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Nanofiber membranes from cellulose triacetate for chiral separation

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ABSTRACT

Nanofiber membranes and molecularly imprinted nanofiber membranes were prepared from cellulose triacetate (CTA) by electrospray deposition. CTA nanofiber membrane incorporated L-Glu in preference to D-Glu from racemic mixture of Glu. Z-L-Glu molecularly imprinted nanofiber membranes showed adsorption selectivity toward the enantiomer, of which absolute configuration was same as that of the print molecule. Adsorption isotherms revealed that specific adsorption sites toward L-Glu were found in the control CTA nanofiber membrane and the Z-L-Glu molecularly imprinted CTA one (CTA-L). The affinity constant between L-Glu and specific adsorption site in the control CTA nanofiber membrane was determined to be $3.8 \times 10^3\,mol^{-1}\,dm^3$ and that for CTA-L one to be $7.9 \times 10^3\,mol^{-1}\,dm^3$, respectively. The control CTA nanofiber membrane selectively transported D-Glu. The permselectivity for the CTA nanofiber membrane was determined to be 1.47. Those nanofiber membranes gave high flux values, and the molar mobility for those was over $1.0 \times 10^{-8}\,mol\,cm\,cm^2\,J^{-1}\,h^{-1}$.

Keywords: Cellulose triacetate; Chiral separation; Electrospray deposition; Isotherm; Nanofiber membrane; Optical resolution; Permslectivity

1. Introduction

In a membrane separation, not only permselectivity but also flux is a couple of important factors so that a given membrane can be applicable to a practical application. High permselectivity and high flux are desirable membrane performances. However, permselectivity and flux often show a trade-off relationship. It is hard to simultaneously enhance not only permselectivity but also flux for a given membrane, in other words, enhancement of flux often leads to decrease in permselectivity and *vice versa*. Breakthrough in such a trade-off relationship in membrane separation has been an unsolved problem or seems to be an unsolvable matter. Against this, nanofiber fabrics have been emerged as a solution strategy, that has been proved by molecularly imprinted nanofiber membranes [1–4]. The membrane form of nanofiber fabric revealed to have potential to simultaneously enhance both flux and permselectivity; at least, nanofiber membrane will enhance flux values two orders of magnitude without concurrent depression of permselectivity [1,2,4].

Cellulose triacetate (CTA) is a microcrystalline material and a derivative of natural polymer. CTA was reported to be promising chiral stationary phases

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[5–11]. Chiral separation is an important chemical process in industries involving pharmaceuticals, agrochemicals, fragrances, food additives, and so forth, since one of paired enantiomers and the corresponding antipode often shows different pharmacological effects [12,13]; in other words, it is often observed that drug enantiomers give desired effect, while the antipodes show undesired one or toxicity [14,15]. It is an interesting subject to prepare chiral separation membranes from CTA. To this end, nanofiber membranes were prepared from CTA and their membrane performances were investigated. Molecularly imprinted nanofiber membranes were also prepared from CTA and their performances were studied.

2. Experimental

2.1. Materials

Cellulose triacetate (CTA), of which degree of substitution being 2.92, was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used without purification. Dichloromethane (DC), ethanol (EtOH), pyridine (Py), sodium azide were used as received. N-α-Benzyloxycarbonyl-D-glutamic acid (Z-D-Glu) and N-α-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu) were purchased from Watanabe Chemical Industries Ltd. (Hiroshima, Japan) and used without purification. Water purified with an ultrapure water system (Simpli Lab. Millipore S.A., Molsheim, France) was used.

2.2. Membrane preparation

The control membrane was prepared as follows: a 0.40 g of CTA was dissolved in 10.0 cm^3 of DC. The solution thus prepared was poured into a flat laboratory dish (11.5 cm diameter) and dried at 50°C for 1 h. The thickness of the membrane was determined to be 28 μm.

