure

Table 4 Some parameters of the various alcohols used in this study

Alcohol	r_d ($\times 10^{-10}$ m)[a]	$\sqrt{S}/2$ ($\times 10^{-10}$ m)[b]	L (Å)[c]	V/L (Å)[d]	ε[e]	η (CP)[e]	Acidity[f]
EtOH	1.98	1.99	4.2	23.1	24.3	1.08	143
n-PrOH	2.13	2.05	5.4	23.3	20.1	2.00	141
i-PrOH	2.16	2.34	4.3	29.6	18.3	2.09	135
t-BuOH	3.36	2.98	–	–	10.9	3.32	123

[a] Stokes' radius[16]

[b] Mean width of the alcohol molecule[16]

[c] Calculated molecular length of the alcohol[17]

[d] Calculated molecular shape of the alcohol, where V = mol.wt./the Avogadro constant[17]

[e] At 25°C, except for t-BuOH (measured at 30°C)[14]; CP = 10^{-3} Pa s

[f] Relative values[12]

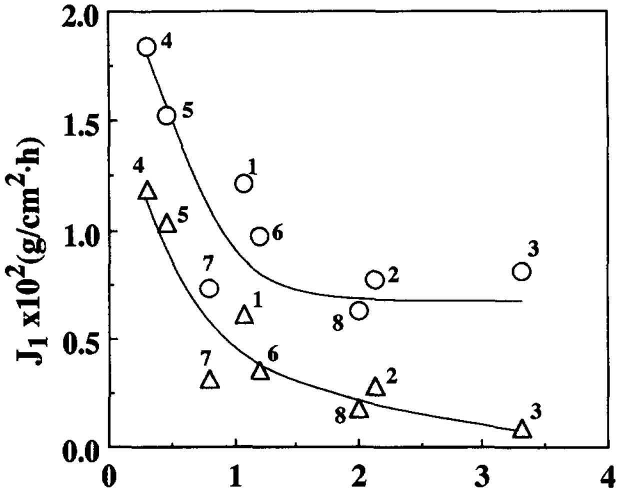

Figure 7 Volumetric flux J_1 vs. the viscosity of various organics for the PS-18Co (○) and PS-18 (△) membranes: (1) EtOH; (2) i-PrOH; (3) t-BuOH; (4) acetone; (5) THF; (6) 1,4-dioxane; (7) DMF; (8) DMSO

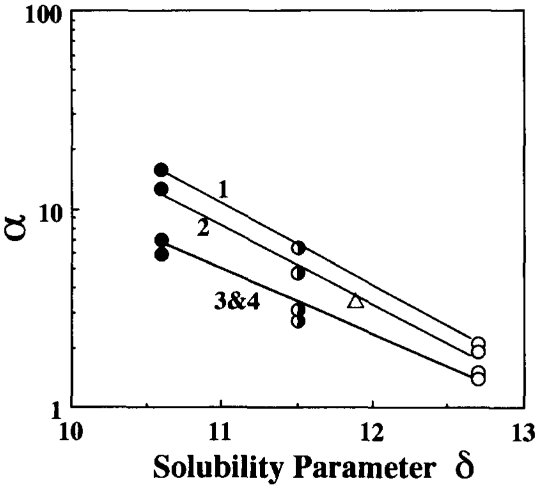

Figure 8 Separation factor α vs. the solubility parameters of various alcohols: (●) t-BuOH; (◑) i-PrOH; (△) n-PrOH for membrane 3; (○) EtOH: (1) PS-16Co; (2) PS-18Co; (3) PS-262Co; (4) PS-12Co

Table 4). The differences in the Stokes' radii, ε and η, between the two structural isomers, n-PrOH and i-PrOH, are very small and further study is necessary to determine which factor of the organics in fact determines the performance of the present membranes. For alcohols of different carbon number, therefore, the molecular sizes, ε, η and the acidity, in addition to δ, all combine to influence the membrane performance.

With respect to the aprotic solutes, neither the molecular size parameter, nor ε and η, yielded any parallel relationship with α, except for δ, probably because the aprotic organics treated in this study cover a wide range of different types of compounds, such as ketones, cyclic ethers, amides and sulfoxides. In such a case, δ, which consists of the three kinds of interaction (see above) may play a role as a universal or common parameter among those organics.

