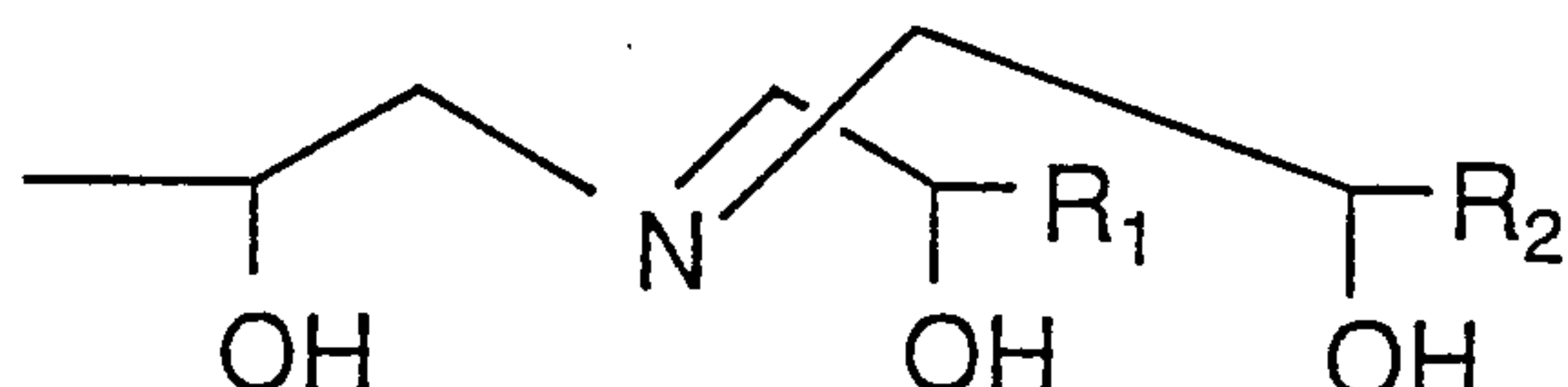




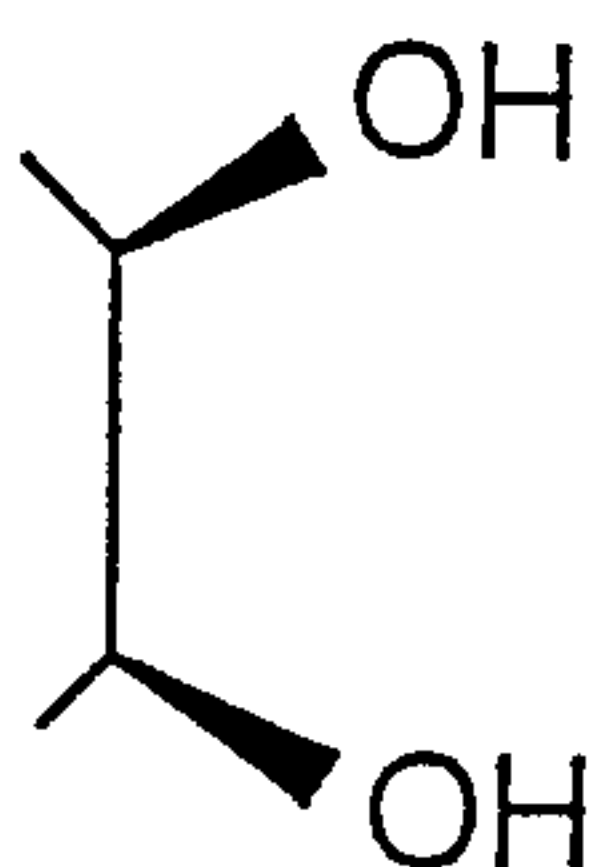


本発明はキレート形成能を有する多孔性中空糸膜及び該多孔性中空糸膜による酸化ゲルマニウムの回収方法に関するものである。

本発明の多孔性中空糸膜は、ポリエチレン製多孔性中空糸膜の表面に放射線グラフト重合されたエポキシ基を含有する化合物の残基と、該残基と反応して式



又は、式



で表される構造を含む残基を与える化合物とを反応させて得られることを特徴とするものであり、また、本発明の酸化ゲルマニウムの回収方法は、前記多孔性中空糸膜により水溶液中の酸化ゲルマニウムを捕集し、その後、溶出することを特徴とするものである。

PCTに基づいて公開される国際出願のパンフレット第一頁に掲載されたPCT加盟国を同定するために使用されるコード(参考情報)

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## DESCRIPTION

Porous Hollow Fiber Membrane Having Chelate Formability and  
Method for Recovery of Germanium Oxide Using the Porous  
5 Hollow Fiber Membrane

## Technical Field

The present invention relates to a porous hollow fiber membrane having chelate formability, as well as  
10 to a method for recovery of germanium oxide using the porous hollow fiber membrane.

## Background Art

Germanium is an element indispensable in various fields, for development of materials for high-  
15 technology industries such as optical fiber, solar cell and the like, or as a polymerization promotion catalyst in production of polyethylene terephthalate resin, or as a raw material for production of biologically active substance.

Recently, the supply of germanium has been unable to meet the demand and the demand and supply has become unbalanced, and this situation has been taken up as a serious problem. In Japan, the supply of germanium has been almost dependent upon import. Therefore, if the used germanium which has been entirely disposed as a waste, can be recovered by any method, it will improve the demand and supply balance of germanium and moreover is preferred from the standpoint of reutilization of resource.

Up to now, however, there has been made no proposal on any effective method for recovery of germanium, particularly germanium oxide which is used as a catalyst per se or as a raw material for germanium of various applications; and development for such an effective method has been desired.

The present invention aims at solving the above-mentioned problems of the prior art and providing a porous hollow fiber membrane capable of economically and efficiently recovering used germanium, particularly used

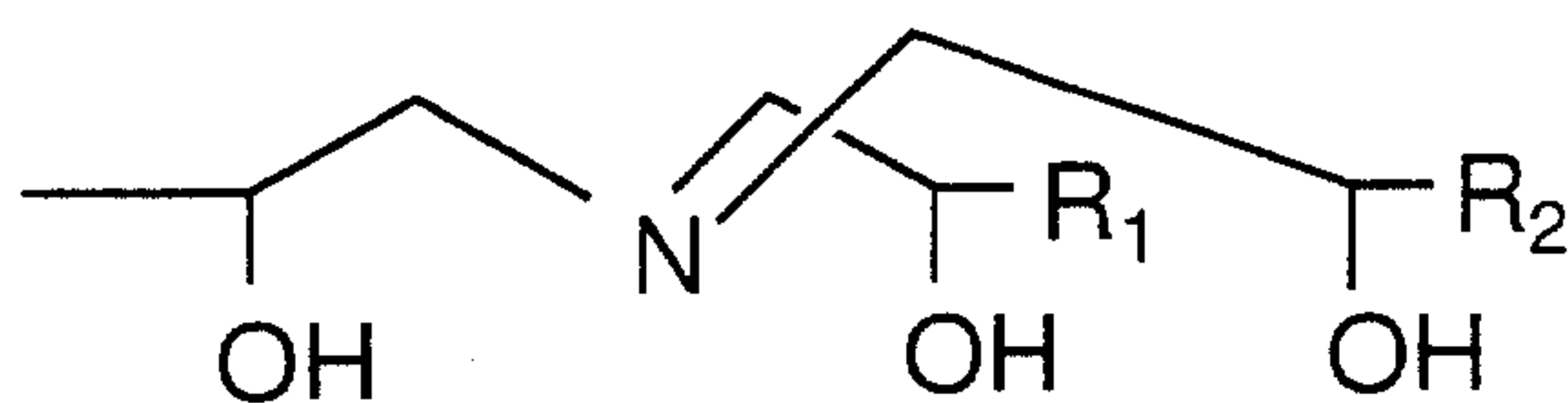
germanium oxide heretofore disposed entirely as a waste and a method for economical and efficient recovery of germanium, particularly germanium oxide using such a porous hollow fiber membrane.

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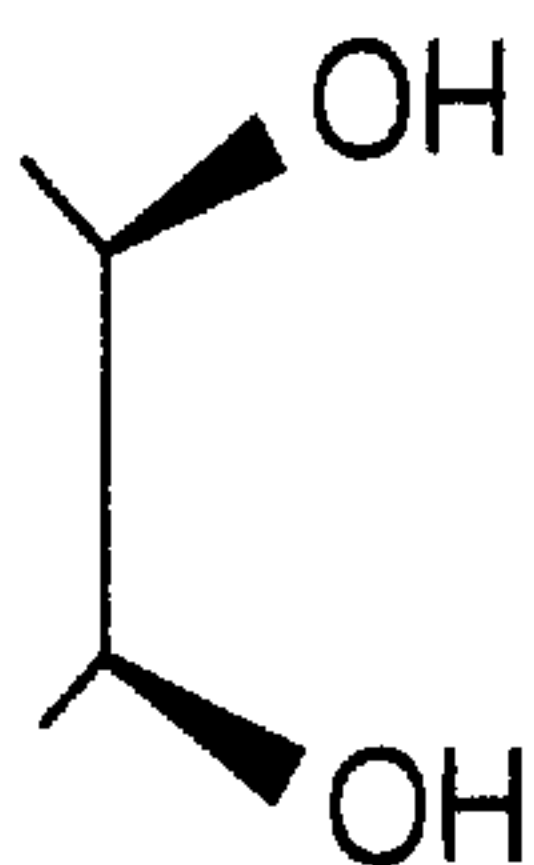
#### Disclosure of the Invention

The porous hollow fiber membrane employed by the present invention in order to achieve the above aim is characterized by being obtained by reacting the residue of an epoxy group-containing compound subjected to irradiation-induced graft polymerization on a polyethylene-made porous hollow fiber membrane, with a compound capable of reacting with said residue to give a residue containing a structure represented by the following formula:

15



(wherein R<sub>1</sub> and R<sub>2</sub> are a hydrogen atom or a lower alkyl group) or the following formula:



The method for recovering germanium oxide using a porous hollow fiber membrane, also employed by the present invention is characterized by contacting an aqueous germanium oxide solution with the above-mentioned porous hollow fiber membrane having chelate formability, to allow the porous hollow fiber membrane having chelate formability to capture the germanium oxide contained in the aqueous solution, and then dissolving the captured germanium oxide into an acidic solution.

#### Brief Description of the Drawings

Fig. 1 is a conceptual drawing of a permeation apparatus used for examining the germanium oxide adsorbability of a porous hollow fiber membrane.

Fig. 2 is a graph of adsorption curves each showing the adsorption amount of germanium when an aqueous

germanium solution was allowed to permeate through a porous hollow fiber membrane.

Fig. 3 is a graph showing the pH dependency of germanium adsorbability of IDE membrane.

5 Fig. 4 is a graph showing the germanium oxide adsorbability of high-capacity IDE membrane.

Fig. 5 is a graph showing the flow amount dependency of adsorbability of IDE membrane.

10 Fig. 6 is a graph showing the adsorbability of IDE membrane in repeated use.

Fig. 7 is a graph showing the dissolvability from IDE membrane.

