Synthesis and Characterization of Soluble Poly(amide-imide)s Bearing Triethylamine Sulfonate Groups as Gas Dehumidification Membrane Material

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ABSTRACT: A series of soluble poly(amide-imide)s (PAIs) bearing triethylammonium sulfonate groups were synthesized directly using trimellitic anhydride chloride (TMAC) polycondensation with sulfonated diamine such as 2,2′-benzidinedisulfonic acid (BDSA), 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS), and nonsulfonated diamine 4,4-diaminodiphenyl methane in the presence of triethylamine. The resulting copolymers exhibited high molecular weights (high inherent viscosity), and a combination of desirable properties such as good solubility in dipolar aprotic solvents, film-forming capability, and good mechanical properties. Wide-angle X-ray diffraction revealed that the polymers were amorphous. These copolymers showed high permeability coefficients of water vapor because of the presence of the hydrophilic triethylammonium sulfonate groups. The water vapor permeability coefficients (P_w) and permselectivity coefficients of water vapor to nitrogen and methane [$\alpha(H_2O/N_2)$ and $\alpha(H_2O/CH_4)$] of the films increased with increasing the amount of the triethylammonium sulfonated groups. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3179–3184, 2007

Key words: synthesis; gas dehumidification; membrane; poly(amide-imide)s; sulfonate

INTRODUCTION

Membrane dehumidification of gases, air, and organic vapors have been found wide applications in the drying of natural gas,[1] drying of compressed air,[2] removing water from organic vapor,[3] and the humidity control in closed spaces (air conditioning in buildings, aviation, and space flight). The process offers low capital and operating costs, along with low energy consumption compared with other conventional methods, such as compression, cooling, and absorption. Various hydrophilic polymers, including Cellulose triacetate,[3] sulfonated poly(phenylene oxide),[4] polyether-polyurethane,[5] sulfonated poly(ether ether ketone),[6] have been investigated and used as a selective membrane material for the transport of water vapor. Poly(amide-imide)s (PAIs) are one of the most useful and important polymers because of their excellent thermal stability, good chemical resistance, and mechanical strength. From chemical point of view,

PAIs contain polar amide groups which should facilitate water molecules transport through PAI membranes. However, PAIs are often characterized by the poor solubility and high softening or melting temperatures which limited their application as membrane materials. Considerable efforts have been made to modify their chemical structure to improve their processability and solubility, and to change their properties with regard to a specific application or to a particular property. The introduction of bulky substituents[7–17] or bulky pendant groups[18–22] into rigid polymer backbones has been a general approach to increase solubility and processability of PAIs without sacrifying thermostability.[23–25] It has been shown that the sulfonation of polymers is an effective method to increase both the permeation coefficient of water vapor and the separation factor of water vapor over inert gases.[6]