The molecularly imprinted membrane was prepared as follows: prescribed amounts of Z-D-Glu or Z-L-Glu and CTA were dissolved in 10.0 cm^3 DC/EtOH (9/1, v/v). The molecular imprinting ratio, the ratio of the mol number of the print molecule to that of the constitutional repeating unit of CTA was fixed to be around 1.0. Each CTA solution was poured into a flat laboratory dish (11.5 cm diameter) and dried at 50°C for 1 h. After drying, the print molecule was extracted from the resultant membrane by a large volume of 50 vol.% aqueous ethanol solution until the print molecule was hardly detectable in aqueous ethanol solution by UV analysis. The thickness of the Z-D-Glu imprinted membrane was determined to be 39 μm and that of the Z-L-Glu one to be 41 μm.

2.3. Preparation of nanofiber membrane

DC/EtOH/Py (8/1/1, v/v/v) was adopted as a solvent for the preparation of control nanofiber membrane and DC/EtOH (8/2, v/v) as that for the preparation of molecularly imprinted one. A prescribed amount of CTA for the preparation of the control nanofiber membrane and those of CTA and print molecule for the preparation of molecularly imprinted nanofiber membranes were dissolved in 10.0 cm^3 of mixture of solvent. The molecular imprinting ratio, the ratio of the mol number of the print molecule to that of the constitutional repeating unit of CTA was fixed to be around 1.0. Esprayer ES-2000 (Fuence Co. Ltd., Wako, Japan) was adopted as the electrospray deposition device. Polymer solution was electrosprayed at ambient temperature using a prescribed applied voltage. The applied voltage of 25 kV was applied for the preparation of the control nanofiber membrane and that of 27 kV for those for molecularly imprinted ones. The syringe used in this study had a capillary tip of 0.52 mm diameter. The feeding rate was fixed to be 10.0 mm^3. A grounded aluminum foil used as a counter electrode was placed 10.0 cm from the tip of the capillary.

The morphology, such as diameter and thickness of the electrosprayed nanofiber membranes, was determined with KEYENCE VE-7800 scanning electron microscope (SEM). A small section of the nanofiber membrane was placed on the SEM sample holder. The fiber diameter of nanofiber membrane was determined using Image J software program by measuring at least 30 fibers from each SEM image.

2.4. Adsorption selectivity

The membrane samples were immersed in a racemic Glu solution, which was the same racemic mixture studied in the membrane transport, that is, an aqueous solution of racemic Glu (concentration, 1.0×10^{-3} mol dm^{-3}) and the membranes were allowed to equilibrate at 40°C for 2 weeks; 0.02 wt.% of sodium azide was added as a fungicide. In this study, the amount of racemic Glu adsorbed in the membrane was too low to be determined precisely by the aliquots of the solution after equilibrium had been reached. From this, the amount of racemic Glu adsorbed in the membrane was determined as follows: the membrane, which had reached equilibrium with racemic Glu solution, was taken out from the immersing solution, blotted free solution adhering on

the surface and then transferred to 0.02 wt.% sodium azide aqueous solution to desorb the racemic Glu from the membrane. Aliquots of the solution of adsorption at the initial stage and that for desorption were used for quantitative estimation by liquid chromatography (LC) (Jasco PU1580, equipped with a UV detector (Jasco UV1570) employing Chiralpak MA(+) column (50 × 4.6 mm (id), Daicel Chemical Ind.). Aqueous cooper solution was used as a mobile phase.

The adsorption selectivity $S_{A(i/j)}$ is defined as

$$S_{A(i/j)} = ((\text{i-Glu})/(\text{j-Glu}))/([\text{i-Glu}]/[\text{j-Glu}]) \quad (1)$$

where (i-Glu) and [i-Glu] are the amount of i-Glu adsorbed in the membrane and concentration in the solution after equilibrium had been reached, respectively.

2.5. Adsorption isotherms of D-Glu and L-Glu

The membrane samples were immersed in various concentrations of optically pure D-Glu or L-Glu solution and allowed to equilibrate at 40°C for 2 weeks. The quantitative analyses were carried out as described previously. The concentration of Glu in the membrane $[\text{i-Glu}]_M$ or $[\text{j-Glu}]_M$ (i = D, j = L or i = L, j = D) was determined adopting the amount of Glu adsorbed in the membrane and the volume of membrane phase, including that of membrane and that of the solution in the membrane.