#### Best Mode for Carrying Out the Invention

15 Hereinafter, the present invention is described in detail.

The polyethylene-made porous hollow fiber membrane used in the present invention is a polyethylene-made hollow fiber membrane (this is also called "hollow yarn" or

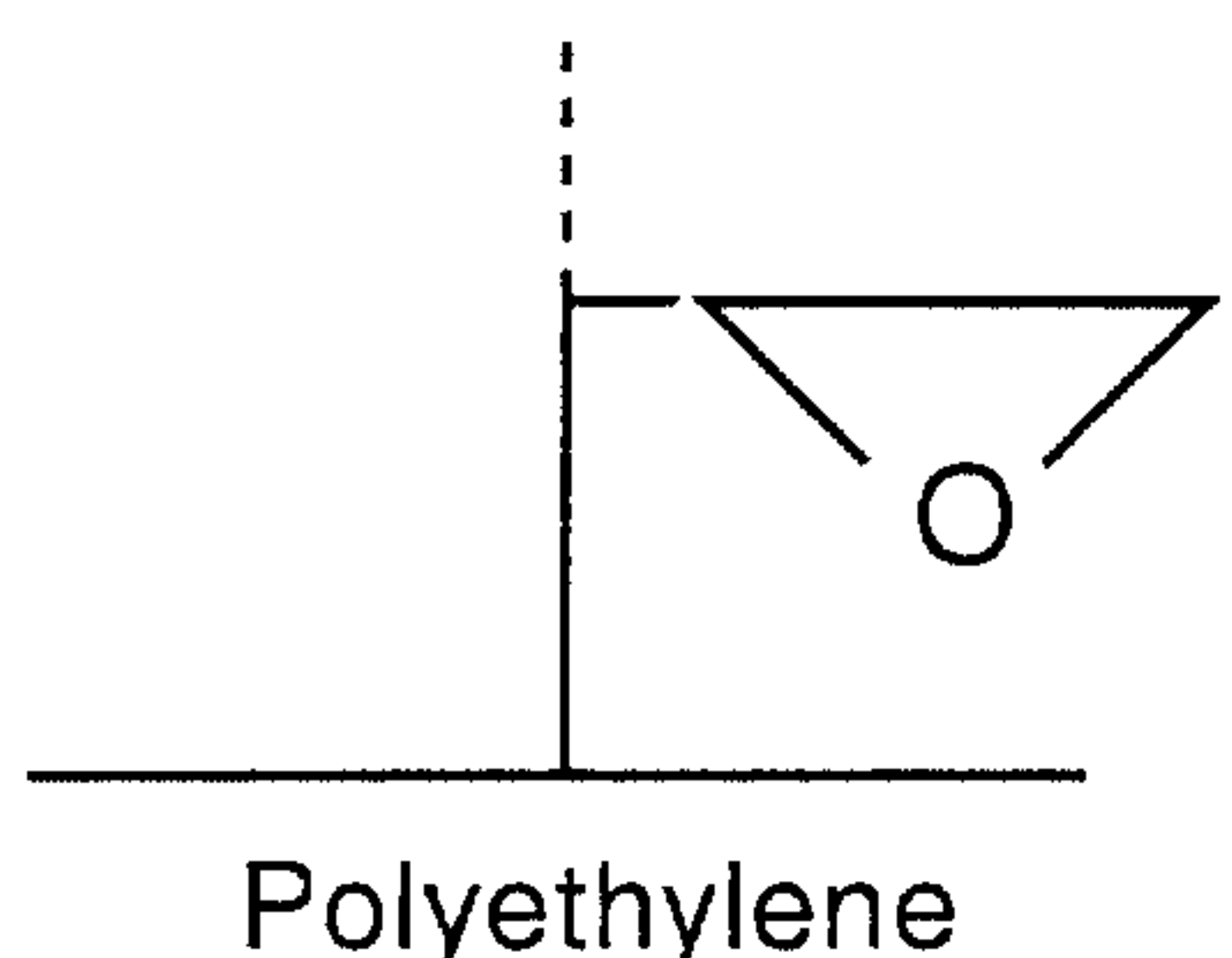
"hollow fiber") having a large number of pores communicating from the inner wall to the outer wall, and can be produced by an extraction method or a stretching method. It is convenient to use a commercial product as such a membrane.

In order to produce a porous hollow fiber membrane having chelate formability, of the present invention, an epoxy group-containing compound is polymerized on the above-mentioned polyethylene-made porous hollow fiber membrane. This polymerization is conducted by irradiation-induced graft polymerization.

In the irradiation-induced graft polymerization, a polyethylene radical is generated by the use of a radiation such as electron beam, gamma-ray or the like and it is reacted with a monomer (an epoxy group-containing compound in the present invention).

As the epoxy group-containing compound, there can be mentioned, for example, glycidyl methacrylate. When this compound is subjected to irradiation-induced graft po-

lymerization on the above-mentioned polyethylene-made porous hollow fiber membrane, there can be obtained a polyethylene-made porous hollow fiber membrane having the residue of an epoxy group-containing compound, which has the following structure.



The amount of the epoxy group-containing compound used is, when the compound is, for example, glycidyl methacrylate, about 4.0 moles in terms of epoxy group amount per kg of the resulting porous hollow fiber membrane. By controlling the amount of the epoxy group-containing compound used, the epoxy group amount in the resulting porous hollow fiber membrane can be controlled.

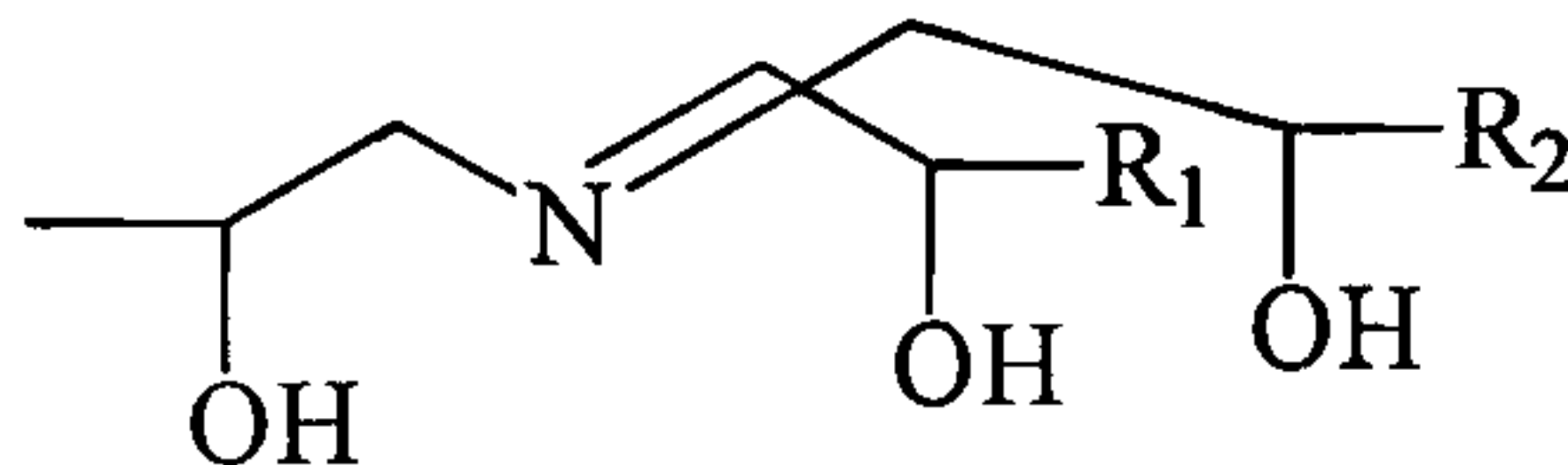
Then, the residue of an epoxy group-containing compound in the polyethylene-made porous hollow fiber mem-

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brane having the residue of an epoxy group-containing compound is reacted, in the first case, with a compound capable of reacting with the residue to give a residue containing a structure represented by the following formula:

5



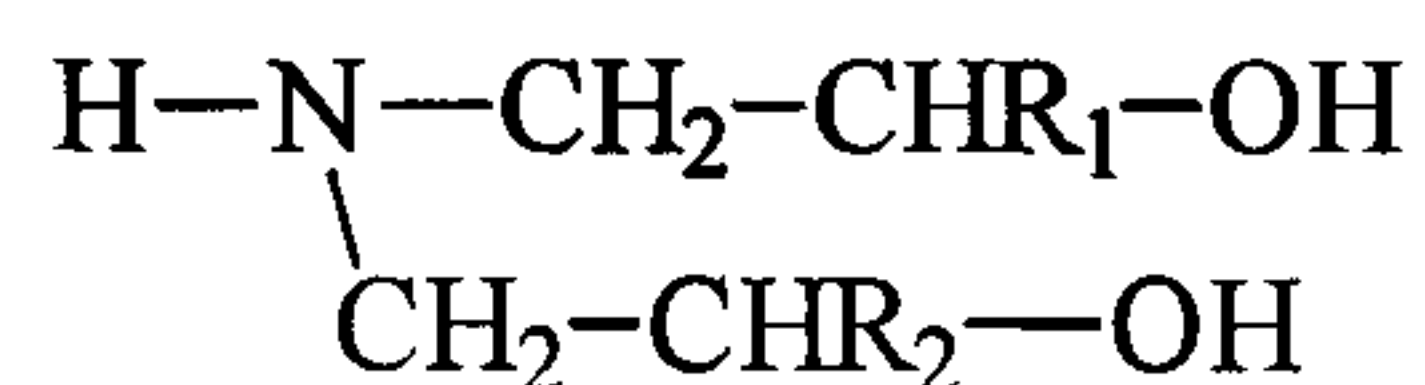
whereby is obtained a first porous hollow fiber membrane having chelate formability, of the present invention.

10

In the above formula,  $R_1$  and  $R_2$  may be the same or different and are each a hydrogen atom or a lower alkyl group.

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The compound used for obtaining the above first porous hollow fiber membrane is not critical as long as it can give a residue containing a structure represented by the above formula. The compound has the formula:

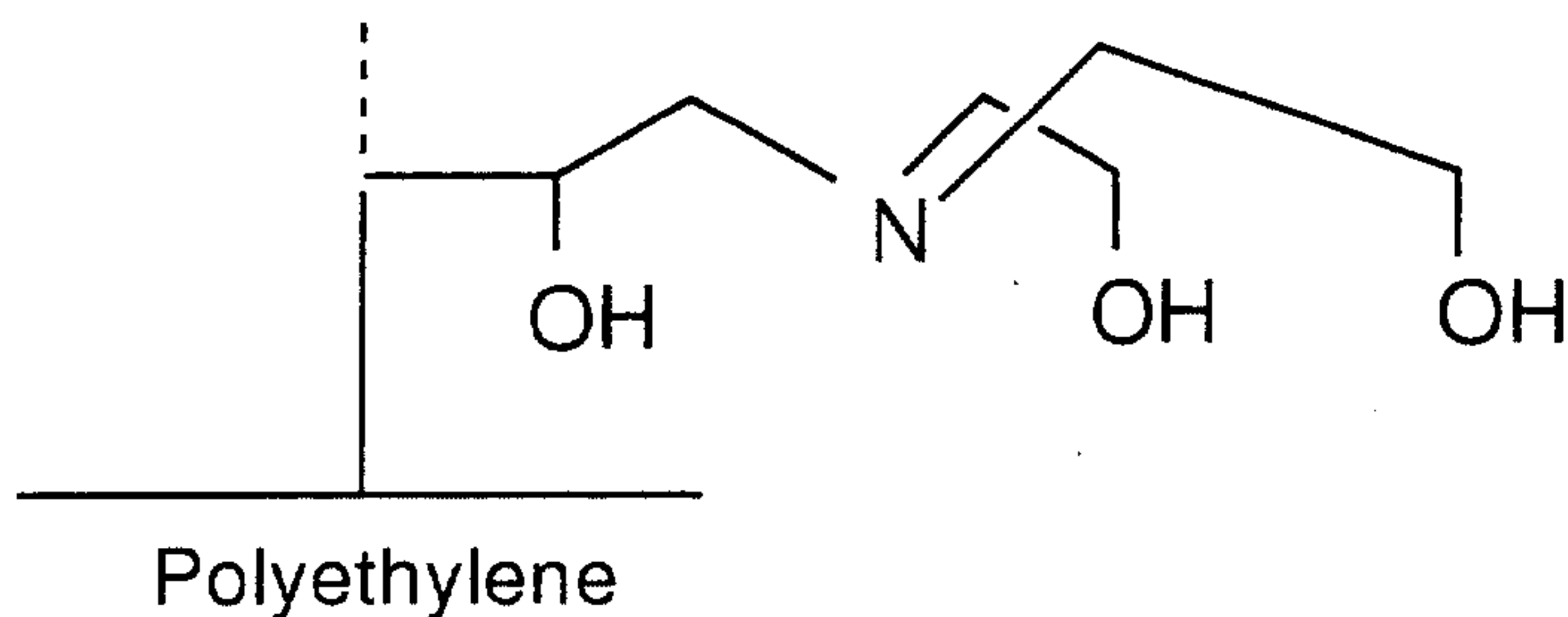


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and includes, for example, 2,2-iminodiethanol and di-2-propanolamine.

