Separation of Alcohol–Water Mixture by Pervaporation through a Reinforced Polyvinylpyridine Membrane

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SYNOPSIS

A membrane consisted of cross-linked poly(4-vinylpyridine) and reinforced by a nonwoven cloth made of poly(ethylene terephthalate) was prepared by copolymerization of 4-vinylpyridine with divinylbenzene in the presence of the nonwoven cloth. Pervaporation performance of this polyvinylpyridine membrane was examined at several feed alcohol concentrations and temperatures. The membrane showed water selectivity, and the permselectivity, $\alpha_{W/A}$, for the alcohol–water mixture was in the order isopropyl > propyl > tert-butyl > ethyl > methyl. The membrane showed a large permeability, and the pervaporation flux, ϕ, for the ethanol–water mixture was 7–13 kg/h per square meter of the membrane in pervaporation with sweeping of carbon dioxide under atmospheric pressure and at 40°C. The membrane was durable and long lasting for a prolonged-period, and permselectivity and permeability of the membrane did not fall off even after repeated use for 1000 h.
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INTRODUCTION

Separation of the ethanol–water mixture by pervaporation through membranes has received increasing attention in industry. The method may provide an economical alternative to distillation for ethanol–water separations[1,2] and avoids the limitation of osmotic pressure imposed on reverse osmosis processes by maintaining the permeate below its saturated vapor pressure. Although this membrane process requires the vaporization of a part of the liquid charge, the permeation pressure can be reduced by vacuum pumping, gas sweeping, or condensation and removal as a liquid. In general, however, pervaporation can be of practical use only when the selectivity of the transfer is much higher than for an ordinary vaporization and when the rate of permeation is satisfactorily large.

From a practical standpoint, it is also necessary to use durable and long-lasting membranes for a prolonged period. Membranes obtained by the conventional casting method are apt to lack mechanical strength sufficient for continuous and repeated operations of the pervaporation, even though the membrane showed excellent permselectivity and permeability. In this work, we aimed at development of a membrane reinforced by a nonwoven cloth.

Membranes used for pervaporation of the ethanol–water mixture are classified into two categories, i.e., water-selective membranes[3,4] and ethanol-selective membranes.[5,6] Water-selective membranes are generally hydrophilic and would be of interest for solutions concentrated in ethanol, whereas ethanol-selective membranes are generally hydrophobic and could remove ethanol directly from a fermentation bath. In this work, we attempted to develop a water-selective membrane made of cross-linked poly(4-vinylpyridine), since the polymer was used as a polymeric adsorbent for recovery of ethanol from the ethanol–water mixture.[7]

EXPERIMENTAL

Materials

Commercial products of 4-vinylpyridine, styrene, and 55% divinylbenzene were purified by conventional methods. Gas chromatographic analysis

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showed that the distilled divinylbenzene was a mixture of m-divinylbenzene (41.5%), p-divinylbenzene (14.4%), ethyl styrenes (40.1%), and diethylbenzenes (3.9%). Commercial products of 2,2'-azobisisobutyronitrile (AIBN), alcohols, and other chemicals and solvents were used without further purification.

Nonwoven cloth made of poly(ethylene terephthalate) was provided by Miki Special Paper Manufacturing Co., Kawanoe, Ehime, Japan. The thickness of the nonwoven cloth was 27 μm.

Preparation of Membranes

A membrane consisting of cross-linked poly(4-vinylpyridine) and reinforced by nonwoven cloth made of poly(ethylene terephthalate) (designated as polyvinylpyridine membrane in this article) was prepared by copolymerization of 4-vinylpyridine with divinylbenzene in the presence of the nonwoven cloth. A sample of the nonwoven cloth 7.0 cm long and 7.0 cm wide was soaked in a monomer mixture containing 4-vinylpyridine (16.0 g, 0.152 mol), 55% divinylbenzene (16.0 g, 0.068 mol), and AIBN (130 mg, 0.79 mmol) for 2 h under a nitrogen atmosphere. Thus, treated nonwoven cloth, which was swollen with the monomer mixture, was degassed under reduced pressure at room temperature and then held between two glass plates 7.0 cm long, 7.0 cm wide, and 7 mm thick and placed in a water bath. The copolymerization was performed by heating the water bath at 121°C for 30 min using an autoclave. After the polymerization, the membrane was taken out and was washed with deionized water and dried at room temperature in a hood. The thickness of the membrane was 30 μm. A mercury porosimetry measurement showed that the membrane resisted a pressure of 4.14×10^8 Pa and indicated substantial absence of pores larger than 32 Å in the membrane. A densimetry measurement using air at 2.03×10^4 Pa required 20,000 s for the pass of several milliliters of air through the membrane and indicated substantial absence of pores in the membrane. The surface area of the membrane determined by the BET method was 0.04 m²/g.

