

Gas Permeabilities of CO₂ and CH₄ for Polysulfones Substituted with Bromo and Trimethylsilyl Groups

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Abstract—Bromobisphenol A trimethylsilylated polysulfone (BTMSPSF) was synthesized, and the effect of bromo and trimethylsilyl groups on the pure CO₂ and CH₄ transport properties of polysulfone was examined. The ideal separation factor for BTMSPSF is reduced by about 10% than that for unmodified polysulfone (PSf), but BTMSPSF is about two times more permeable than PSf. The effect of the substituents on chain packing was related to the gas permeation properties. Fractional free volume (FFV) calculation, d-spacing and cohesive energy density were used to judge chain packing. In comparison with PSf, the higher values of permeability coefficients for BTMSPSF are due to higher FFV and d-spacing. The small decrease in ideal separation for BTMSPSF is explained as follows: the potential increase in FFV due to packing-disrupting bulky trimethylsilyl groups is overridden by the increase in cohesive energy density attributed to the addition of bromo substituents.

Key words: Polysulfone, Trimethylsilyl Group, Polar Substituents, Sorption, Permeability

INTRODUCTION

The use of polymeric membranes for CO₂/CH₄ separations has increased for a variety of industrial applications, including enhanced oil recovery, the treatment of landfill gases and the sweetening of natural gases [Bhide and Stern, 1993; Bollinger et al., 1982; Rautenbach and Welsch, 1994; Stern, 1994]. For the membrane processes to be successful, new polymeric materials with higher permeability and selectivity are required. It is generally known that polymeric membrane that has high gas permeability exhibits low selectivity and *vice versa*. The systematic molecular design of polymer structure can lead to materials that can run counter to a certain extent this trade-off relationship, and recent studies have been focused on varying polymer structure to increase permeability with minimal loss of selectivity [McHattie et al., 1991a, b, 1992; Ghosal et al., 1996; Pixton and Paul, 1995; Maier et al., 1998a, b; Aitken et al., 1992]. In our previous works, we studied the preparation and characterization of both trimethylsilylated and brominated polysulfone membrane, and reported that the trimethylsilylation of polysulfone increased permeability, and bromination increased selectivity [Kim and Hong, 1997b, 1999]. Considering these facts, this present work involves the synthesis of bromobisphenol A trimethylsilylated polysulfone (BTMSPSF), in which phenyl rings of bisphenol and sulfone units in polysulfone are substituted with bromo and trimethylsilyl groups, respectively. This work is a part of a study of chemical modifications of polysulfone. It is the purpose of this study to investigate the effect of both bromo and trimethylsilyl substitutions on the gas transport properties.

EXPERIMENTAL

1. Materials and Membrane Preparation

The material synthesized in this study was BTMSPSF. PSf (Udel® P-3500) was obtained from Amoco Chemical Co. Reagent grade tetrahydrofuran (THF) was freshly distilled for each reaction. All other reagents were purchased commercially and used as received without further purification. BTMSPSF was synthesized by bromination of bisphenol A trimethylsilylated polysulfone (TMSPSF). TMSPSF was synthesized by lithiation and trimethylsilylation, and the procedure was discussed in a previous paper in detail [Kim and Hong, 1997b]. Bromine (0.062 mol, 5 g) was added to a stirred solution of TMSPSF (0.029 mol, 15 g) in chloroform (60 mL) at room temperature. The resulting solution was stirred for 24 hr, and then precipitated into methanol, washed, and finally dried to yield BTMSPSF. The resulting solution recovered polymer left standing in fresh methanol, then filtered and dried in a vacuum oven. The chemical structure of BTMSPSF is characterized by ¹H-NMR and ¹³C-NMR. Fig. 1 shows ¹³C-NMR spectrum of BTMSPSF, and Table 1 indicates its chemical shifts and structure.