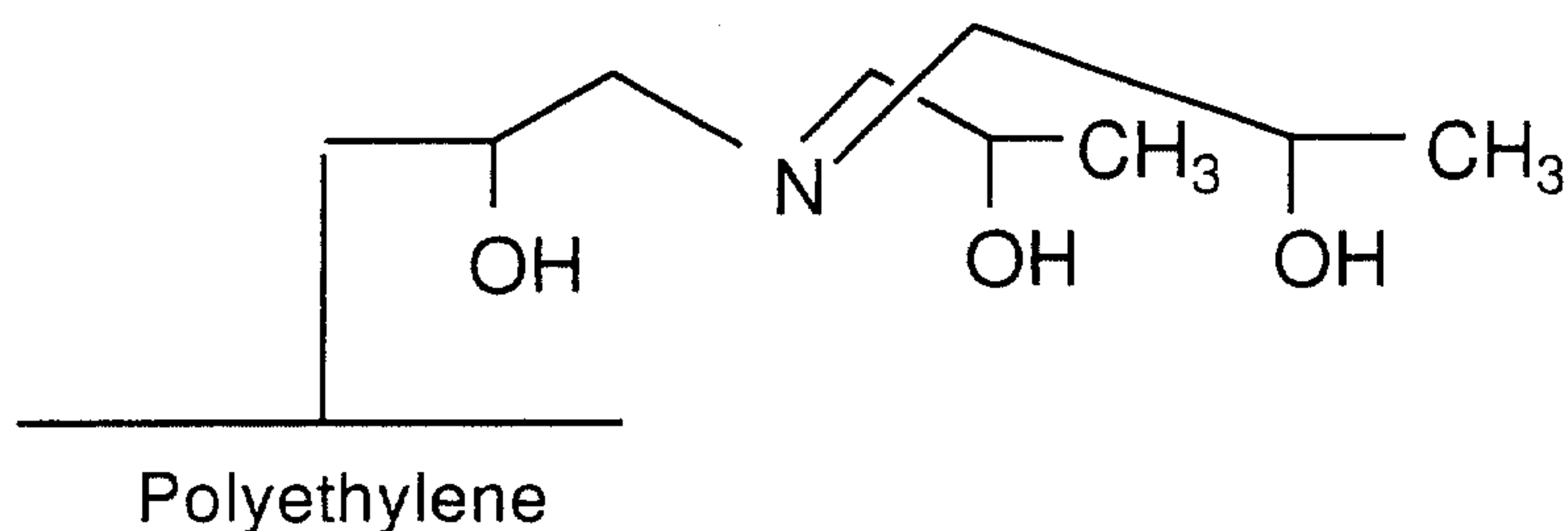
When 2,2-iminodiethanol is used, the first porous hollow fiber membrane having chelate formability, of

the present invention has the following structure:



and, when di-2-propanolamine is used, the following struc-

5 ture.



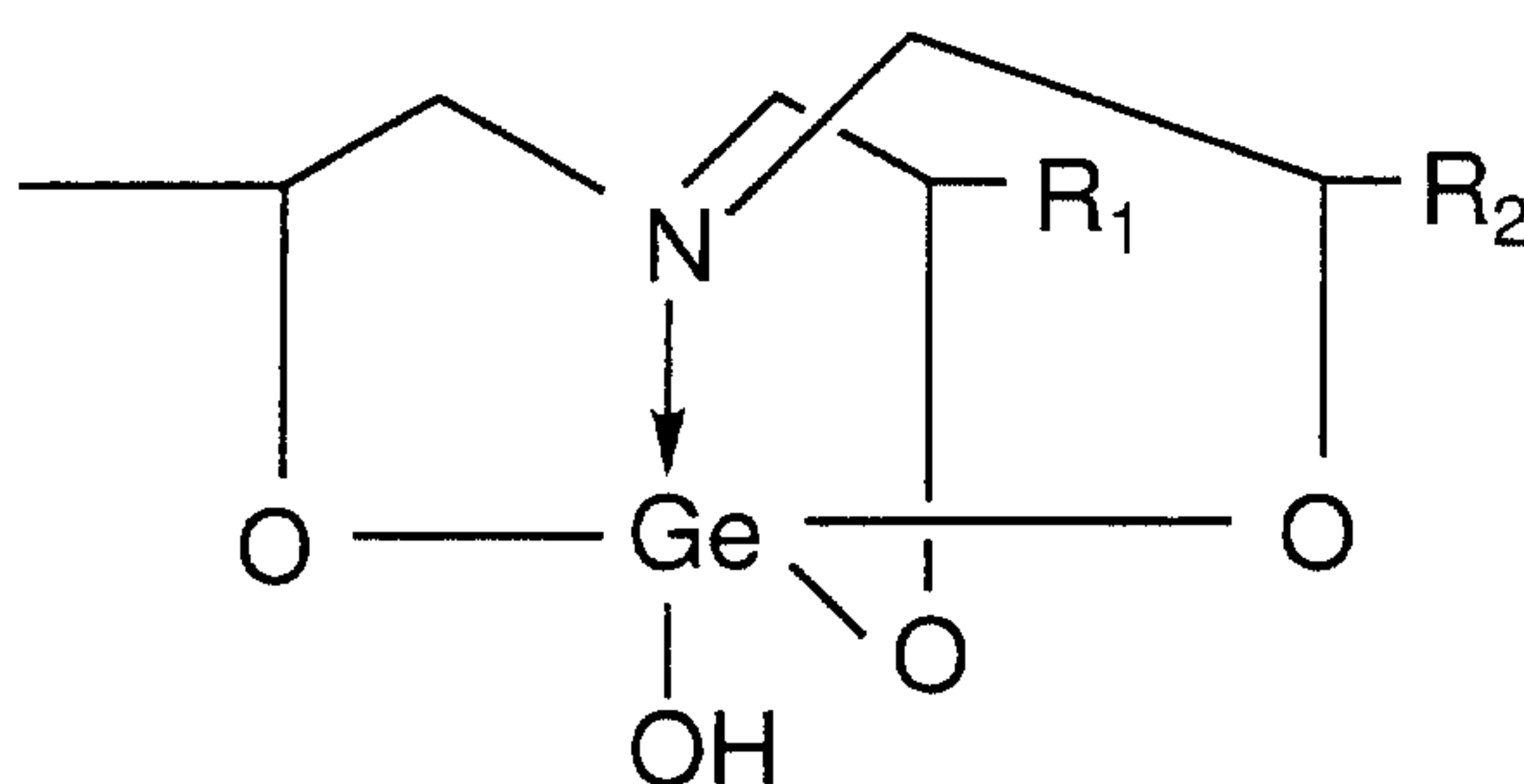
The first porous hollow fiber membrane can be produced, for example, by immersing the polyethylene-made porous hollow fiber membrane having the residue of an epoxy group-containing compound, in a solution of a compound used for obtaining the first porous hollow fiber membrane, to add the latter compound to the epoxy group of the polyeth-

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ylene-made porous hollow fiber membrane. The amount of the structure of chelate formability in the first porous hollow fiber membrane obtained can be controlled by controlling the use amount of the compound used for obtaining the first porous hollow fiber membrane.

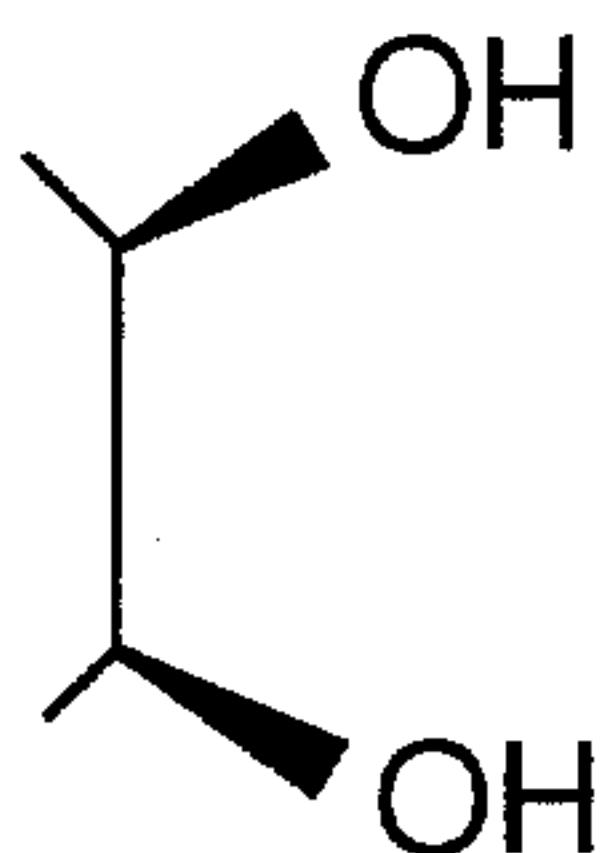
The first porous hollow fiber membrane having chelate formability, of the present invention, when used for germanium oxide, captures germanium oxide to form a germatrane structure as shown below.

10



Meanwhile, in a second case, the residue of an epoxy group-containing compound in the polyethylene-made porous hollow fiber membrane having the residue of an epoxy group-containing compound is reacted with a compound capable of reacting with the residue to give a residue contain-

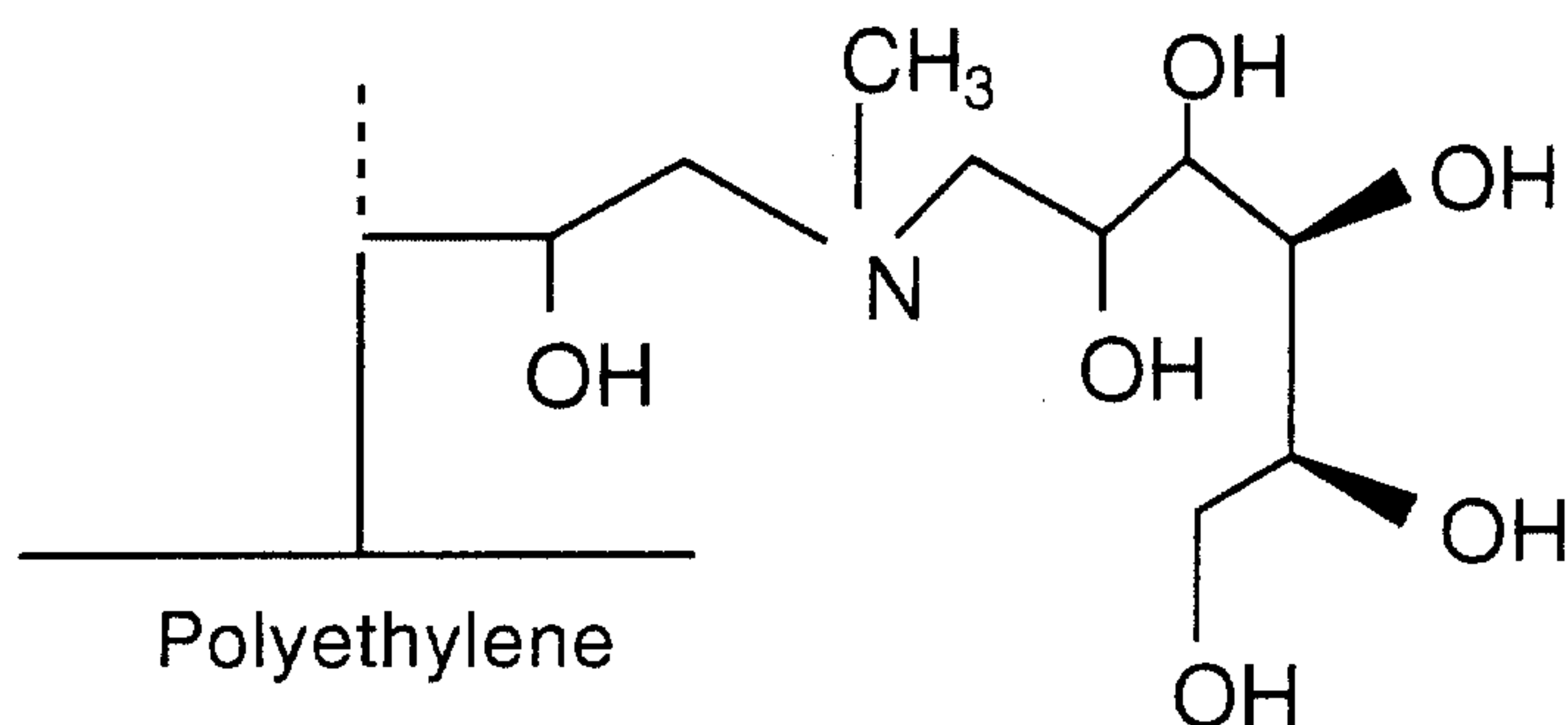
ing a structure (a cis-1,2-diol structure) represented by the following formula:



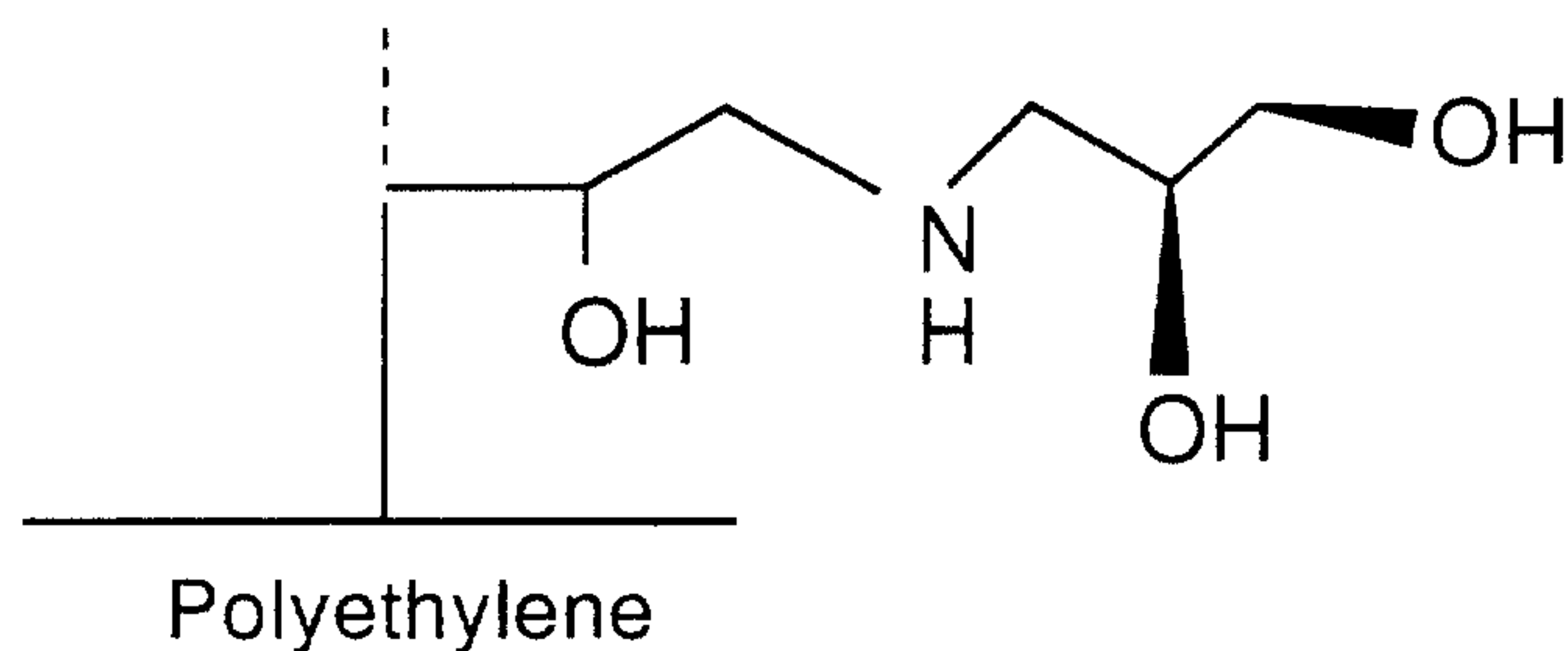
5 whereby can be obtained a second porous hollow fiber membrane having chelate formability, of the present invention.

The compound used for obtaining the above second porous hollow fiber membrane is not critical as long as it can give a residue containing a structure represented by  
10 the above formula. The compound includes, for example, N-methylglucamine and 3-amino-1,2-propanediol.

When N-methylglucamine is used, the second porous hollow fiber membrane having chelate formability, of the present invention, has the following structure:



and, when 3-amino-1,2-propanediol is used, the following structure.

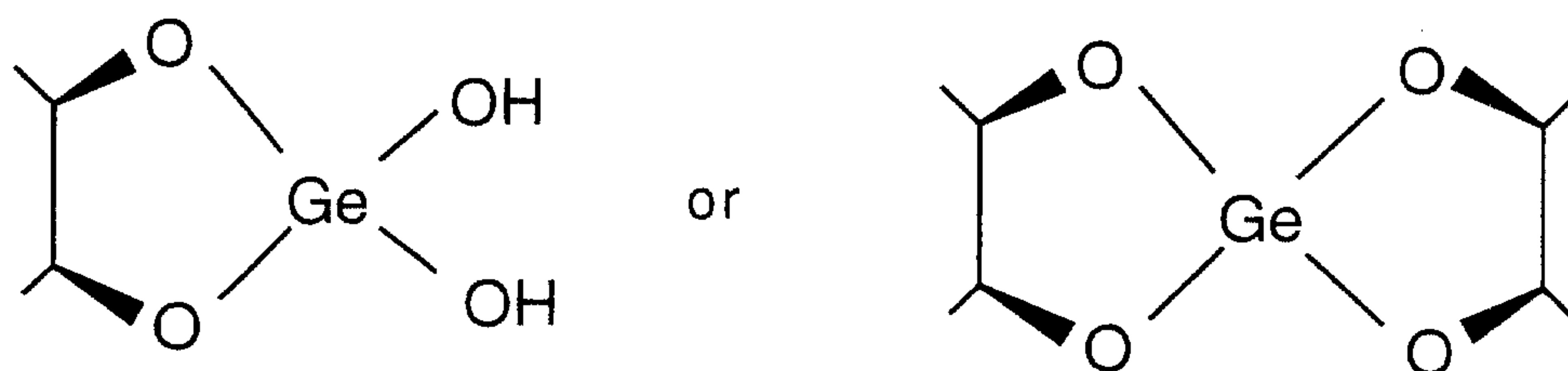


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The second porous hollow fiber membrane can be produced, for example, by immersing the polyethylene-made porous hollow fiber membrane having the residue of an epoxy group-containing compound, in a solution of a compound used for obtaining the second porous hollow fiber membrane, to add the latter compound to the epoxy group of the polyethylene-made porous hollow fiber membrane. The amount of the

structure of chelate formability in the second porous hollow fiber membrane obtained can be controlled by controlling the use amount of the compound used for obtaining the second porous hollow fiber membrane.

5 The second porous hollow fiber membrane having chelate formability, of the present invention, when used for germanium oxide, captures germanium oxide to form a complex with a cis-1,2-diol structure as shown below.



10

In recovering germanium using the thus-obtained porous hollow fiber membrane having chelate formability, of the present invention, first, an aqueous solution containing, for example, germanium oxide is contacted with the porous hollow fiber membrane having chelate formability to allow the membrane to capture germanium oxide. Specifically, the aqueous solution containing, for example, germa-

15

nium oxide is allowed to permeate through the porous hollow fiber membrane having chelate formability, of the present invention from the inner wall to the outer wall.

The permeation of the aqueous solution containing germanium oxide through the porous hollow fiber membrane from the inner wall to the outer wall can be conducted, for example, by allowing a 0.01 wt. % aqueous germanium oxide solution adjusted to pH 3 to 12 with sodium hydroxide or hydrochloric acid, to permeate at a particular pressure and a particular temperature and then, as necessary, washing the resulting membrane with water.

By the above permeation of the aqueous germanium oxide solution through the porous hollow fiber membrane from the inner wall to the outer wall, germanium oxide becomes the above-mentioned germatrane structure or the above-mentioned complex with a cis-1,2-diol structure and is captured by the porous hollow fiber membrane having chelate formability, of the present invention.

Finally, the captured germanium oxide is dis-

solved into an acidic solution to complete recovery of germanium oxide from the aqueous germanium oxide solution. As the acidic solution, there can be mentioned, for example, hydrochloric acid of about 1 M.

5                   The elution of the captured germanium oxide into the acidic solution can be conducted, for example, by allowing the acidic solution to permeate through the porous hollow fiber membrane from the inner wall to the outer wall, as in the case of germanium oxide capture.

10

The present invention is described in more detail below by way of Examples.

1. Production of porous hollow fiber membranes having chelate formability

15

A polyethylene-made porous hollow fiber membrane (inner diameter = 1.8 mm, outer diameter = 3.1 mm, pore diameter = 0.3  $\mu\text{m}$ , porosity = 70%) was irradiated with 200 KGy of a radiation in a nitrogen atmosphere at room temperature. The irradiated membrane was placed in a glass

ampoule containing a methanol solution of glycidyl methacrylate, and graft polymerization of glycidyl methacrylate was allowed to take place at 40°C to obtain a glycidyl methacrylate membrane (hereinafter referred to as GMA membrane) containing 4.0 moles of epoxy group per kg of GMA membrane.

#### 1-1) Production of iminodiethanol membrane

The GMA membrane obtained above by irradiation-induced graft polymerization was immersed in a 50 vol. % aqueous iminodiethanol solution at 338 K (65°C) to add iminodiethanol group to the epoxy group of the GMA membrane (the resulting membrane is hereinafter referred to as IDE membrane).

#### 1-2) Production of diisopropanolamine membrane

The GMA membrane was also immersed in a 1 M aqueous diisopropanolamine solution at 338 K (65°C) to add diisopropanolamine group to the epoxy group of the GMA membrane (the resulting membrane is hereinafter referred to as DPA membrane).

### 1-3) Production of N-methylglucamine membrane

The GMA membrane was also immersed in an aqueous solution containing 0.5 M of N-methylglucamine and 50 v/v % of dioxane-water at 353 K (80°C) to add N-methylglucamine group to the epoxy group of the GMA membrane (the resulting membrane is hereinafter referred to as NMG membrane).

### 1-4) Production of 3-amino-1,2-propanediol membrane

The GMA membrane was also immersed in an aqueous solution containing 1 M of 3-amino-1,2-propanediol and 50 v/v % of dioxane-water at 353 K (80°C) to add 3-amino-1,2-propanediol group to the epoxy group of the GMA membrane (the resulting membrane is hereinafter referred to as APD membrane).

## 2. Confirmation of structures of porous hollow fiber membranes having chelate formability

The structures of the membranes obtained above were confirmed using the IR spectra of the membranes. That is, by converting the GMA membrane into the IDE membrane,

the DPA membrane, the NMG membrane and the APD membrane, the absorption of epoxy group at  $847\text{ cm}^{-1}$  and  $909\text{ cm}^{-1}$  disappeared and new absorption of hydroxyl group appeared at  $3,000$  to  $3,500\text{ cm}^{-1}$ . The IR spectral data of the individual  
5 membranes are given below.

GMA membrane (grafting degree of base material =  
155.5%).

2920  $\text{cm}^{-1}$ , 2851  $\text{cm}^{-1}$  (stretching vibration of CH)  
1734  $\text{cm}^{-1}$  (CO group)  
10 1490  $\text{cm}^{-1}$ , 1262  $\text{cm}^{-1}$ , around 1150  $\text{cm}^{-1}$ , 995  $\text{cm}^{-1}$   
762  $\text{cm}^{-1}$   
909  $\text{cm}^{-1}$  (antisymmetric ring stretching  
vibration of epoxy)  
847  $\text{cm}^{-1}$  (antisymmetric ring stretching  
15 vibration of epoxy)

IDE membrane (conversion percentage = 98%)

3000 to 3500  $\text{cm}^{-1}$  (OH group)  
2917  $\text{cm}^{-1}$ , 2851  $\text{cm}^{-1}$  (stretching vibration of CH)  
1725  $\text{cm}^{-1}$  (CO group)

1474  $\text{cm}^{-1}$ , 1250  $\text{cm}^{-1}$ , around 1163  $\text{cm}^{-1}$ , 1068  $\text{cm}^{-1}$

The absorption of antisymmetric ring stretching vibration of epoxy disappeared.

DPA membrane (conversion percentage = 90%)

5. 3000 to 3500  $\text{cm}^{-1}$  (OH group)

2919  $\text{cm}^{-1}$ , 2851  $\text{cm}^{-1}$  (stretching vibration of CH)

1728  $\text{cm}^{-1}$  (CO group)

1474  $\text{cm}^{-1}$ , 1271  $\text{cm}^{-1}$ , 1150  $\text{cm}^{-1}$ , 995  $\text{cm}^{-1}$

The absorption of antisymmetric ring stretching vibration of epoxy disappeared.

NMG membrane (conversion percentage = 82%)

3000 to 3500  $\text{cm}^{-1}$  (OH group)

2919  $\text{cm}^{-1}$ , 2851  $\text{cm}^{-1}$  (stretching vibration of CH)

1717  $\text{cm}^{-1}$  (CO group)

15. 1474  $\text{cm}^{-1}$ , 1260  $\text{cm}^{-1}$ , 1170  $\text{cm}^{-1}$ , 1084  $\text{cm}^{-1}$

The absorption of antisymmetric ring stretching vibration of epoxy disappeared.

APD membrane (conversion percentage = 68%)

3000 to 3500  $\text{cm}^{-1}$  (OH group)

2919  $\text{cm}^{-1}$ , 2851  $\text{cm}^{-1}$  (stretching vibration of CH)

1725  $\text{cm}^{-1}$  (CO group)

1474  $\text{cm}^{-1}$ , 1269  $\text{cm}^{-1}$ , 1168  $\text{cm}^{-1}$

The absorption of antisymmetric ring stretching  
5 vibration of epoxy disappeared.