In the present article, we describe the synthesis of organic soluble PAIs bearing triethylammonium sulfonate groups (SPAIs) by copolymerization of BDSA, ODADS, and commercially available diamine such as 4,4-diaminodiphenyl methane (MDA), respectively. Because of the hydrophilicity of triethylammonium sulfonate groups, the resulting sulfonated PAIs show high permeability of water vapor and good permselectivity of water vapor over inert gases. Their other properties such as, thermal stability, mechanical properties, are also discussed.
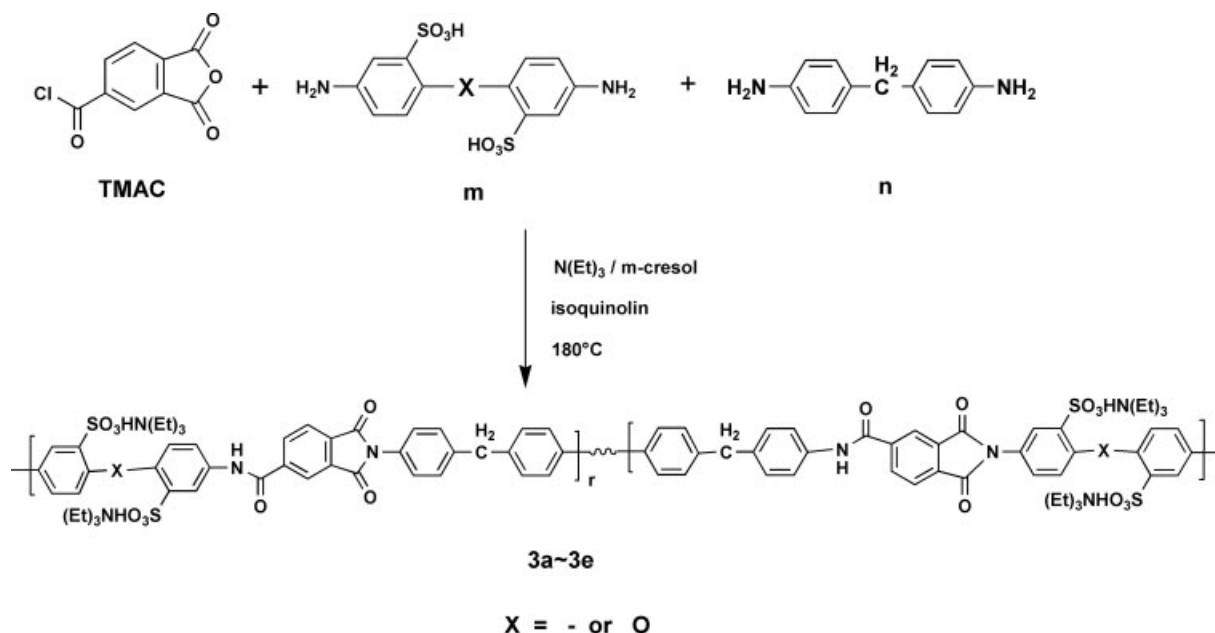
Scheme 1 Synthesis of the polymers.

EXPERIMENT

Materials

Trimellitic anhydride chloride (TMAC) was obtained from Aldrich, and was purified by dissolving it in toluene, the insoluble impurities like trimellitic anhydride were removed by filtration. 4,4′-Oxydianiline (ODA) and 4,4′-diaminophenylmethane (MDA) were purified by recrystallization from ethanol. 2,2′-Benzidinedisulfonic acid (BDSA), 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) were synthesized in our laboratory according to the method reported by Okamoto et al.[26] Triethylamine (Et₃N), N,N-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP) were distilled under reduced pressure and dried with molecular sieve of 4 Å. m-Cresol were distilled before use. All the other chemicals were regent grade and used as received.

Measurements

Fourier transform infrared (FTIR) spectra were determined with a Bio-Rad Digilab Division FTS-80 spectrometer. Inherent viscosities of all polymers were determined at 30°C with 0.5 g/dL concentration using Ubbelodhe viscometer. Solubility was determined at a 2% (w/w) concentration. Thermogravimetric analysis (TGA) was conducted with a SDT 2960 thermal analysis station. Measurements were performed under flowing nitrogen at a heating rate of 10°C/min. Dynamic mechanical thermal analysis (DMTA) were performed on a dynamic mechanical thermal analyzer (Rheometric Scientific, USA) in a tensile mode at a heating rate of 5°C/min and a frequency of 1 Hz.

Wide-angle X-ray diffraction measurements were obtained on a Rigaku Max 2500 V PC X-ray diffract meter (Japan) with Cu-Kα radiation (40 kV, 200 mA) with a scanning rate of 8°/min. The tensile measurements were carried out on an Instron Model 1122 at room temperature. The samples were tested at an average cross head speed of 5.0 mm/min. Generally, five samples were tested and the results were averaged. Contact angles (θ) were determined using a KRUSS DSA10-MK2 contact angle measuring system at ambient temperature. The probe fluid used was deionized water and drop volumes were 2 μL. Permeability coefficient of inert gas was measured by means of a vacuum time-lag method. The ideal permselectivity of water vapor was calculated from the ratio of permeability coefficients:

TABLE I
Synthesis of the Copolymers

Copolymer	m : n[a]	Yield (%)	(η)[b] (dL/g)
BDSA-20%[c]	2 : 8	99	0.76
BDSA-30%	3 : 7	97	0.48
BDSA-40%	4 : 6	97	0.46
BDSA-50%	5 : 5	95	0.43
ODADS-40%[d]	4 : 6	98	0.92