2.6. Membrane transport

A membrane with an area of 3.0 cm^2 was tightly secured with Parafilm between two chambers of a permeation cell. The volume of each chamber was 40.0 cm^3. A racemic mixture of Glu solution was placed in the left-hand side chamber (L-side) and 0.02 wt.% sodium azide aqueous solution in the right-hand side chamber (R-side). Each concentration of Glu was 1.0×10^{-3} mol dm^{-3}. Membrane transport experiments were carried out at 40°C with stirring. An aliquot was drawn from the permeate side at each sampling time. The amounts of D-Glu and L-Glu transported through the membrane were determined by LC as described above.

The flux, J (mol cm cm^{-2} h^{-1}), is defined as

$$J = Q\delta/At \quad (2)$$

where Q (mol) is the amount of transported Glu, δ (cm) the membrane thickness, A (cm^2) the effective membrane area, and t (h) means the transport time.

The permselectivity $\alpha_{i/j}$ is defined as the flux ratio, J_i/J_j, divided by the concentration ratio [i-Glu]/[j-Glu]

$$\alpha_{i/j} = (J_i/J_j)/([\text{i-Glu}]/[\text{j-Glu}]) \quad (3)$$

3. Results and discussion

3.1. Morphology of nanofiber membranes

In the preparation of control nanofiber membrane, DC/EtOH/Py mixture was adopted as solvent for CTA, though DC/EtOH mixed solvent was reported as a solvent for electrospray deposition [16,17]. The mixture of DC and Py is capable of forming adducts, such as 1,1′-methylenebispyridinium dichloride and 1-chloromethylpyridinium chloride under ambient conditions [18,19]. But the reaction was slow and it was reported that 9 mol dm^{-3} solution of Py in DC formed 1,1′-methylenebispyridinium dichloride in 1% yield over two months [19]. To prevent from the formation of such adducts between Py and DC during elctrospray deposition process, the polymer solution for the preparation of control nanofiber membrane was used within 1 week after preparation.

The SEM photographs of three types of nanofiber membrane are shown in Fig. 1. In all nanofiber membranes in the present study, beads are hardly observed. Fig. 1(a) shows the SEM image of the control nanofibefr membrane. The nanofiber membrane shown in Fig. 1(b) was electrosprayed in the presence of Z-D-Glu as a print molecule. That shown in Fig. 2 (c) was fabricated adopting Z-L-Glu as a print molecule. In the present study, strict optimization of electrospray deposition condition was not conducted though the morphology and diameter of nanofiber membrane would be widely controlled [20,21].

Table 1 summarizes membrane thickness of each membrane and fiber diameter of each nanofiber membrane together with membrane preparation conditions. As for the last alphabet in the membrane code, C, D, and L mean control, D-isomer imprinted, and L-isomer imprinted nanofiber membrane, respectively.

3.2. Adsorption selectivity

Adsorption selectivity of nanofiber membranes was studied adopting racemic mixture of Glu as model racemates. Results are summarized in Table 2. Contrary to adsorption selectivity of nanofibers from cellulose acetate (CA) with acetyl content of 40% (degree of substitution of 1.20) [2], the control CTA nanofiber membrane, CTA-C, adsorbed L-Glu in preference to D-Glu. The adsorption selectivity of CTA-C