3. Adsorption of germanium oxide by porous hollow fiber  
membranes having chelate formability

Each of the four kinds of porous hollow fiber  
membranes having chelate formability, produced above, i.e.  
10 the IDE membrane, the DPA membrane, the NMG membrane and  
the APD membrane was set in a permeation apparatus shown in  
Fig. 1. Then, the following three kinds of solutions were  
allowed to permeate through each apparatus set with these  
membranes in the following order at a constant pressure  
15 (0.1 MPa) and a constant temperature (24°C) for the follow-  
ing three kinds of operations.

1) Adsorption operation: a 0.01 wt. % aqueous germa-  
nium oxide solution (adjusted to pH 3 to 12 using sodium  
hydroxide or hydrochloric acid)

2) Washing operation: water

3) Elution operation: 1 M hydrochloric acid

For each operation, the solution after permeation was continuously collected into a test tube; the final solution after permeation was determined for germanium concentration by a phenylfluorone method; and the amount of germanium adsorbed by the porous hollow fiber membrane was calculated from a difference between the germanium concentration in feeding solution and the germanium concentration in solution after permeation.

#### 4. Results

##### 4-1) Comparison of germanium amounts adsorbed

The adsorbed amount of germanium when an aqueous germanium oxide solution was allowed to permeate through each porous hollow fiber membrane (the IDE membrane, the DPA membrane, the NMG membrane or the APD membrane), is shown in Fig. 2 as a adsorbed amount curve; and the adsorbability of each porous hollow fiber membrane when the initial pH of the aqueous germanium oxide solution was 4.6, is

shown in Table 1.

Table 1

Hollow fiber membrane (functional group)	Initial pH	Adsorbed amount (mmol/g)	Elution amount (mmol/g)	Elution percentage (%)	Bonded mole ratio (Ge amount / functional amount)
DPA membrane	4.6	1.0	1.0	99	0.74
NMG membrane	4.6	0.6	0.6	100	0.55
APD membrane	4.6	0.6	0.5	73	0.42
IDE membrane	4.6	1.2	1.2	99	0.85
	3.2	1.1	1.1	100	0.70
	7.8	1.2	1.2	100	0.88
	11.7	0.1	0.1	99	0.26

As is clear from Fig. 2 and Table 1, the IDE membrane gave the highest adsorbed amount (1.2 mol per kg of the membrane), and the adsorbabilities of the IDE membrane and the DPA membrane were higher than those of the NMG membrane and the APD membrane.

The above "DEV (Dimensionless Effluent Volume)" refers to (amount of solution after permeation)/(membrane volume excluding hollow portion).

The elution percentage was nearly 100% in all the porous hollow fiber membranes, which indicated that they allow repeated adsorption and desorption.

4-2) pH dependency of germanium adsorbability of IDE membrane

In Fig. 3 is shown the pH dependency of adsorbed germanium amount of IDE membrane when the initial (when fed to IDE membrane) pH of aqueous germanium oxide solution was varied from 3.2 to 11.7. As is clear from Fig. 3 and Table 1, the adsorbed amount of germanium oxide varied in an initial pH range of 3 to 12. The mole ratio of bonded germanium to IDE group at pH 7.8 was 0.88 and about 3.4 times that at pH 11.7. These matters indicated that the adsorbed germanium

oxide amount varies depending upon the initial pH of the aqueous germanium oxide solution and is optimum at pH 7.8.

5. Adsorption of germanium oxide by high-capacity IDE membrane

5 5-1) Comparison of adsorbed germanium oxide amounts

A high-capacity IDE membrane having a higher GMA grafting degree and a higher degree of conversion to IDE group (functional group density = 2.9 mol/kg) for higher adsorption was subjected to the same adsorption test as in 10 above, at an initial pH of 7.1. The resulting break-through curve of germanium oxide is shown in Fig. 4. In Fig. 4 is also shown, for comparison, the break-through curve obtained at the optimum condition (functional group density = 1.3 mol/kg) in the above adsorption test.

15 As is clear from Fig. 4, the high-capacity IDE membrane enables high-capacity adsorption of germanium oxide.

5-2) Comparison with chitosan resin with mannose side chain or with N-2,3-dihydroxypropylchitosan resin

Adsorbed germanium oxide amounts were compared 20 between a high-capacity IDE membrane and a chitosan resin

with mannose side chain or an N-2,3-dihydroxypropylchitosan resin (these resins are known to adsorb metals and described in Chitin-Chitosan Study, Vol. 4, No. 2, 1998). The results are shown in Table 2. It is clear from Table 2 that the

5 high-capacity IDE membrane gave an adsorbed Ge amount of 2.7 mol/kg (196 g/kg) which is about 2.3 times that of ordinary IDE membrane and higher than those of the chitosan-based res-

ins.

Table 2

Germanium adsorbent	Base resin	Initial pH	Adsorbed amount (mol/kg)	Elution amount (mol/kg)	Elution percentage (%)	Grafting degree (%)	Conversion percentage (%)
IDE membrane	Polyethylene	7.1	2.7	2.7	100	213	86
Chitosan resin with mannose side chain	Chitosan	7.2	2.4				
N-2,3-dihydroxy-propylchitosan resin	Chitosan	3.9	1.4				

## 5-3) Flow amount dependency of adsorption of IDE membrane

An aqueous germanium oxide solution (initial pH = 6.3) was allowed to permeate through an IDE membrane at a flow rate of 5, 10, 25 and 50 ml/min. The resulting breakthrough curves of Ge are shown in Fig. 5. When the flow rate varied up to tenfold, there was no change in shape of breakthrough curve and therefore in adsorbed amount. This indicates that the diffusion transfer resistance in a direction perpendicular to the thickness direction of membrane is negligibly small. Incidentally, the adsorbed amount of germanium oxide was 0.99 mol/kg (72.1 g/kg) (a four-time average) and the mole ratio of bonded germanium oxide to DetA (Diethyl amino moiety) group was 0.72.

## 5-4) Adsorbability of IDE membrane in repeated use

An adsorption-elution-regeneration cycle was repeated six times (six cycles) for an IDE membrane. The elution percentage after each cycle and the bonded mole ratios after the third, fourth, fifth and sixth cycles are shown in Fig. 6. The elution percentages after individual cycles were constant at about 100% and there was no change in the ad-

sorbed Ge amounts after the third, fourth, fifth and sixth cycles. As a result, it became clear that the IDE membrane enables repeated adsorption-elution-regeneration cycles, the adsorption capacity and the elution ratio remain unchanged even when the times of the adsorption-elution-regeneration cycle increase, and the IDE membrane is an industrially usable adsorbent.

#### 5-5) Dissolvability from IDE membrane

In order to examine the dissolvability from IDE membrane, an aqueous germanium oxide solution (initial pH = 6.3) was allowed to permeate through an IDE membrane and then a elution operation was conducted in such a condition that the volume of the solution after elution operation became 1/10 of the volume of the solution after permeation. The resulting elution curve is shown in Fig. 7. It was possible to concentrate from the peak concentration of the solution after elution to about 45 times the concentration of the feeding solution; and 90% of the adsorbed germanium oxide could be dissolved using 1 M hydrochloric acid of 3 times the membrane volume (about 0.4 ml) and 100% could be dissolved using 1 M

hydrochloric acid of 30 times the membrane volume (about 0.4 ml).

Thus, the porous hollow fiber membrane having chelate formability, of the present invention can adsorb germanium oxide efficiently. By using this porous hollow fiber membrane in the form of a module, germanium oxide can be recovered quickly and in a large amount, and the membrane can be used repeatedly.

#### 10 Industrial Applicability

The porous hollow fiber membrane having chelate formability, of the present invention has a functional group having chelate formability, for example, a triethanolamine structure or a di- or polyol structure and can therefore adsorb germanium oxide at a high efficiency.

Further, the germanium oxide adsorbed by the porous hollow fiber membrane having chelate formability, of the present invention, when subjected to an acid treatment, can be dissolved substantially by 100%; therefore, the present membrane can be used repeatedly for adsorption and

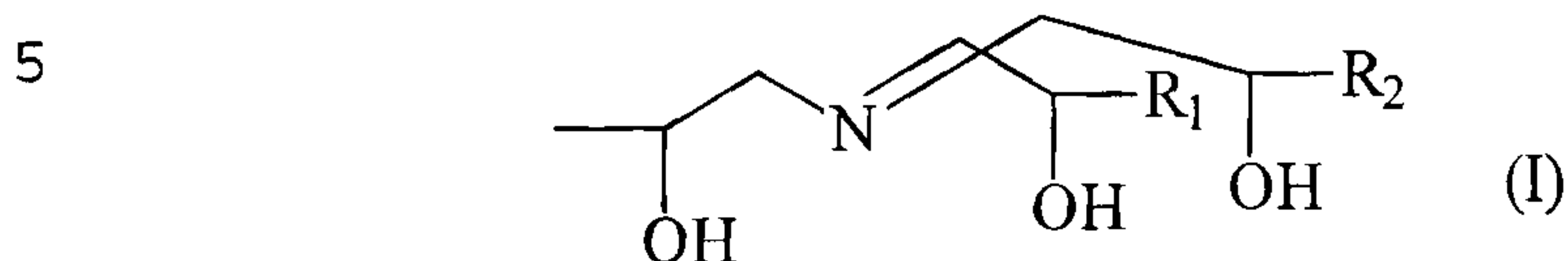
desorption of germanium oxide.

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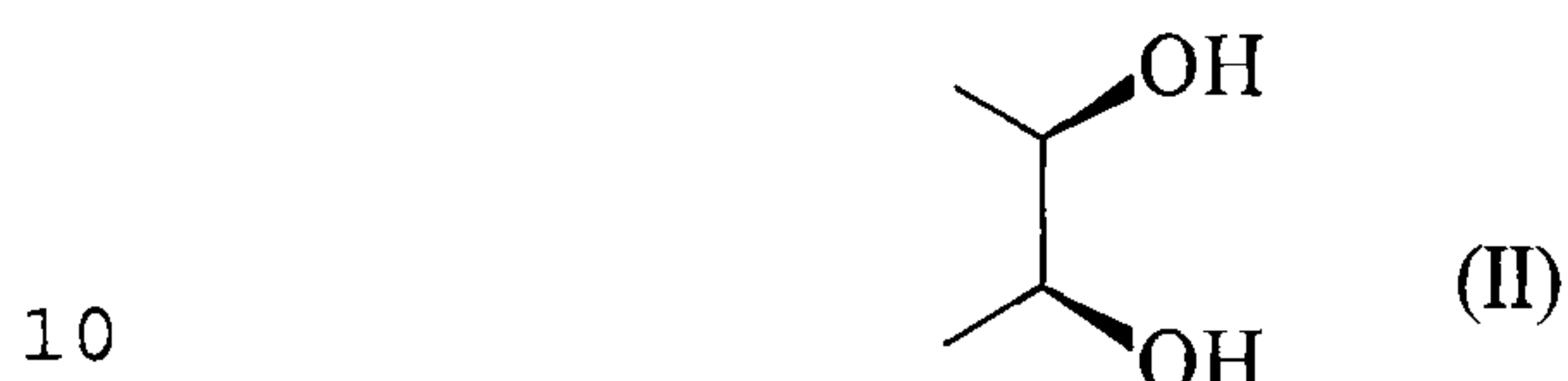
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CLAIMS:

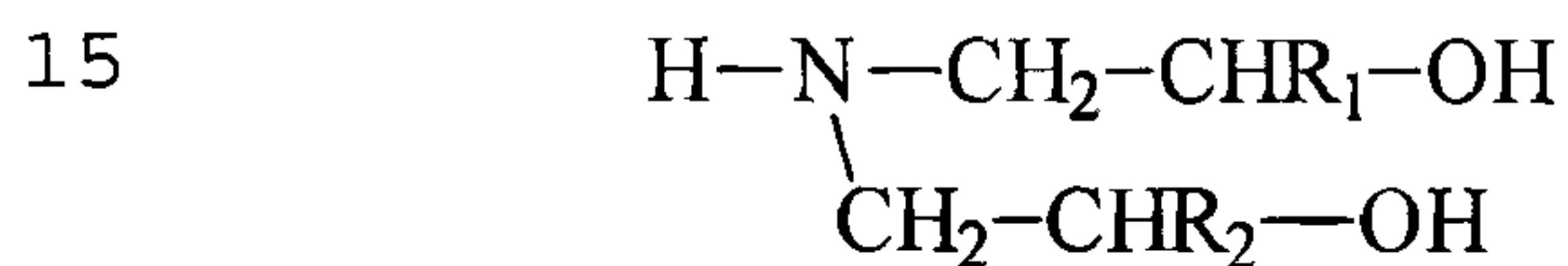
1. A porous hollow fiber membrane which has a chelate-forming residue containing a structure represented by the following formula:



(wherein  $R_1$  and  $R_2$  are a hydrogen atom or a lower alkyl group) or a structure represented by the following formula:



and is obtained by reacting an epoxy residue of an epoxy group-containing compound subjected to irradiation-induced graft polymerization onto a polyethylene-made porous hollow fiber membrane, with a compound of the formula:



(wherein  $R_1$  and  $R_2$  are as defined above), N-methylglucamine or 3-amino-1,2-propanediol.