[a] The ratio of sulfonated diamine and 4,4′-diaminophenylmethane (MDA).
[b] Measured at a concentration of 0.5 g/dL in DMAc at 30°C.
[c] BDSA-20% denotes that copolymer based on BDSA, and the molar fraction of BDSA is 20%.
[d] ODADS-40% denotes that copolymer based on ODADS, and the molar fraction of ODADS is 40%.
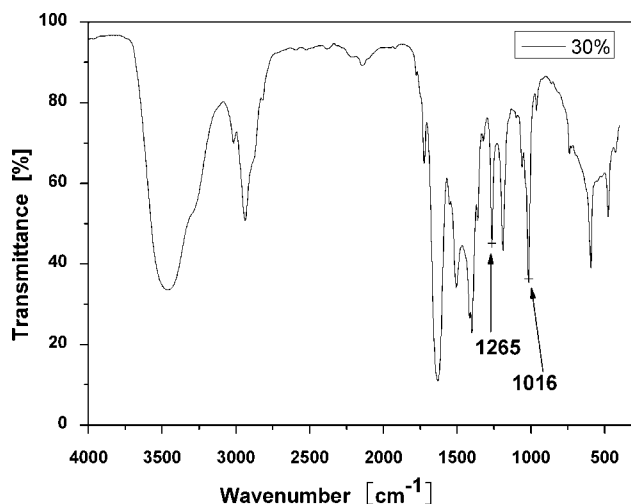
Figure 1 IR spectrum for the polymer BDSA-40%.

$$\alpha(H_2O/X_2) = P_w/P(X_2)$$

where $\alpha(H_2O/X_2)$ refers to permselectivity coefficients of water vapor to inert gas, and P_w and $P(X_2)$ refers to the permeability coefficients of water vapor and inert gas, respectively. Water vapor permeation was measured by the "cup method," which was probably the most frequently used technique to determine the transport rate of water vapor through a polymeric material.[27]

Synthesis of SPAI based on ODADS

Poly(amide-imide) copolymers were synthesized by direct solution polycondensation of TMAC with ODADS. The route was illustrated in Scheme 1. To a 100 mL three-necked round-bottom flask were added 1.4400 g (4 mmol) of ODADS, 1.1896 g (6 mmol) of MDA, 10 mL of triethylamine, and 20 mL of m-cresol under nitrogen atmosphere. After the ODADS and MDA were dissolved completely, 2.1057 g (10 mmol) of TMAC and 1.2916 g (10 mmol) of isoquinolin were charged to the flask. The mixture was stirred at room temperature for 2 h, and at 180°C for 8 h. After cooling to room temperature, the reaction mixture was poured into 250 mL ethanol. The resulting copolymer

(ODADS-40%) was collected by filtration, and dried in vacuum at 200°C for 12 h. All the other SPAIs were prepared based on BDSA with different molar fraction (X) of BDSA similarly (BDSA-X). The yield and the inherent viscosity of the polymers were shown in Table I. The FTIR spectrum (Fig. 1) of the polymer BDSA-40% exhibited absorptions at 1265 cm^{-1} (asymmetric O=S=O stretching), 1016 cm^{-1} (symmetric O=S=O stretching), 1720 cm^{-1} (imide C=O stretching),[26] 1340 cm^{-1} (imide C—N stretching), 720 cm^{-1} (imide ring deformation) and 3500 cm^{-1} (N=H stretching).

Preparation of PAI films

About 10 wt % solutions of SPAIs in NMP were cast onto glass substrate at 80°C. The semidried films were heated at 120°C for 24 h in vacuum, and then at 200°C for 24 h in vacuum. All films were transparent, soft, and ~0.025 mm in thickness. These SPAIs films were cut into strips about 4 cm length and 5 mm width for stress–strain and thermal measurements.

RESULTS AND DISCUSSION

Synthesis of copolymers

The preparation of the SPAIs was carried out according to a one-step polymerization method using m-cresol as the solvent in the presence of Et$_3$N. In this case Et$_3$N was employed to improve the solubility of ODADS and BDSA by liberating the protonated amino groups (Scheme 1). All the polymerization reactions proceeded readily in a homogeneous solution, and these polymers were obtained in almost a quantitative yield with inherent viscosities of 0.43–0.76 dL/g.