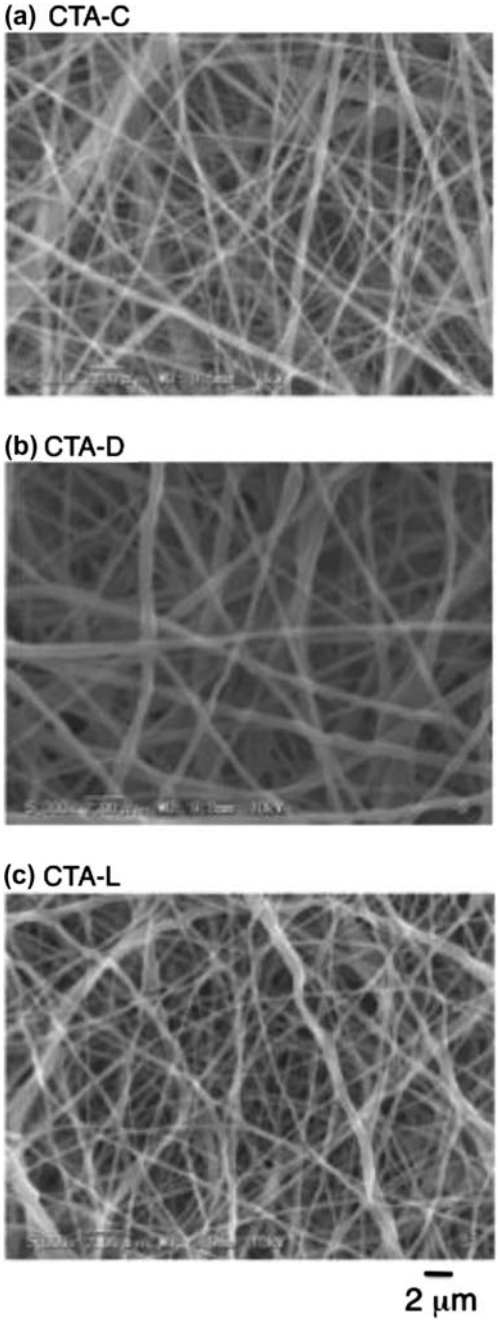

Fig. 1. SEM images of surface of the control nanofiber membrane (CTA-C) (a) Z-D-Glu imprinted nanofiber membrane (CTA-D), and (b) Z-L-Glu imprinted nanofiber membrane (CTA-L) (c).

toward L-Glu was determined to be 1.80, while CA nanofiber membrane hardly showed adsorption selectivity [2]. The Z-D-Glu molecularly imprinted CTA nanofiber membrane (CAT-D) slightly showed adsorption selectivity toward D-Glu. CTA-L nanofiber membrane showed the L-isomer adsorption selectivity, but the value of adsorption selectivity was lower than that expected from the previous results [1,2,4]. To study the expression mechanism of adsorption selectivity, substrate specificity of those nanofiber membranes was investigated by adsorption isotherms.

3.3. Adsorption isotherms of D-Glu and L-Glu

It is interesting to study substrate specificity of those three types of CTA nanofiber membrane. To this end, adsorption isotherms of D-Glu and L-Glu for those membranes were studied. The adsorption isotherms for those membranes are shown in Fig. 2.

The adsorption isotherm of D-Glu for CTA-C, those of D-Glu and L-Glu for CTA-D, and that of D-Glu for CTA-L are straight lines passing through origin, implying that those enantiomers were adsorbed in the membrane without any specific interaction with the membrane, in other words, those were non-specifically adsorbed in the membrane. The adsorption isotherm of Glu non-specifically adsorbed in the membrane can be represented by the following equation:

$$[\text{j-Glu}]_m = k_A[\text{j-Glu}] \quad (4)$$

where $[\text{j-Glu}]_m$ denotes the concentration of j-Glu in the membrane, which was non-specifically adsorbed in the membrane, k_A is adsorption constant, and [j-Glu] means the concentration of j-Glu in the solution equilibrated with the membrane. On the other hand, the adsorption isotherm of L-Glu for CTA-C and that for CTA-L, which were preferentially adsorbed in the membrane, gave complicated profiles. The straight lines at higher substrate concentration region are parallel to those of antipode non-specifically adsorbed in each membrane. And the extension of those straight lines has positive intercepts and does not pass though origin. Those adsorption isotherms exhibit dual adsorption isotherms, which consists of non-specific adsorption and adsorption on specific recognition sites toward the L-isomer. The isotherm of L-Glu adsorbed specifically in the membrane can be represented by the following equation:

$$[\text{L-Glu}]_m = k_A[\text{L-Glu}] + K_s[\text{Site}]_0[\text{L-Glu}]/(1 + K_s[\text{L-Glu}]) \quad (5)$$

where $[\text{L-Glu}]_m$ denotes the concentration of L-Glu in the membrane, which was specifically adsorbed in the membrane, K_S is the affinity constant between specific adsorption site and L-Glu, [L-Glu] means the concentration of L-Glu in the solution equilibrated with the membrane.