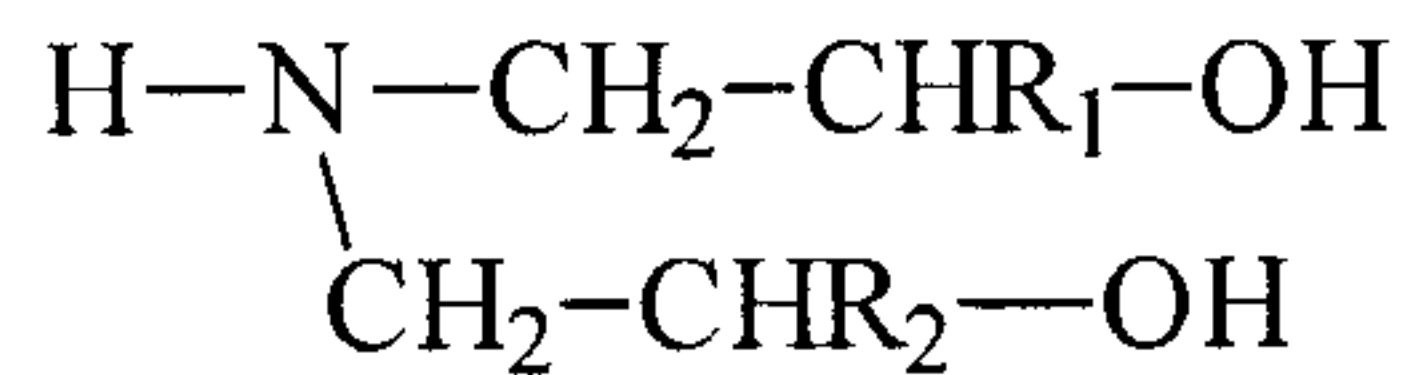
2. The porous hollow fiber membrane according to claim 1, wherein the epoxy group-containing compound subjected to irradiation-induced graft polymerization is glycidyl methacrylate.

3. The porous hollow fiber membrane according to claim 2, wherein about 4.0 moles of glycidyl methacrylate in terms of the epoxy group is graft polymerized per kg of the resulting porous hollow fiber membrane.

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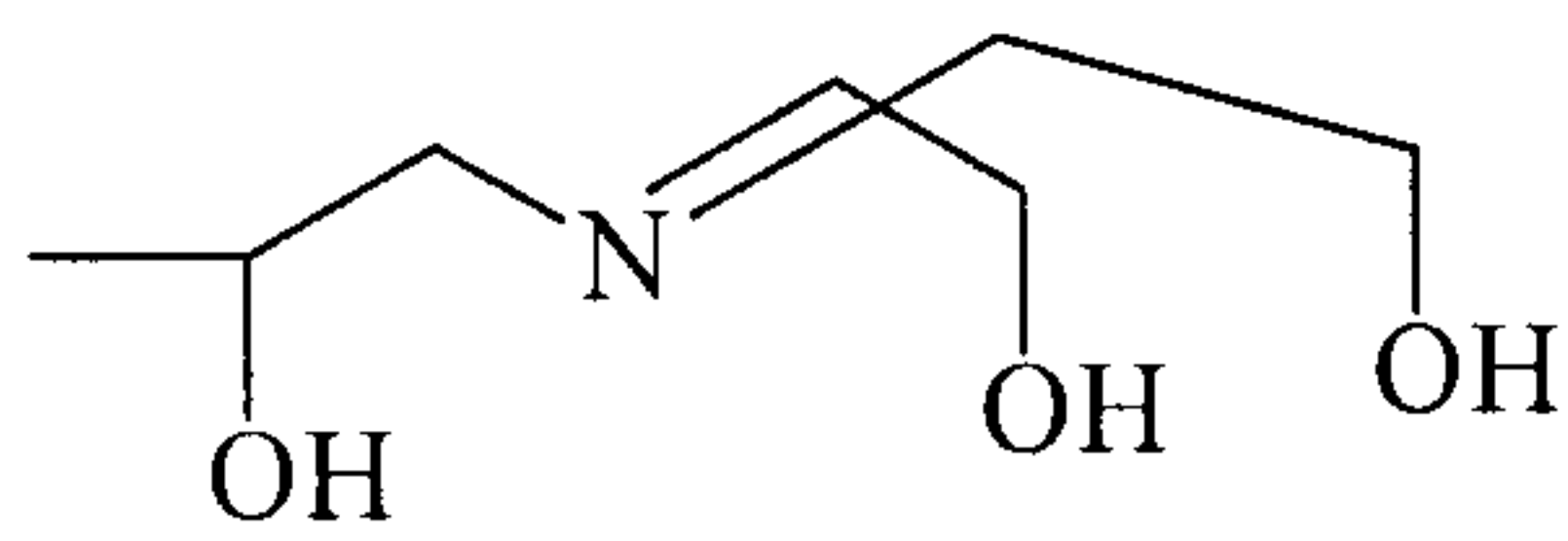
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4. The porous hollow fiber membrane according to claim 1, 2 or 3, wherein the epoxy residue is reacted with the compound of the formula

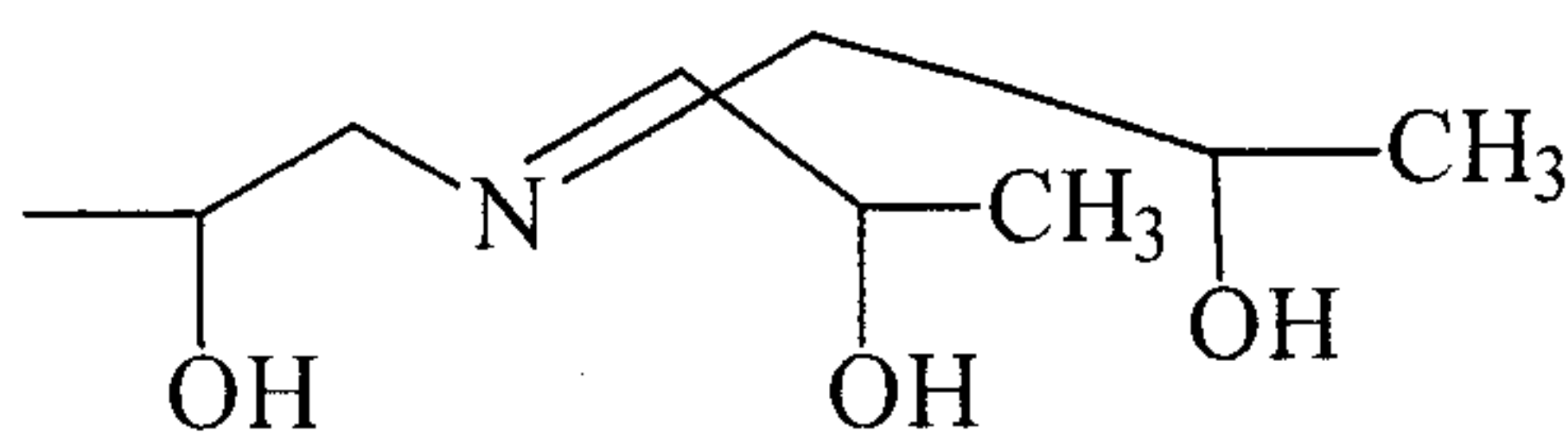


whereby the chelate-forming residue is represented by the formula (I).

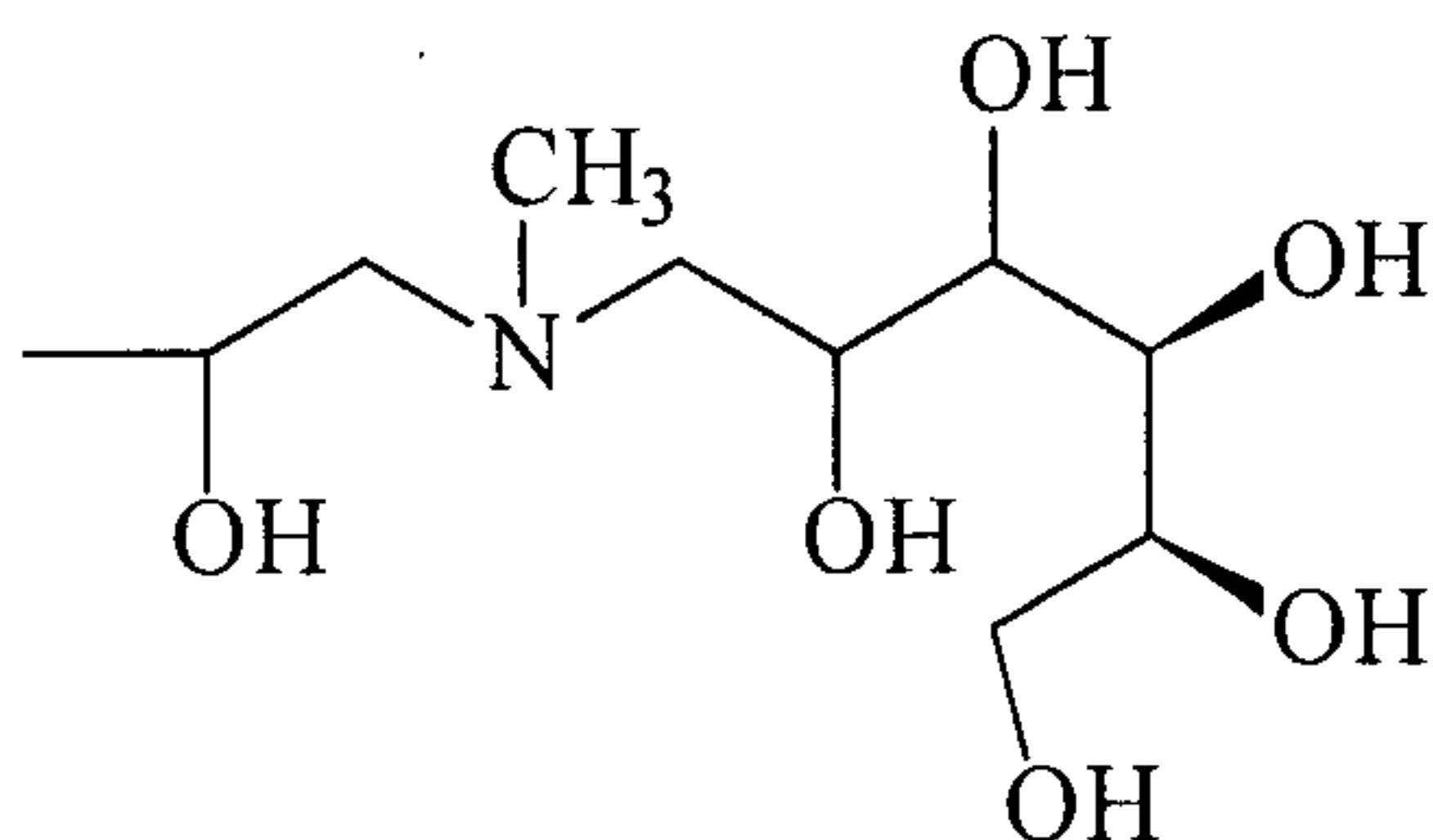
5. The porous hollow fiber membrane according to claim 4, wherein the epoxy residue is reacted with 2,2-iminodiethanol, whereby the chelate-forming residue is represented by the formula:



6. The porous hollow fiber membrane according to claim 4, wherein the epoxy residue is reacted with di-2-propanolamine, whereby the chelate-forming residue is represented by the formula:



7. The porous hollow fiber membrane according to claim 1, 2 or 3, wherein the epoxy residue is reacted with N-methylglucamine, whereby the chelate-forming residue is represented by the formula:

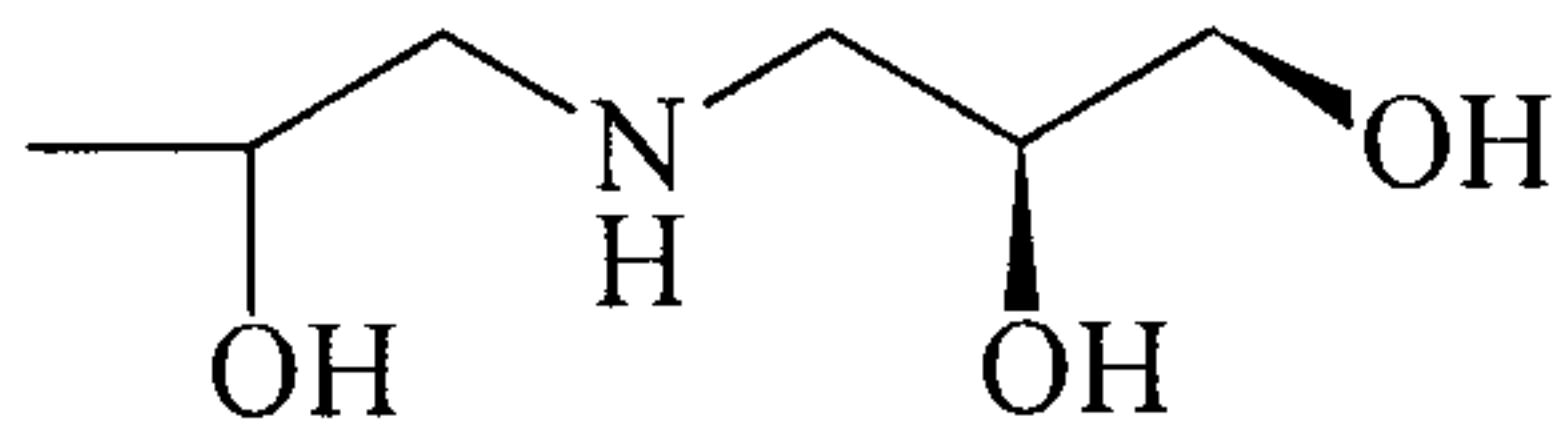


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8. The porous hollow fiber membrane according to claim 1, 2 or 3, wherein the epoxy residue is reacted with 3-amino-1,2-propanediol, whereby the chelate-forming residue is represented by the formula:

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9. The porous hollow fiber membrane according to any one of claims 1 to 8, which has pores communicating from an inner wall to an outer wall.

10. A method for recovering germanium oxide from an aqueous solution thereof, which comprises:

contacting the aqueous solution with the porous hollow fiber membrane as defined in any one of claims 1 to 9 to allow the porous hollow fiber membrane to capture the germanium oxide contained in the aqueous solution, and

then dissolving the captured germanium oxide with an acidic solution.

11. The method according to claim 10, wherein the aqueous solution has a pH of 3 to 12 and the porous hollow fiber membrane is washed with water after being contacted with the aqueous solution and before the captured germanium oxide is dissolved with the acidic solution.

12. The method according to claim 10 or 11, wherein the acidic solution used to dissolve the captured germanium oxide is hydrochloric acid.

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Fig.1

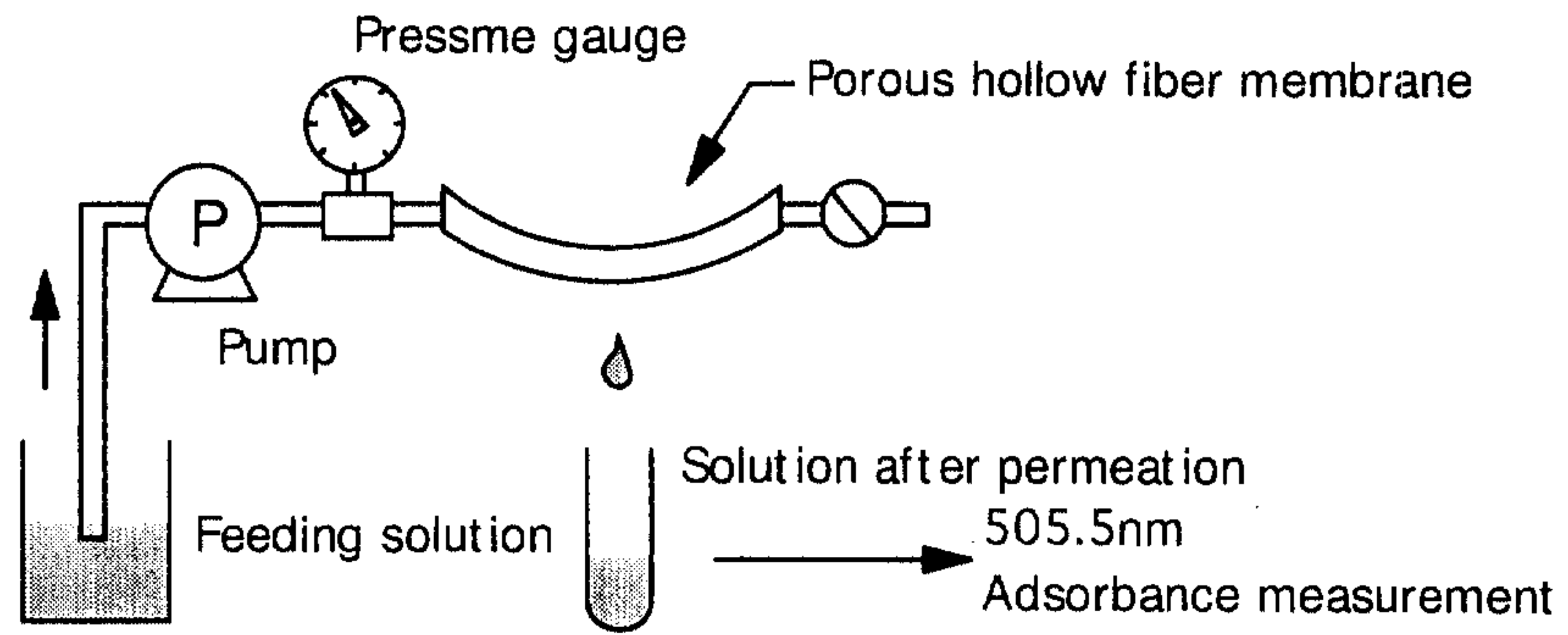
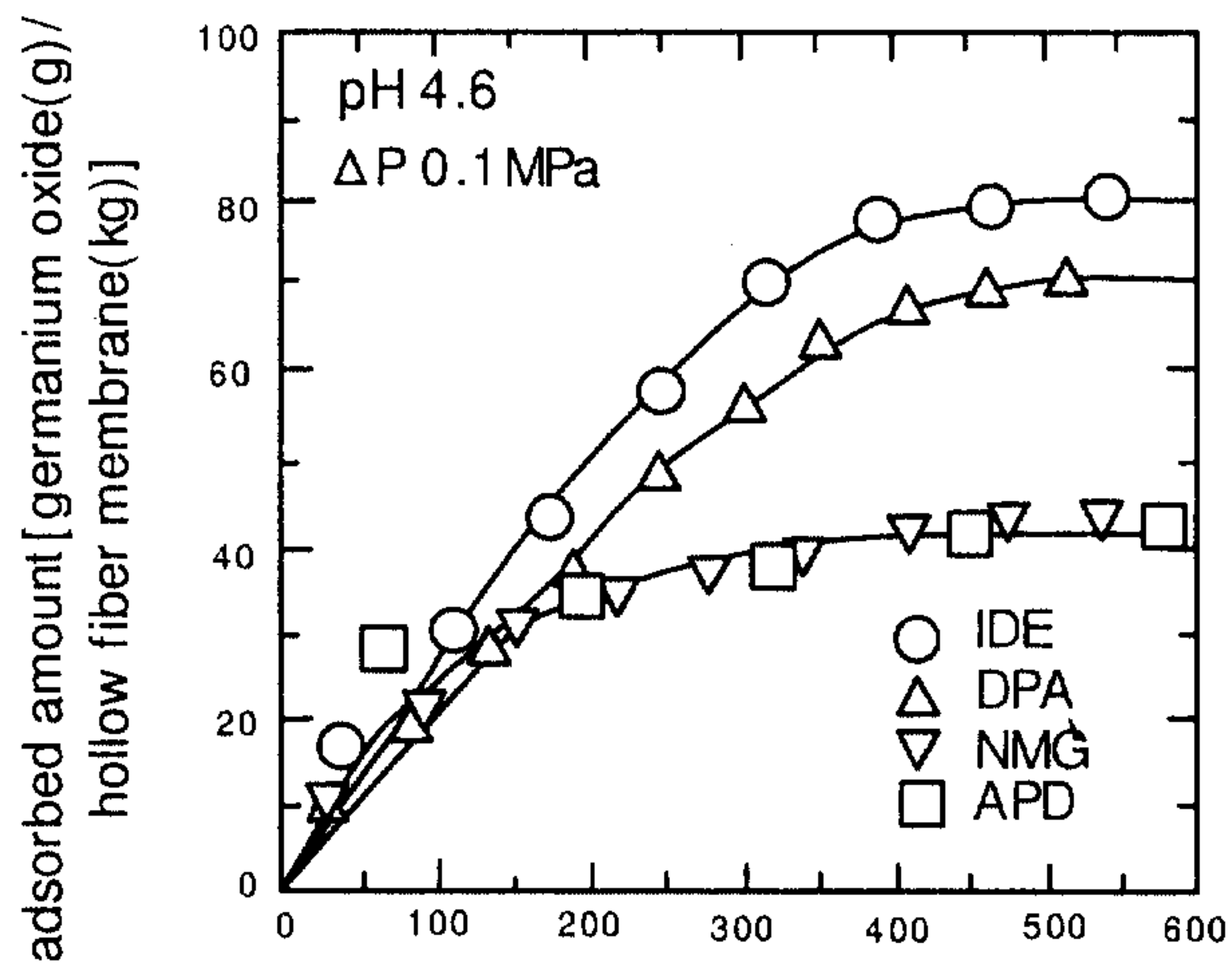


Fig.2



$$DEV = \frac{\text{amount of solution after permeation}}{\text{membrane volume excluding hollow portion}}$$