For comparison, a membrane consisting of cross-linked polystyrene and reinforced by the nonwoven cloth (designated as polystyrene membrane) was also prepared by copolymerization of styrene with divinylbenzene in a similar manner. A sample of nonwoven cloth 7.0 cm long and 7.0 cm wide was soaked in a monomer mixture containing styrene (15.8 g, 0.152 mol), 55% divinylbenzene (16.0 g, 0.068 mol), and AIBN (130 mg, 0.79 mmol) for 2 h

under a nitrogen atmosphere. The treated nonwoven cloth was submitted for the polymerization procedure at 121°C for 30 min using an autoclave. The thickness of the membrane was 28 μm. A mercury porosimetry measurement and a densimetry measurement showed substantial absence of pores in the membrane. The surface area of the membrane determined by the BET method was 0.018 m²/g.

In addition, a membrane consisting of cross-linked poly(4-vinylpyridine-co-styrene) and reinforced by the nonwoven cloth [designated as poly(vinylpyridine-co-styrene) membrane] was prepared by copolymerization of 4-vinylpyridine and styrene with divinylbenzene in a similar manner. A sample of nonwoven cloth 7.0 cm long and 7.0 cm wide was soaked in a monomer mixture containing 4-vinylpyridine (15.0 g, 0.143 mol), styrene (15.0 g, 0.144 mol), 55% divinylbenzene (15.0 g, 0.064 mol), and AIBN (90 mg, 0.55 mmol) for 2 h under a nitrogen atmosphere. The treated nonwoven cloth was submitted for the polymerization procedure at 121°C for 30 min using an autoclave. The thickness of the membrane was 30 μm. A mercury porosimetry measurement and a densimetry measurement showed substantial absence of pores in the membrane. The surface area of the membrane determined by the BET method was 0.025 m²/g.

Pervaporation

A schematic diagram of the apparatus used for pervaporation experiments is shown in Figure 1. Two 240 mL glass cells were used for the feed alcohol-water mixtures and the pervaporates, respectively. The diameter of the membrane was 50 mm, and the effective membrane area was 20 cm². The temperature of the cells was kept constant by a water bath. The alcohol-water mixture was placed in the upstream cell. In pervaporation with vacuum pumping, pressure of the downstream side was maintained at 133 Pa. In pervaporation with gas sweeping under the atmospheric pressure, the sweeping gas was passed through the downstream cell. The permeated vapor was collected in a dry-ice trap.

We determined the permeation flux, ϕ, expressed in kg/h per square meter of the membrane, and the permselectivity, $\alpha_{W/A}$, defined as