Properties of copolymer

All these SPAIs are easily soluble in polar solvents such as DMAc and NMP, but not soluble in less polar solvents such as CHCl$_3$, THF, and pyridine (Table II). The excellent solubility of these SPAIs could be attributed to the presence of triethylammonium sulfonate

TABLE II
Solubility of SPAIs[a]

Copolymer	DMAc	NMP	DMF	DMSO	m-Cresol	THF	Py	CHCl$_3$
BDSA-20%	+	+	+	+	+	−	−	−
BDSA-30%	+	+	+	+	+	−	−	−
BDSA-40%	+	+	+	+	+	−	−	−
BDSA-50%	+	+	+	+	+	−	−	−
ODADS-40%	+	+	+	+	+	−	−	−

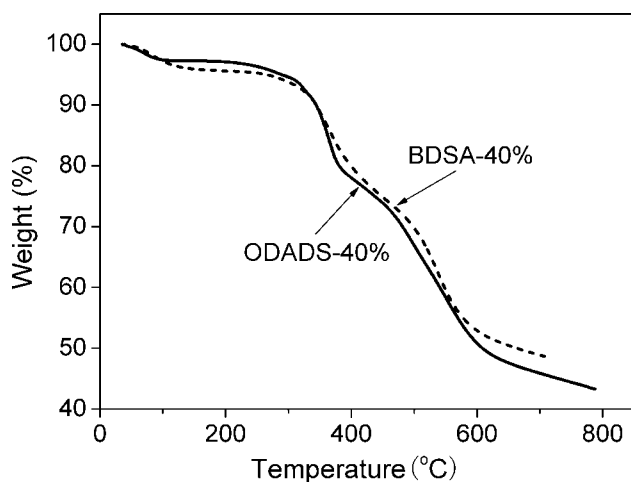[a] Solubility: (+) soluble; (−) insoluble.

Figure 2 TGA thermograms of the polymer BDSA-40% and ODADS-40%.

groups, which exhibit strong interaction with polar solvent and then serve to solubilize the material. Figure 2 showed the thermal stability of the polymer BDSA-40% and ODADS-40% investigated by TGA. The initial weight loss from 100 to 200°C is ascribed to the loss of water molecules, absorbed by the highly hydrophilic triethylammonium sulfonate groups. The second weight loss around 300°C is due to the decomposition of the triethylammonium sulfonate groups. The third stage weight loss around 450°C[13] is assigned to the decomposition of polymer main chain. The char yields of all the polymers in nitrogen are above 45% even at 700°C. Figure 3 displayed the dynamic storage modulus (E′) and tan δ as a function of temperature for the copoly(amide-imide)s. Regarding peak temperature in the tan δ curves (Fig. 4) as the glass transition temperature, these SPAIs show a glass-transition temperature (T_g) in the range of 290–317°C, depending on the diamine monomers used. In general, T_g is mainly determined by the interchains

interaction and rigidity of polymer backbones. With the increase of the contents of triethylammonium sulfonate groups, the interchains interaction was increased because of the strong electrostatic interaction between polymer chains, and restricted the free motion and rotation of polymer backbone. Hence, the obtained polymers containing the more contents of triethylammonium sulfonate groups could show higher glass transition temperature. Among all the PAIs synthesized, polymer BDSA-50% contained the most contents of triethylammonium sulfonate groups, so it showed the highest T_g of 317°C. The similar effect of ionomers' on T_g induced by electrostatic interactions have been reported by Adi Eisenberg and Joon-Seop Kim.[28] Additionally, the T_g value of ODADS-40% is about 10°C lower than that of BDSA-40%, although they had comparable contents of triethylammonium sulfonate groups. The reason was that the soft ether bonds introduced by ODADS descreased the rigidity of polymer backbones.