Two parameters in Eqs. (4) and (5), which were determined to fit each adsorption isotherm best, are

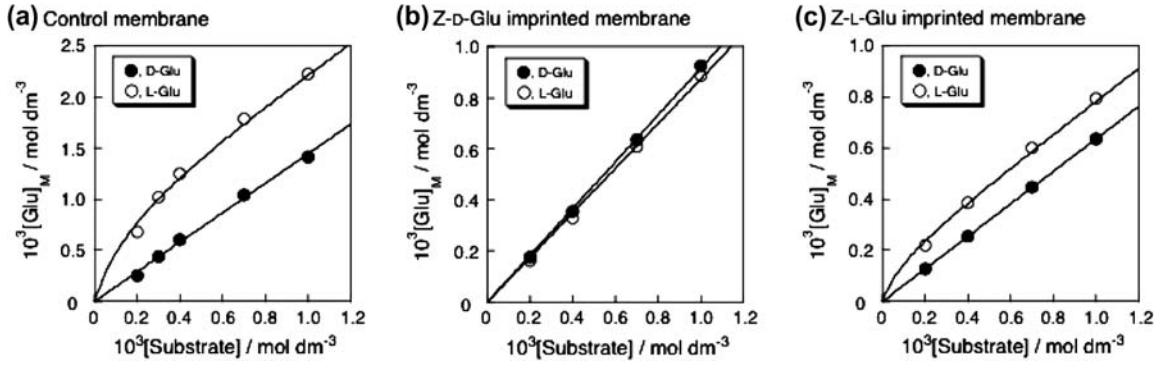

Fig. 2. Adsorption isotherms of D-Glu and L-Glu in the control membrane (CTA-C) (a), the nanofiber membrane imprinted by Z-D-Glu (CTA-D) (b) and that imprinted by Z-L-Glu (CTA-L) (c).

summarized in Table 3. In the previous study on molecularly imprinted nanofiber membranes from cellulose acetate [2], both Z-D-Glu and Z-L-Glu effectively worked as a print molecule; Z-D-Glu was effective to construct molecular recognition site toward D-Glu during preparation process of molecularly imprinted nanofiber membrane and *vice versa*. Contrary to the previous study [2], in the present study, Z-D-Glu hardly constructed the D-isomer recognition site like molecularly imprinted membranes from tetrapeptide derivatives [22–24]. The adsorption isotherm of L-Glu for CTA-C revealed that the control CTA nanofiber membrane essentially possessed specific adsorption sites toward L-Glu. The fact that CTA-C nanofiber membrane was fabricated without a print molecule of Z-L-Glu supports the above speculation. At the moment, there were not any other additional experimental results to elucidate whether the specific adsorption site toward L-Glu was a chiral recognition site or a molecular recognition site.

The presence of Z-D-Glu during the membrane preparation process led to the disappearance of specific adsorption site toward the L-isomer in CTA nanofiber membrane imprinted by Z-D-Glu (CTA-D). Both adsorption isotherms in Fig. 2(b) gave straight lines passing through origin. The slope for the adsorption isotherm of D-Glu was slightly higher than that for L-Glu. The ratio of the slope for D-Glu to that of L-Glu was determined to be 1.05, which was close to the adsorption selectivity of 1.03 in Table 2. Destruction of specific adsorption site toward the L-isomer in CTA might be induced by the presence of Z-D-Glu during nanofiber formation process, and Z-D-Glu hardly worked as a print molecule to construct the specific adsorption site toward the D-isomer. However, the presence of Z-D-Glu during the fabrication process of nanofiber membrane was thought to be contribute to make the adsorption constant for D-Glu slightly higher than that for L-Glu. CTA consists of $\beta(1\rightarrow4)$ linked D-glucose. If CTA consisting of $\beta(1\rightarrow4)$ linked L-glucose was adopted as a raw material, Z-D-Glu would work as a print molecule and the antipode print molecule would not work.