Fig.3

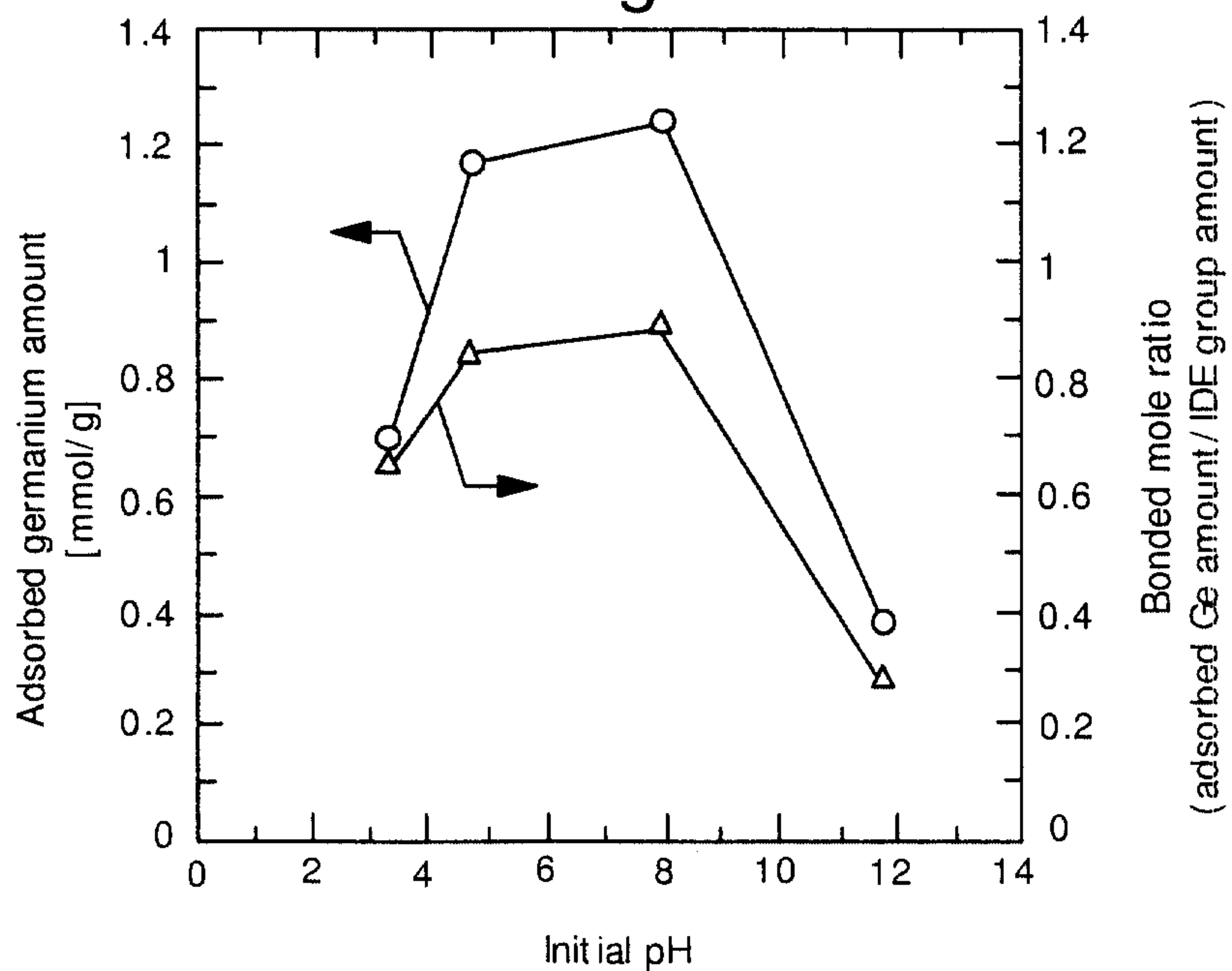


Fig.4

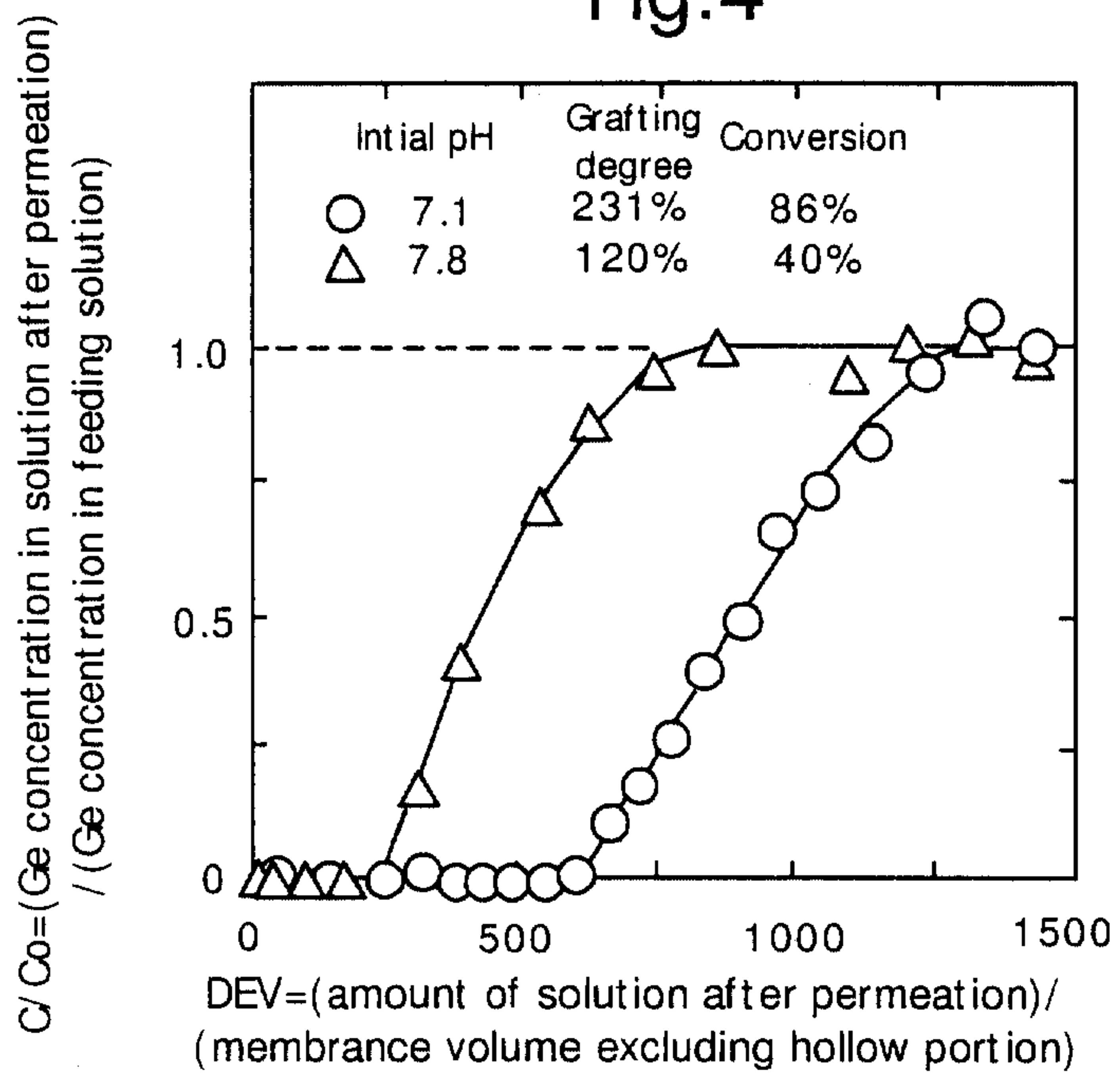


Fig.5

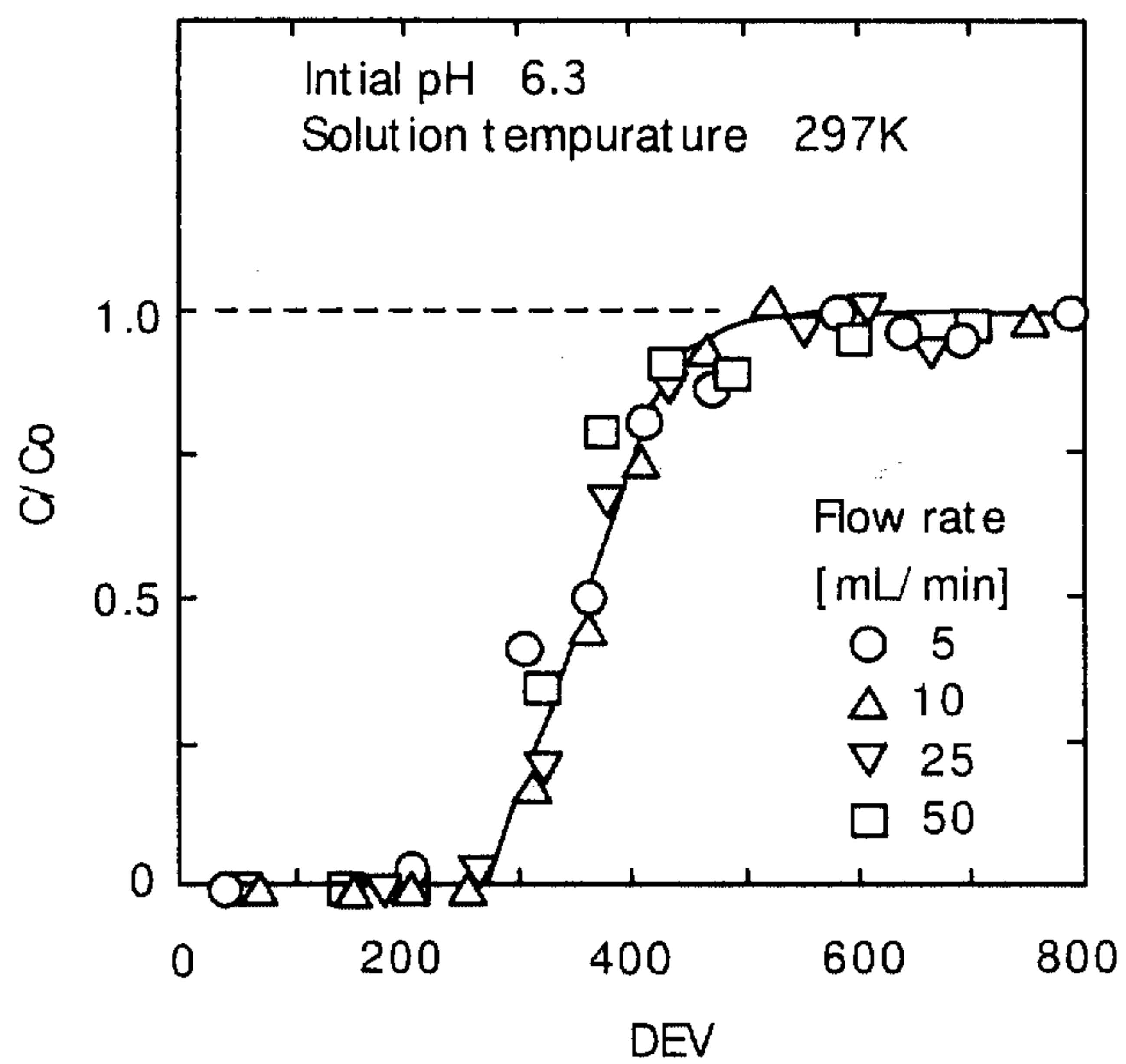


Fig.6

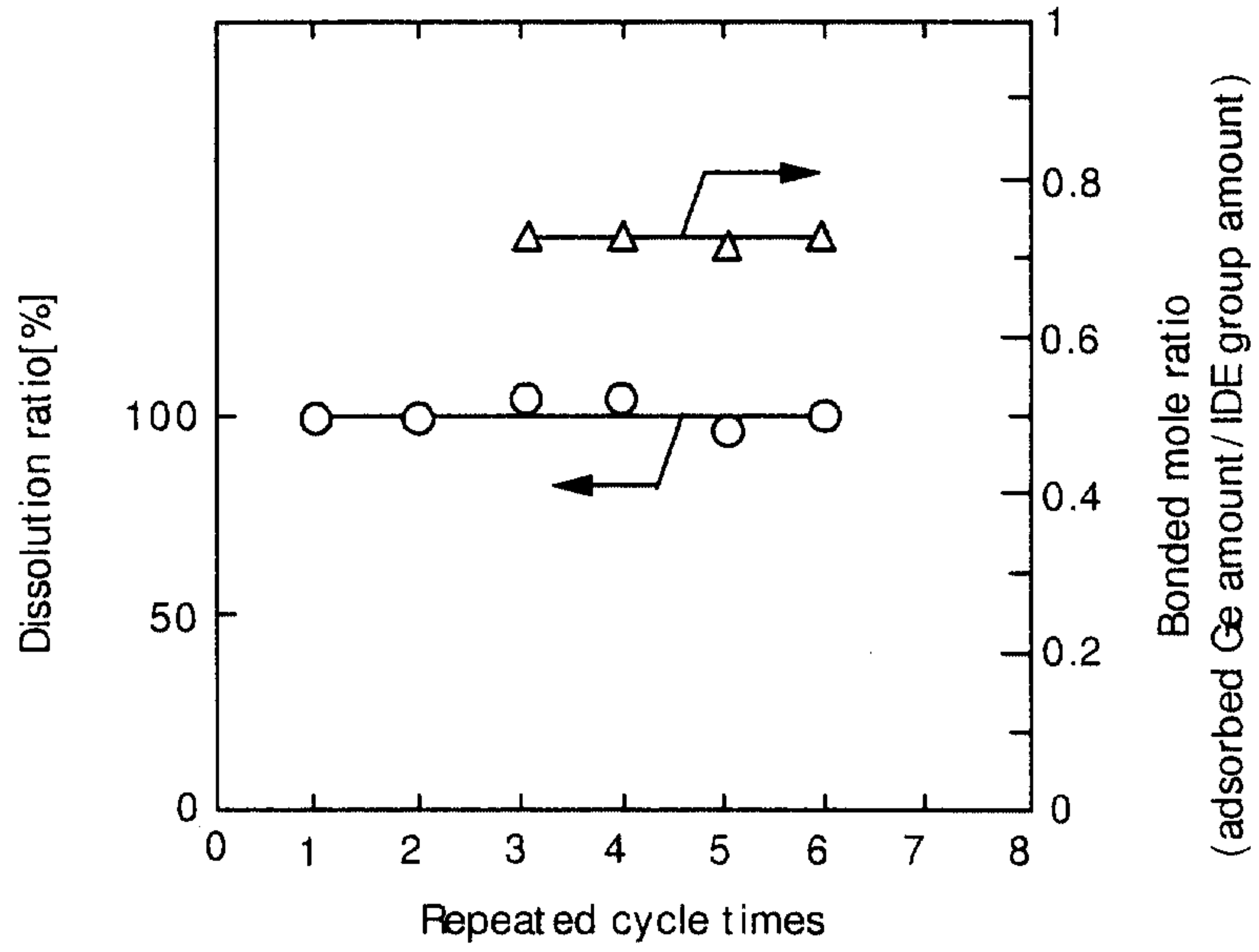


Fig.7