$$\alpha_{W/A} = \frac{Y_{water}/Y_{alcohol}}{X_{water}/X_{alcohol}}$$

where X and Y are the weight fractions of feed and pervaporate, respectively. Water is the species that is preferentially pervaporated.
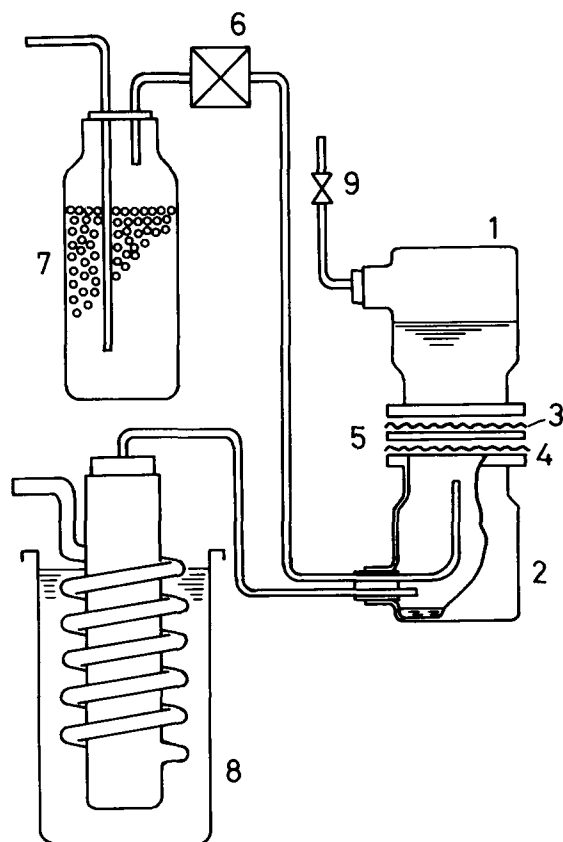
Figure 1 Schematic diagram of the glass apparatus used for the pervaporation experiments: (1) glass cell containing feed mixture of alcohol and water; (2) glass cell for the pervaporate; (3,4) gaskets; (5) membrane; (6) flow meter; (7) drying agent (silica gel); (8) cooling trap; (9) valve.

Adsorption of Ethanol-Water Mixture by the Polyvinylpyridine Membrane

Adsorption of the ethanol-water mixture by the polyvinylpyridine membrane was performed at 30°C by a batch method. A membrane sample was soaked in a beaker containing a 50 : 50 (w/w) mixture of ethanol and water with stirring at the prescribed temperature. After a prescribed time, the membrane was taken out, and the amount of the adsorbed ethanol-water mixture was determined based on the increase of weight. Composition of the ethanol-water mixture adsorbed by the membrane was determined by gas chromatography.

Analysis

Composition of the feed mixture and the pervaporate were determined by a Shimadzu GC-QA gas chromatograph equipped with a 1 m-long column packed

with Porapak Q. Concentration of water was determined by the Karl-Fischer method.

RESULTS AND DISCUSSION

Pervaporation of the Ethanol-Water Mixture through the Polyvinylpyridine Membrane with Vacuum Pumping

Pervaporation experiments for ethanol-water mixtures of various compositions through the polyvinylpyridine membrane with conventional vacuum pumping at 133 Pa were performed at 25, 40, and 55°C. Permselectivity and permeability are summarized in Table I. Permselectivity ($\alpha_{W/A}$) for ethanol increased with the content of ethanol in the feed liquid and was in the range 2-13 at 40°C. The permselectivity decreased with increase of the pervaporation temperature and was in the range 7-28 in the case where the ethanol concentration in the feed liquid was 95 wt %. Pervaporation flux (ϕ) decreased with content of ethanol in the feed liquid and was in the range 10-16 kg/h per square meter of the membrane at 40°C. The pervaporation flux increased with increase of the pervaporation temperature and was in the range 9-11 kg/h per square meter of the membrane in the case where the ethanol concentration in the feed liquid was 95 wt %.

The polyvinylpyridine membrane showed a strong affinity for the ethanol-water mixture and adsorbed

Table I Pervaporation of Ethanol-Water Mixture through the Polyvinylpyridine Membrane with Vacuum Pumping

Ethanol (Wt %)		Temp (°C)	$\alpha_{W/A}$	ϕ (kg/h m^2)
Feed	Permeate			
10.0	2.5	25	4.3	12.5
10.0	4.4	40	2.4	16.4
10.0	6.2	55	1.7	18.8
20.0	4.7	25	5.1	11.6
20.0	8.1	40	2.8	15.5
20.0	11.9	55	1.9	17.6
50.0	10.2	25	8.8	10.2
50.0	16.9	40	5.2	13.0
50.0	25.4	55	2.9	15.5
80.0	16.9	25	20.5	9.7
80.0	28.9	40	9.8	10.2
80.0	45.1	55	4.9	12.9
95.0	40.5	25	27.9	8.7
95.0	59.6	40	12.9	9.6
95.0	73.5	55	6.9	11.0

a considerable amount of the liquid at equilibrium. The mechanical strength of the swollen membrane appeared to be insufficient for repeated pervaporation with vacuum pumping. For example, significant cracking of the swollen membrane was observed during the repeated pervaporation procedure, although the pervaporation showed a good permselectivity for water and a sufficient permeability. Therefore, we attempted to perform the pervaporation through the polyvinylpyridine membrane with sweeping of gas under atmospheric pressure.