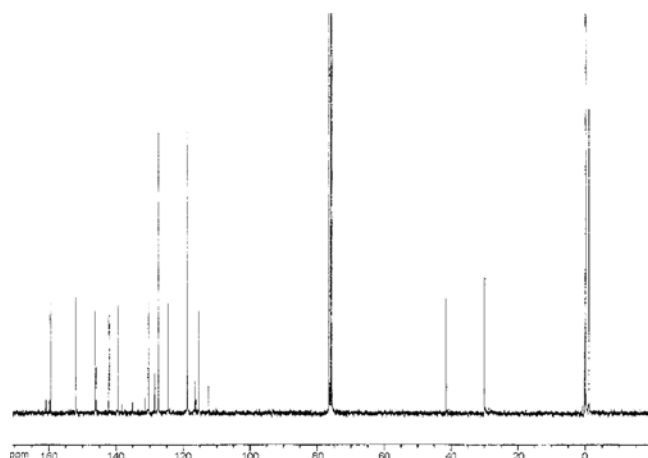
The membranes were cast from 10 wt% solution in chloroform on a clean glass plate at room temperature. The membranes were dried under atmosphere for 24 hr. After drying, the membranes were lifted from the glass plate and completely dried in a vacuum oven at 150 °C for several days.

2. Gas Sorption and Permeation

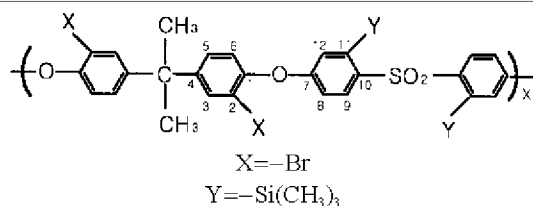
Pure gas sorption measurements were made for CO₂ and CH₄ up to 25 atm and at 30 °C. Equilibrium sorption was measured by the pressure decay method. The sorption cell is similar to one designed by Koros and Paul [1976], and described in an earlier paper [Kim and Hong, 1997a]. Permeability measurements were also made for pure CO₂ and CH₄ using the appara-

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Fig. 1. ¹³C-NMR spectrum of BTMSPSF.Table 1. ¹³C-NMR chemical shifts of BTMSPSF

| Carbon no. | ppm |
|-------------------------------------|-------|
| 1 | 151.0 |
| 2 | 119.0 |
| 3 | 127.4 |
| 4 | 146.3 |
| 5 | 131.4 |
| 6 | 115.4 |
| 7 | 159.5 |
| 8 | 116.4 |
| 9 | 128.4 |
| 10 | 142.0 |
| 11 | 139.5 |
| 12 | 124.7 |
| -C- | 41.4 |
| -C(CH ₃) ₂ - | 30.0 |
| -Si(CH ₃) ₃ | 0.4 |



tus employed in our laboratory, and the procedure was discussed in previous paper in detail [Hong et al., 1996].

3. Characterization

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker DRX-500 spectrophotometer. The glass transition temperature (*T_g*) for each material was measured using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 20 °C/min. Polymer density was measured using a density gradient column filled with aqueous solutions of calcium nitrate at 23 °C. Fractional free volume of the polymers was calculated by the group contribution method proposed by Bondi [1964; Van Krevelen, 1990]. The wide-angle X-ray diffraction (WAXD) measurements were carried out using a Rigaku WAXD-D/MAX III X-ray diffractometer with Cu Kα radiation with wavelength of 1.54 Å.

Table 2. Physical properties for modified polysulfones at 30 °C and 10 atm

| Polymer | <i>T_g</i> (°C) | ρ (g/cm ³) | d-spacing (Å) | δ (cal/cm ³) ^{1/2} | FFV |
|---------------------|------------------------------|---------------------------|------------------|--------------------------------------------|-------|
| PSf ^a | 190.3 | 1.243 | 5.2 | 12.4 | 0.158 |
| TMSPSF ^a | 164.0 | 1.126 | 5.6 | 11.0 | 0.167 |
| BPSf ^b | 190.9 | 1.514 | 4.7(9.5) | 12.9 | 0.156 |
| BTMSPSF | 169.5 | 1.244 | 5.3(10.4) | 11.5 | 0.168 |

^a Data from Kim and Hong, 1997b.

^b Data from Kim and Hong, 1999.

The average intersegmental distances or “d-spacings” were calculated from the Bragg equation [Balta-Cajella and Vonk, 1989], $n\lambda = 2d \sin\theta$, at the angle of maximum peak of scan. Cohesive energy density (CED) was estimated by the group contributions published by Fedors [Van Krevelen, 1990]. The characterized physical properties related to permeation properties are listed in Table 2.