From the fact that there can be found specific adsorption sites toward the L-Glu in the control CTA nanofiber membrane, the Z-L-Glu molecularly imprinted CTA nanofiber membrane would show higher adsorption selectivity and more specific recognition site than the control nanofiber membrane. Against expectation, the adsorption selectivity toward L-Glu for CTA-L was lower than that for CTA-C as summarized in Table 2. The adsorption constant for CTA-L (k_A) was lower than that for CTA-C, and furthermore, the concentration of specific adsorption site toward the L-isomer for CTA-L was decreased to around 43% of that for CTA-C. But the affinity constant between L-Glu and specific adosrption site was increased. The presence of Z-L-Glu during electrospray deposition process is thought to support the construction of solider specific adsorption site toward L-Glu. The specific adsorption site found in the CTA-L can be a molecular recognition site toward L-Glu, since Z-L-Glu was simultaneously electrosprayed with CTA in the electrospray deposition process. The specific recognition site in CTA-L might be constructed by more functional groups than that in CTA-C. And this led to the increase in affinity constant from 3.8 to $7.9\times10^3\,\mathrm{mol^{-1}\,dm^3}$ and to the decrease in concentration of specific recognition site toward L-Glu [33].

From adsorption isotherms, the adsorption selectivity at $1.0\times10^{-3}\,\mathrm{mol\,dm^{-3}}$ for CTA-C was calculated to be 1.53 and that for CTA-L to be 1.22, respectively. There are small difference in adsorption selectivity between calculated value and observed one.

Table 1
Membrane thickness, fiber diamter, and membrane preparation conditions

Membrane		CTA g (mol[a]) $\times 10^{-3}$		Z-D-Glu g (mol) $\times 10^{-3}$		Z-L-Glu g (mol) $\times 10^{-3}$		Solvent[b]	Imprinting ratio[c]	Thickness (μm)	Diameter (nm)
Usual mem.	CTA-C	0.3962	(1.39)	–	–	–	–	DC	–	28	–
	CTA-D	0.4018	(1.41)	0.3980	(1.42)	–	–	DC/EtOH[d]	1.01	39	–
	CTA-L	0.3970	(1.39)	–	–	0.3891	(1.38)	DC/EtOH[d]	0.99	41	–
Nanofiber mem.	CTA-C	0.5005	(1.76)	–	–	–	–	DC/EtOH/Py[e]	–	360	340 ± 110
	CTA-D	0.4983	(1.75)	0.4966	(1.77)	–	–	DC/EtOH[f]	1.01	310	390 ± 80
	CTA-L	0.4952	(1.74)	–	–	0.4920	(1.75)	DC/EtOH[f]	1.01	330	380 ± 60

[a]Mole number for constitutional repeating unit of CTA.
[b]10.0 cm^3.
[c](Z-Glu)/(CTA).
[d]9/1, (v/v).
[e]8/1/1 (v/v/v).
[f]8/2 (v/v).

3.4. Enantioselective membrane transport

From adsorption study, those nanofiber membranes were expected to show chiral separation ability. To this end, membrane transport of racemic mixture of Glu through those nanofiber membranes was investigated. Three types of usual cast membrane hardly transported racemic mixture of Glu. Contrary to this, membrane transport of Glu's through nanofiber membranes was observed as expected. Time-transport curves of racemic mixture of Glu through three types of nanofiber membrane are shown in Fig. 3. Those nanofiber membranes were anticipated to give high flux values from previous results [1,2,4]. Therefore, in the present study, the concentration gradient was adopted as a driving force for membrane transport of racemic mixture of Glu.