Pervaporation of the Ethanol–Water Mixture through the Polyvinylpyridine Membrane with Sweeping of Air under Atmospheric Pressure

Pervaporation experiments for ethanol–water mixtures of various compositions were performed at 25, 40, and 55°C, and the results are summarized in Table II. Much the same order of magnitude was observed for permselectivity ($\alpha_{W/A}$), and the value for ethanol was in the range 2–14 at 40°C. On the other hand, the pervaporation flux (ϕ) was very low and was around 0.5 kg/h per square meter of the membrane at 40°C.

In the pervaporation with sweeping of air under atmospheric pressure, the polyvinylpyridine membrane was durable and long-lasting for a prolonged period, and cracking of the membrane was not ob-

served during the procedure. However, the permeability was considerably low, although there was no significant difference in permselectivity. Therefore, pervaporation with gas sweeping appears to be more desirable than that with vacuum pumping for the pervaporation of the alcohol–water mixture through the polyvinylpyridine membrane, although permeability of the membrane needs to be improved.

Pervaporation of the Ethanol–Water Mixture through the Polyvinylpyridine Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure

As has been mentioned above, pervaporation with gas sweeping appears to be more suitable than that with vacuum pumping for the pervaporation of the alcohol–water mixture through the polyvinylpyridine membrane, provided that an excellent permeability is realized by employing an appropriate sweeping gas. In a process for recovering ethanol from dilute aqueous solutions employing solid sorbent, carbon dioxide was successfully used as the eluate to recover ethanol from the sorbent.[7] Therefore, we attempted to use carbon dioxide as the sweeping gas for the pervaporation.

Pervaporation experiments were performed using an ethanol–water mixture of various compositions at 25, 40, and 55°C, and results are summarized in Table III. Permselectivity ($\alpha_{W/A}$) for ethanol was in the range 2–13 at 40°C. A significant difference in permselectivity was not observed between the pervaporation with vacuum pumping and that with sweeping of carbon dioxide under atmospheric pressure.

On the other hand, the pervaporation flux (ϕ) was remarkably improved and was a good match for that obtained by the pervaporation with vacuum pumping. The pervaporation flux decreased with the content of ethanol in the feed liquid and was 7–13 kg/h per square meter of the membrane at 40°C. The pervaporation flux increased with increase of the pervaporation temperature and was in the range 2–10 kg/h per square meter of the membrane in the case where ethanol concentration in the feed liquid was 95 wt %.

The polyvinylpyridine membrane showed durableness and to be long-lasting for a prolonged period of the pervaporation. Formation of a crack was not observed even after repeated pervaporation for 1000 h. Permselectivity and permeability of the membrane also did not fall off even after repeated use for 1000 h; i.e., in pervaporation of a 50 : 50 (w/w) mixture of ethanol and water at 40°C, the perme-

Table II   Pervaporation of Ethanol–Water Mixture through Polyvinylpyridine Membrane with Sweeping of Air under Atmospheric Pressure

Ethanol (Wt %)		Temp (°C)	$\alpha_{W/A}$	ϕ (kg/h m²)
Feed	Permeate			
10.0	2.6	25	4.2	0.29
10.0	5.6	40	1.9	0.42
10.0	6.5	55	1.6	0.45
20.0	5.0	25	4.8	0.29
20.0	7.6	40	3.0	0.44
20.0	10.9	55	2.0	0.41
50.0	10.0	25	9.0	0.26
50.0	16.3	40	5.1	0.45
50.0	25.2	55	3.0	0.55
80.0	19.1	25	16.9	0.30
80.0	28.4	40	10.1	0.50
80.0	45.4	55	4.8	0.51
95.5	40.1	25	28.4	0.35
95.5	58.6	40	13.6	0.46
95.5	70.9	55	7.8	0.45

Table III   Pervaporation of the Ethanol–Water Mixture through the Polyvinylpyridine Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure

Ethanol (Wt %)		Temp (°C)	$\alpha_{W/A}$	ϕ (kg/h m^2)
Feed	Permeate			
10.0	2.9	25	3.7	5.8
10.0	4.7	40	2.3	12.5
10.0	6.1	55	1.7	15.5
20.0	5.0	25	4.8	4.6
20.0	7.6	40	3.0	10.6
20.0	8.7	55	2.6	14.7
50.0	9.8	25	9.3	2.8
50.0	16.3	40	5.1	9.8
50.0	25.2	55	3.0	12.9
80.0	18.7	25	19.5	1.5
80.0	28.4	40	10.1	9.6
80.0	45.4	55	4.8	12.9
95.0	42.1	25	26.1	1.9
95.0	58.6	40	13.4	7.5
95.0	68.1	55	8.9	10.4

ability ($\alpha_{W/A}$) was 5.0 at the beginning and 5.4, 4.9, and 4.9 after 150, 500, and 1000 h, respectively. The pervaporation flux was 9.8 kg/h per square meter of the membrane at the beginning and 8.8, 8.5, and 8.2 kg/h per square meter of the membrane after 150, 500, and 1000 h, respectively.

Pervaporation of Other Alcohol–Water Mixtures through the Polyvinylpyridine Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure

Pervaporation through the polyvinylpyridine membrane with sweeping of carbon dioxide was performed using mixtures of water and other alcohols in a similar manner at 40°C. Methanol, propyl alcohol, isopropyl alcohol, and *tert*-butyl alcohol were used as the test alcohols. Results are summarized in Table IV.

Permselectivity of methanol through the polyvinylpyridine membrane was close to unity, indicating essentially nonselective permeation of the methanol–water mixture in the pervaporation. On the other hand, separation of mixtures of water and higher alcohols was more effective. The permselectivity was in the following order: isopropyl alcohol > *tert*-butyl alcohol > ethanol > methanol. This result suggests the significance of hydrophobicity of alcohol in the pervaporation of the water–alcohol mixture through the polyvinylpyridine membrane.

Adsorption of the Ethanol–Water Mixture by the Polyvinylpyridine Membrane

As has been mentioned above, the polyvinylpyridine membrane showed water selectivity. To obtain additional information on this subject, adsorption experiments were performed by soaking the membrane in a 50 : 50 (w/w) mixture of ethanol and water at 25, 40, and 55°C. At equilibrium, the membrane adsorbed 300–900 wt % of the mixture. Composition of the ethanol–water mixture adsorbed by the membrane at equilibrium was analyzed by gas chromatography and the Karl–Fischer method. Results are given in Table V. Composition of the mixture adsorbed by the polyvinylpyridine membrane clearly indicated the water selectivity of the membrane. However, the water selectivity decreased at higher temperature. Composition of the ethanol–water mixture adsorbed by the membrane was close to that

Table IV   Pervaporation of Alcohol–Water Mixture through the Polyvinylpyridine Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure[a]

Alcohol (Wt %)		$\alpha_{W/A}$	ϕ (kg/h m^2)
Feed	Permeate		
Methanol			
10.0	10.5	0.95	14.1
20.0	20.1	0.99	14.0
50.0	50.1	1.00	13.8
80.0	80.0	1.00	13.9
Ethanol			
10.0	4.7	2.3	12.5
20.0	7.6	3.0	10.6
50.0	16.3	5.1	9.8
80.0	28.4	10.1	9.6
Propyl alcohol			
10.0	3.1	3.5	8.8
20.0	3.0	8.1	7.5
50.0	7.8	11.8	7.6
80.0	19.5	16.5	5.9
Isopropyl alcohol			
10.0	1.8	6.1	10.2
20.0	3.6	6.7	9.1
50.0	7.2	12.9	8.2
80.0	12.6	27.7	8.2
tert-Butyl alcohol			
10.0	4.1	2.6	8.9
20.0	7.1	3.3	6.2
50.0	6.2	15.1	5.8
80.0	14.8	23.0	3.9

[a] Performed at 40°C.