The effect of complexation of membranes

In order to clarify the effect of membrane complexation with $CoCl_2$ the separation performances of the PS-18 and PS-26 membranes were compared (see *Figures 4* and *5*). PS-18 and PS-18Co are identical membranes; after the study of the NaCl and organics feeds (PS-18), the $CoCl_2$ and organics feeds were studied, in that order (PS-18Co). PS-261 and PS-262Co membranes were prepared separately, under the same conditions, to give nearly the same thickness. The r.o. data for a NaCl feed are close to each other, as listed in *Table 2*. The PS-261 membrane was used for feeds of organics solutions without any contact with $CoCl_2$, while the PS-262Co membrane was first fed with $CoCl_2$ and, after determination of R and J_1 for $CoCl_2$, was then fed with organics. In a comparison between the PS-18 and PS-18Co membranes, the α-values in *Figure 4* are close to each other, with those of PS-18Co being somewhat higher. However, for the PS-26 membranes (see *Figure 5*), the α-values of PS-261 are apparently higher than the α-values of PS-262Co, while the value of J_1 of PS-262Co are increased considerably. The improvement in J_1 in the PS-18Co membrane is also apparent in *Figure 4*, which is shown more clearly in *Figure 7*, in a comparable

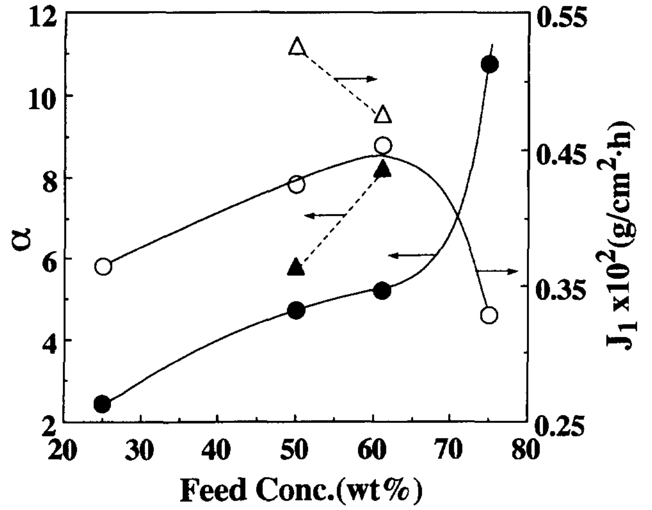

Figure 9 Separation factor α and volumetric flux J_1 vs. the feed concentration of THF: (○, ●) membrane PS-28; (△, ▲) membrane PS-28Co

fashion. *Figure 9* shows the performance of the uncomplexed membrane PS-28 for aqueous THF, where the increase in α with an increasing feed concentration, and a drastic decrease in J_1 at a 75% feed level, after a slight increase in the range from 30 to 75%, indicates the hydrophilicity of the membrane. In this case, also, when the membrane was complexed (PS-28Co), J_1 was enhanced, to a larger extent at lower feed concentrations. This dependence of J_1 on the concentration is similar to that seen in *Figure 1*. An interesting feature in the case of the PS-28 membrane is the concurrent increase in α along with the complexation. This may be attributed to a very high membrane thickness, which forms a tight swollen and gelled matrix under pressure after the repair of any defects[9]. Therefore, increasing the thickness of the PS-262Co membrane would bring about enhanced values of α. Consequently, metal complexation of the membrane generally yields an increase in J_1, as a result of an improved hydrophilicity due to the fixed charge, along with a simultaneous increase in α in the case of a thick membrane.