Transparent, flexible, and yellow films of SPAIs were subjected to a tensile test by an Instron machine. The tensile properties of these polymers were summarized in Table III. These films show tensile strengths of 111–135 MPa, elongation to break of 8.0–21%, and an initial modulus of 2.98–3.43 GPa. Figure 5 displayed the Wide-angle X-ray diffraction of SPAI films. All of the films have typical Gaussian distribution curves, broad, and structureless, suggesting that all the polymers tested are amorphous. Values of hydrophilicity, measured by water contact angle (θ value), were showed in Table III. The order of the θ values is BDSA-20% > BDSA-30% ≈ ODADS-40% > BDSA-40% > BDSA-50%, and it reaches to 68.8° by polymer BDSA-50% owing to the static electricity interaction between triethylamine sulfonate groups and water vapor molecule which resulting in stronger hydrophilicity when the content of triethylamine sulfonate groups increased.
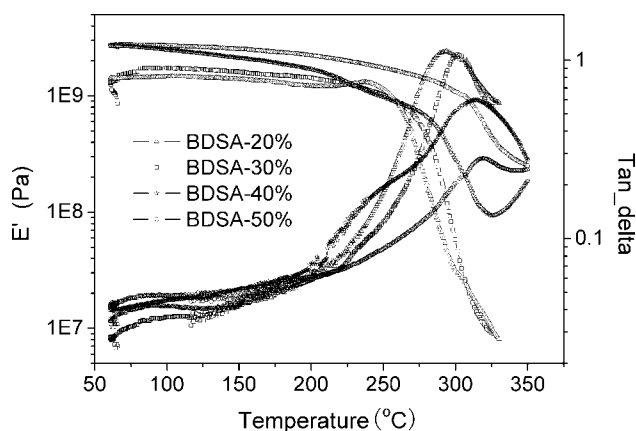

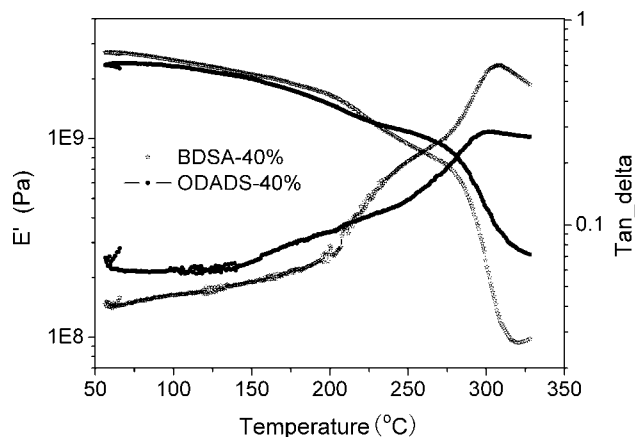**Figure 3** DMTA curves of the polymers BDSA-20% to BDSA-50%.

Figure 4 DMTA curves of the polymers BDSA-40% and ODADS-40%.

TABLE III
Physical Properties of the SPAIs

Polymer	Tensile strength (MPa)	Elongation (%)	Initial modulus (GPa)	$T_g{}^a$ (°C)	Contact angle (°)
BDSA-20%	135 ± 2	20.9 ± 0.3	3.43 ± 0.05	291	94 ± 3
BDSA-30%	123 ± 2	18.7 ± 0.3	3.26 ± 0.05	301	80 ± 3
BDSA-40%	113 ± 2	16.6 ± 0.3	3.04 ± 0.05	311	72 ± 3
BDSA-50%	110 ± 2	8.3 ± 0.3	2.98 ± 0.05	317	68 ± 3
ODADS-40%	73 ± 2	24.5 ± 0.3	1.57 ± 0.05	299	78 ± 3

[a] Obtained by defining the peak of tan δ curves from DMTA at the heating rate of 5°C/min at 1 Hz.