The control CTA nanofiber membrane, CTA-C membrane, transported D-Glu in preference to the corresponding L-Glu, though CTA-C nanofiber membrane selectively incorporated L-Glu into the membrane. Permselectivity toward D-Glu was determined to be 1.47. Such a discrepancy between adsorption selectivity and permselectivity was often observed in enantioselective membrane transport [24–32]. Even in optical resolution with nanofiber membrane [4], such a discrepancy was also observed. This was rationalized by the retarded membrane transport of the enantiomer L-Glu, which was preferentially incorporated into the membrane. The diffusion of L-Glu preferentially adsorbed in the membrane was retarded by a relatively strong interaction between L-Glu and the membrane.

In the case of enantioselective membrane transport with CTA-D nanofiber membrane, the permselectivity reflected its adsorption selectivity, though the selectivity was not so prominent. In other words, CTA-D showed adsorption selectivity toward D-Glu and D-Glu was selectively transported through the membrane. The adsorption isotherms of racemic Glu for the CTA-D nanofiber membrane revealed that both enantiomers were incorporated into the membrane without specific interaction, that is, D-Glu and L-Glu were adsorbed in the membrane by a relatively weak interaction. Therefore, the enantiomer preferentially adsorbed in the membrane was selectively transported as observed.

CTA-L nanofiber membrane, which was molecularly imprinted by Z-L-Glu, selectively transported the D-isomer of Glu, though the membrane preferentially incorporated L-Glu from racemic mixture. The adsorption isotherms of L-Glu for CTA-L nanofiber membrane revealed that there was a specific recognition site toward L-Glu, of which affinity constant was

Table 2
Adsorption selectivity toward a racemic mixture of Glu

Membrane	D-Glu		L-Glu		$S_{A(D/L)}$	$S_{A(L/D)}$
	(D-Glu)/mem mol/g-mem.	(D-Glu)/(CTA)* mol/mol × 10^{-4}	(L-Glu)/mem. mol/g-mem. × 10^{-6}	(L-Glu)/(CTA)* mol/mol × 10^{-4}		
CTA-C	8.52×10^{-7}	2.43	1.53	4.37	0.56	1.80
CTA-D	1.87×10^{-6}	5.33	1.81	5.16	1.03	0.97
CTA-L	1.23×10^{-6}	3.50	1.69	4.81	0.73	1.38

*Amount for constitutional repeating unit of CTA.

Table 3
Parameters for adsorption isotherm

	k_A	$[Site]_0$ mol dm^{-3}	K_S mol^{-1} dm^3 × 10^3
CTA-C	1.5	1.0×10^{-3}	3.8
CTA-D	0.46[a]	–	–
	0.44[b]		
CTA-L	0.64	1.6×10^{-4}	7.9

[a]k_A for D-Glu.
[b]k_A for L-Glu.

around 2.1 times higher than that for CTA-C nanofiber membrane. In this case, the transport of L-Glu selectively adsorbed in the membrane was retarded because of a relatively strong interaction between L-Glu and CTA-L nanofiber membrane.

As described in the introduction, both flux and permselectivity is a couple of important factors in membrane separation. In the present study, it is impossible to compare membrane performances for two types of membrane, such as a usual cast membrane and nanofiber membrane, since three types of usual cast membrane hardly transported racemic mixture of Glu. But it is interesting to compare the present data and those previously reported. To this end, membrane performances for those nanofiber membranes are summarized in Table 4. To compare fluxes for the present nanofiber membranes and previous nanofiber membranes, the molar mobility, u (mol cm cm^2 J^{-1} h^{-1}), of Glu for each membrane was determined by the following equation [2,4,34].