Dependence of separation factor on the polymer composition

As shown in *Figures 2* and *4–6*, the membranes examined in this study exhibited a high separation factor with t-BuOH and THF. The high rejection against t-BuOH can be explained in terms of δ, η, the acidity, and the molecular size as described above. The rejection against t-BuOH was also shown to be the highest among the alcohols with a cellulose acetate membrane[12]. However, to our knowledge, there has been no membrane reported that exhibits such a high separation factor or rejection against THF at high concentrations, as can be seen in *Figures 2, 4–6* and *9*. The dependence of α, normalized with respect to the membrane thickness, on the polymer composition (as denoted by x/z) for THF and other organics, is shown in *Figure 10*. It can be observed that α tends to increase with an increasing x/z value or an increasing content of pyridine moieties. The uncomplexed membrane of PS-29 showed a relatively high value of α. Since THF is the most basic material among the organics in this study[18], it is probable that the repulsion becomes most significant for membranes with increasing x/z ratios. The results shown in *Figure 8* can similarly be discussed from the acid–base interaction; the slope is the largest for PS-16Co (0.42 $(\text{cc cal}^{-1})^{1/2}$), the smallest for PS-12Co (0.33 $(\text{cc cal}^{-1})^{1/2}$) and intermediate for the other membranes, implying that the membrane of a stronger base (PS-12Co, $x/z=4.01$) has a greater affinity to acids, thus lowering α, but more poorly distinguishes alcohols (acids) than a weaker base (PS-16Co, $x/z=0.84$).

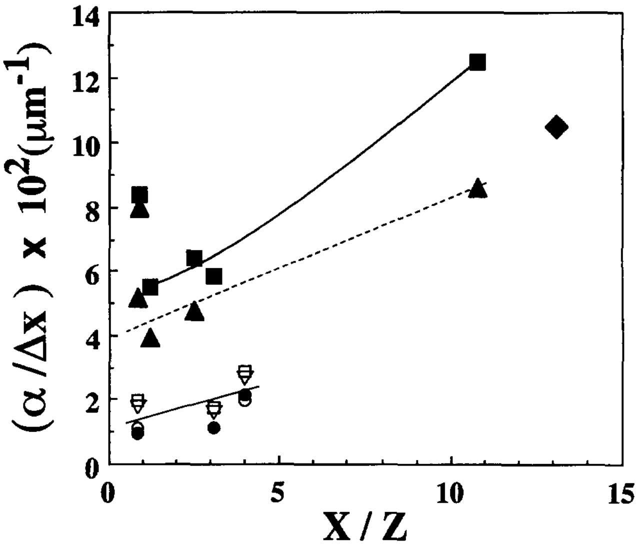

Figure 10 Normalized separation factor $\alpha/\Delta x$ vs. composition x/z for complexed membranes: (■) THF; (□) 1,4-dioxane; (▽) acetone; (●) DMF; (○) DMSO; (◆) THF for a PS-29 membrane. All feed concentrations are 28.1 mol%, except for (▲), 20.0 mol% (50 wt%) THF

To summarize, these basic types of polymer membranes, particularly metal-complexed membranes, are capable of effectively rejecting basic organics having δ-values that are very different to those of the membrane itself and having poor swelling ability.

CONCLUSIONS

An investigation of the performance in separating water-soluble organics by the EGE-crosslinked membranes prepared from the hybrid Schiff bases of PAAm gave the following findings in relation to various parameters of the organic solutes:

1. The membrane had a δ-value of 12.1–12.5 $(\text{cal cc}^{-1})^{1/2}$ (24.7–25.5 $\text{J}^{1/2}\,\text{cm}^{-3/2}$) and was essentially hydrophilic. The hydrophilicity was enhanced by complexation with $CoCl_2$, as shown in *Figures 7* and *9*.
2. The complexed membranes exhibited a remarkably high rejection against t-BuOH and THF, applications in separating water from their water solutions at high concentrations, and a potential for separating t-BuOH or THF from mixtures with other organics in aqueous solutions.
3. The volumetric flux J_1 was significantly influenced by the viscosity η of the organics, tending to increase as η decreased: other parameters of the organics had little effect.
4. The α-values increased as the difference in δ between the polymer and solute became larger, both in the case of alcohols and aprotic organics, with the order of the values being approximately parallel to the reverse

order of the degree of swelling, The solubility parameter appears to be a realistic parameter when comparing the separation factors among organic solutes.

5. In addition to δ, the molecular dimensions, ε, η and the acidity values had an influence on α for alcohols with different carbon numbers, whereas only δ had an influence on aprotic solutes. The difference in the behaviour between alcohols and aprotic solutes was interpreted in the first instance in terms of the difference in properties of the two species, namely the proton-releasing or acidic character of the alcohols and the essentially basic character of both the aprotic solutes and the membrane polymers.

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