Table V Adsorption of Ethanol–Water Mixture by the Polyvinylpyridine Membrane[a]

Temp (°C)	Amount Adsorbed (Wt %)	Composition of the Adsorbed Liquid (Wt %)	
		Ethanol	Water
25	298	10.5	86.0
40	540	14.5	83.0
55	850	20.5	78.0

[a] Adsorption experiments were performed by soaking the polyvinylpyridine membrane in a 50 : 50 (w/w) mixture of ethanol and water for 24 h.

of the permeated liquid obtained during the pervaporation experiments.

Pervaporation of the Alcohol–Water Mixture through the Polystyrene Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure

For comparison with pervaporation through the polyvinylpyridine membrane, pervaporation experiments through the polystyrene membrane were performed for mixtures of water and various alcohols in a similar manner at 40°C. Results are summarized in Table VI.

Except for the case of the methanol–water mixture, the permselectivity ($\alpha_{W/A}$) through the polystyrene membrane was lower than that through the polyvinylpyridine membrane. Permeability of the alcohol–water mixture through the polystyrene membrane was considerably smaller than that through the polyvinylpyridine membrane. In addition, the polystyrene membrane was brittle and formed many cracks after 100 h of pervaporation experiments. The presence of vinylpyridine as a component of the membrane appears to improve the mechanical strength of the membrane.

Pervaporation of the Alcohol–Water Mixture through the Poly(vinylpyridine-co-styrene) Membrane

For comparison, pervaporation experiments through the poly(vinylpyridine-co-styrene) membrane were performed for mixtures of water and various alcohols

Table VI Pervaporation of Alcohol–Water Mixture through the Polystyrene Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure[a]

Alcohol (Wt %)			
Feed	Permeate	$\alpha_{W/A}$	ϕ (kg/h m^2)
Methanol			
50.0	5.5	17.3	0.02
Ethanol			
50.0	18.5	4.4	0.03
Propyl alcohol			
50.0	32.2	2.1	0.02
Isopropyl alcohol			
50.0	35.7	1.8	0.02
tert-Butyl alcohol			
50.0	34.5	1.9	0.03

[a] Performed at 40°C.

in a similar manner at 40°C. Results are summarized in Table VII.

Permselectivity ($\alpha_{W/A}$) through the poly(vinylpyridine-co-styrene) membrane was larger than that through the polyvinylpyridine membrane. However, permeability of the alcohol–water mixture through the poly(vinylpyridine-co-styrene) membrane was considerably smaller than that through the polyvinylpyridine membrane. In addition, the poly-

Table VII Pervaporation of Alcohol–Water Mixture through the Poly(vinylpyridine-co-styrene) Membrane with Sweeping of Carbon Dioxide under Atmospheric Pressure[a]

Alcohol (Wt %)			
Feed	Permeate	$\alpha_{W/A}$	ϕ (kg/h m^2)
Methanol			
50.0	28.6	2.5	1.2
Ethanol			
50.0	9.5	9.5	0.87
Propyl alcohol			
50.0	2.4	40.2	0.72
Isopropyl alcohol			
50.0	2.6	36.9	0.85
tert-Butyl alcohol			
50.0	0.5	186.8	0.53

[a] Performed at 40°C.

(vinylpyridine-co-styrene) membrane was brittle and formed many cracks after 100 h of pervaporation. The presence of styrene as a component of the membrane seems to decrease permeability and mechanical strength of the membrane.

REFERENCES

1. P. Aptel, N. Challard, J. Cuny, and J. Neel, *J. Membr. Sci.*, **1**, 271 (1976).
2. I. Blume, J. G. Wijmans, and R. W. Baker, *J. Membr. Sci.*, **49**, 253 (1990).
3. Y. S. Kang, S. W. Lee, U. Y. Kim, and J. S. Shim, *J. Membr. Sci.*, **51**, 215 (1990).
4. Y. M. Lee and W. J. Wang, *Makromol. Chem.*, **191**, 3131 (1990).
5. P. Schissel and R. A. Orth, *J. Membr. Sci.*, **17**, 109 (1984).
6. P. Radovanovic, S. W. Thiel, and S. T. Hwang, *J. Membr. Sci.*, **48**, 55 (1990).
7. J. Feldman, U.S. Pat. 4,450,294, 1984; *Chem. Abstr.*, **101**, 40512d (1984).