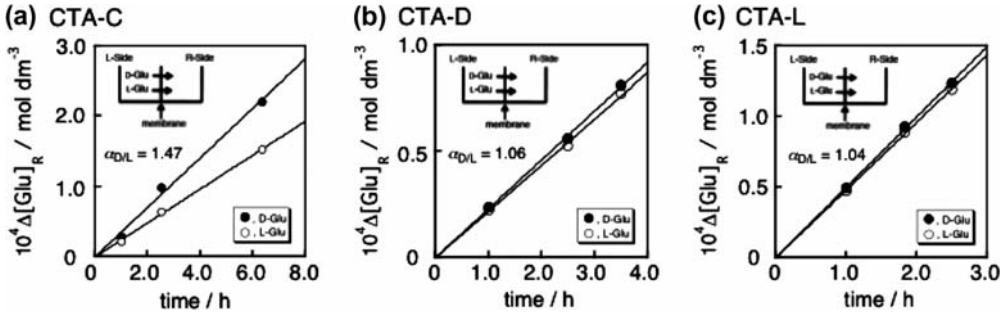

Fig. 3. Time-transport curves of racemic mixture of Glu through CTA-C (a), CTA-D (b), and CTA-L (c) at 40°C in H_2O solution adopting concentration gradient as a driving force for membrane transport.

Table 4
Results of enantioselective membrane transport

Membrane	J_D[a]	J_L[a]	$\alpha_{D/L}$	$\alpha_{L/D}$	u[b] × 10^8
CTA-C	1.70×10^{-8}	1.16×10^{-8}	1.47	0.68	3.43
CTA-D	9.51×10^{-9}	9.00×10^{-9}	1.06	0.94	1.91
CTA-L	2.19×10^{-8}	2.11×10^{-8}	1.04	0.96	4.73

[a][mol cm cm^{-2} h^{-1}].
[b]$u = (-J/c)/(d\mu/dx)$ [{(mol cm cm^{-2} h^{-1})}/(mol cm^{-3})}/(J mol^{-1} cm^{-1}) = mol cm cm^2 J^{-1} h^{-1}].

$$u = (-J/c)/(d\mu/dx) \quad (6)$$

where J means the sum of D-Glu and L-Glu fluxes, c is the concentration of each Glu in the upstream side, and $d\mu/dx$ is the potential gradient at that point. The molar mobility is defined as the mobility and is simply the flux per unit driving force, per unit concentration, per unit membrane area, per unit membrane thickness. In the calculation of the electrochemical potential difference due to the concentration gradient, the concentration of Glu in the downstream side was determined to be $1.0 \times 10^{-8}\,\mathrm{mol\,dm^{-3}}$. Because the lowest limit of the detection of Glu in the present study, the concentration was around $1.0 \times 10^{-8}\,\mathrm{mol\,dm^{-3}}$. The molar mobilities for the present nanofiber membranes gave similar ones for the previous studies [2,4]. The molar mobility for the present nanofiber membranes was one order of magnitude higher than previous results.

4. Conclusions

Nanofiber membranes and molecularly imprinted nanofiber membranes were prepared from CTA. Nanofiber control membrane, which was prepared from CTA in the absence of a print molecule, incorporated L-Glu in preference to D-Glu from racemic mixture of Glu. Z-L-Glu molecularly imprinted nanofiber membranes showed adsorption selectivity toward the enantiomer, of which absolute configuration was same as that of the print molecule. Adsorption isotherms revealed that specific adsorption sites toward L-Glu were found in the control CTA membrane and the Z-L-GLu molecularly imprinted CTA nanofiber membrane (CTA-L). The affinity constant between L-Glu and specific adsorption site in the control CTA nanofiber membrane was determined to be $3.8 \times 10^{3}\,\mathrm{mol^{-1}\,dm^{3}}$ and that for CTA-L one to be $7.9 \times 10^{3}\,\mathrm{mol^{-1}\,dm^{3}}$, respectively. The control CTA nanofiber membranes selectively transported D-Glu. The permselectivity for the control CTA nanofiber membrane was determined to be 1.47. Those nanofiber membranes gave high flux values and the molar mobility for those was over $1.0 \times 10^{-8}\,\mathrm{mol\,cm\,cm^{2}\,J^{-1}\,h^{-1}}$.

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