Gas separation and dehumidification

Gas permeability and permselectivity of SPAIs were investigated at 30°C, and the results were shown in Table IV. All polymers show low inert gas permeability coefficients $P(N_2)$ and $P(CH_4)$ but high water vapor permeability coefficients (P_w) in the range of 5.0–9.8 × 10^3 barrers for BDSA-20% to BDSA-50%, and 6.1 × 10^3 barrers for ODADS-40%. $P(N_2)$ and $P(CH_4)$ decrease with increasing the content of the hydrophilic triethylammonium sulfonate groups, but P_w increase. It is well-known, permeation of gas molecules in polymers occurs via the "solution–diffusion" mechanism.[29] In this mode, permeation occurs in two distinct steps: solvation of the gas molecule in the polymer matrix and subsequent diffusion through the polymer. Hence, the permeability P can be written as $P = DS$, where D is the diffusivity and S is the solubility of the gas. Obviously, introducing of triethylamine sulfonate groups bearing strong polarity into polymers will play two opposite roles on the gas permeability of polymer. One is to improve hydrophilicity of membrane, and it is favorable for the solubility and permeability o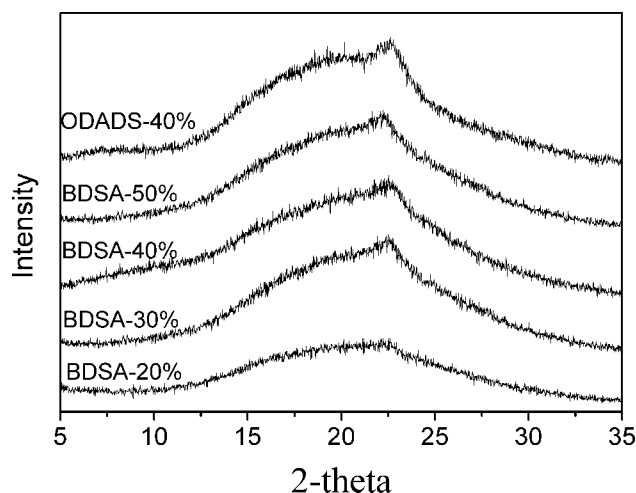f water vapor molecule.[29] On the other hand, it improves the interaction of polymer chains, which results in an increased packing density of polymers and decreased free volume. The $P(N_2)$ and $P(CH_4)$ of SPAIs is lower than nonsulfonated polyimide and PAIs because the compact structure hinders gas molecules diffusing through the membranes freely.[30] However, for the water vapor molecule, the former effect is more evident and then brings on high P_w. With increasing of the content of triethylamine sulfonate groups sequentially, the later effect becomes more evident. The reason is that the tighter structure of polymer decreases the free volume remarkably. In result, the copolymer BDSA-50% with highest amount of sulfonate groups exhibits lower P_w than that of BDSA-40% although the former's hydrophilicity is stronger than that of later. Additionally, the $P(N_2)$ and P_w of ODADS-40% are lower than that of BDSA-40%, although they contain the comparable contents of triethylamine sulfonate. The reason is that the gas molecular diffuses more easily through membrane from BDSA-40% than ODADS-40% owing to rigid, noncoplanar of BDSA in the former.

As can be seen from Table IV, these polymers show good permselectivity of water vapor to nitrogen and methane because of high P_w and low $P(N_2)$ and $P(CH_4)$, which indicates that these SPAIs have excellent separation effect on gas dehumidification. The separation coefficients of water vapor to nitrogen and methane are all above 10^5. Additionally, $\alpha(H_2O/N_2)$

Figure 5 WAXD curves of the polymers BDSA-20% to ODADS-40%.

TABLE IV
Gas Permeability and Permselectivity of SPAIs

Polymer	Permeability (barrer)[a]			Permselectivity (×10^5)	
	$P(N_2)$	$P(CH_4)$	P_w	$\alpha(H_2O/N_2)$	$\alpha(H_2O/CH_4)$
BDSA-20%	0.027	0.023	4966	1.83	2.14
BDSA-30%	0.023	0.021	7569	4.30	3.49
BDSA-40%	0.020	0.006	9767	4.89	16.28
BDSA-50%	0.018	0.006	8922	4.96	15.38
ODADS-40%	0.021	0.020	6100	2.91	3.05

[a] Gas permeation coefficient (barrers) 1 barrer = 10^{-10} cm^3 (STP).cm/cm^2 s cm.

and $\alpha(H_2O/CH_4)$ of BDSA-50% reach 4.9×10^5 and 1.63×10^6, respectively, and the former is five times higher than that of sulfonated PPO.[31]

CONCLUSION

We obtained organic-soluble PAIs containing triethyl-amine sulfonate with inexpensive and facile mono-mers by ''one-step'' method successfully, and these SPAIs can be cast into transparent and flexible films with high thermal stability and good mechanical per-formance. Furthermore, the results exhibit that the SPAIs are potential membrane materials for gas sepa-ration especially for gas dehumidification because of their ascendant selectivity of water vapor over inert gases which are up to 4.9×10^5 and 1.63×10^6 for $\alpha(H_2O/N_2)$ and $\alpha(H_2O/CH_4)$, respectively.

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