RESULTS AND DISCUSSION

Gas sorption isotherms in glassy polymers are generally described by a dual sorption model [Chern and Koros, 1987]. According to the dual sorption model, the equilibrium concentration of sorbed gas in glassy polymers can be described as a function of pressure by Eq. (1).

$$C = C_D + C_H$$

$$C = k_D p + \frac{C'_H b p}{1 + b p} \quad (1)$$

where C [cm³(STP)/cm³] is the equilibrium concentration of the sorbed gas, and C_D and C_H represent Henry's law mode sorption and Langmuir mode sorption, respectively. The parameter k_D [cm³(STP)/cm³ atm] is the Henry's law solubility constant, C'_H [cm³(STP)/cm³] is the Langmuir sorption capacity, and b [atm⁻¹] is the Langmuir affinity constant. These sorption parameters can be obtained by nonlinear least-square regression, and are listed in Table 3. Fig. 2 shows the sorption isotherms of CO₂ and CH₄ in BTMSPSF. The solid curves in Fig. 2 represent the dual mode fits of the actual data, substituting the values of sorption parameters given in Table 3. It is shown that the sorptions of pure CO₂ and CH₄ are well fitted by dual sorption model.

The permeability coefficients of pure CO₂ and CH₄ for BTMSPSF are shown as a function of upstream pressure in Fig. 3. The permeability coefficients of CO₂ and CH₄ decrease with increasing upstream pressure, and this pressure-dependency of permeability coefficients has been generally described as a dual mobil-

Table 3. Dual mode parameters^a for BTMSPSF

| Polymer | Gas | <i>k_D</i> | <i>C_H</i> | <i>b</i> | <i>D_D</i> | <i>D_H</i> |
|---------|-----------------|----------------------|----------------------|----------|----------------------|----------------------|
| BTMSPSF | CO ₂ | 0.643 | 15.906 | 0.257 | 8.502 | 0.327 |
| | CH ₄ | 0.211 | 9.375 | 0.105 | 398 | 0.087 |

^a Units: k_D [cm³(STP)/cm³ atm]; C'_H [cm³(STP)/cm³]; b (atm⁻¹); $D_D \times 10$ (cm²/s); $D_H \times 10$ (cm²/s)

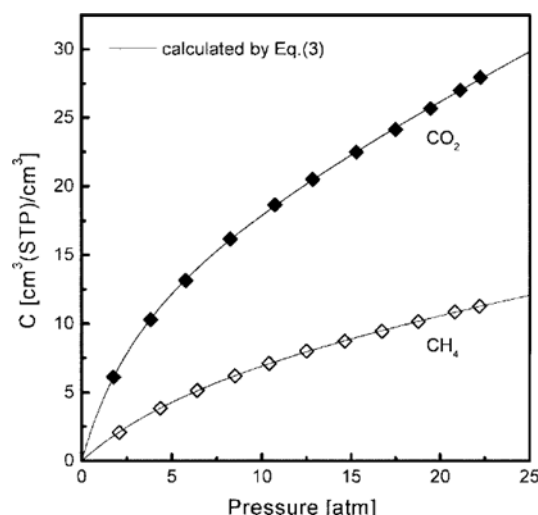


Fig. 2. Sorption isotherms for CO₂ and CH₄ in BTMSPSF at 30 °C. The symbols represent experimental data.

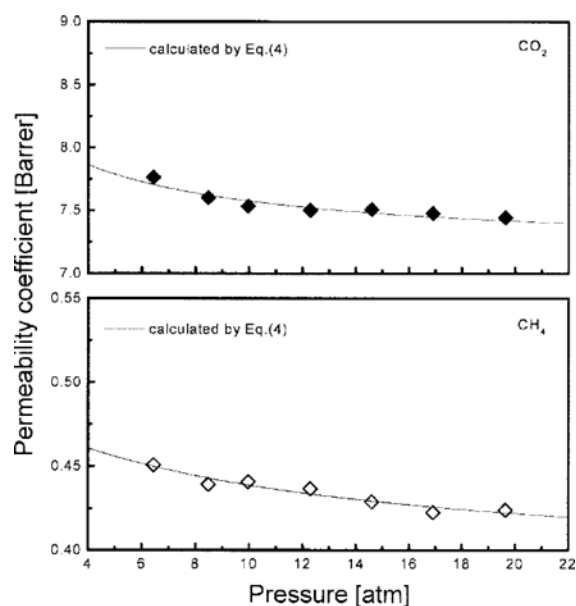


Fig. 3. Pressure dependency of permeability coefficients of CO₂ and CH₄ for BTMSPSF at 30 °C. The symbols represent experimental data.

ity model proposed by Paul and Koros [1976]. The dual mobility model was developed to complement the dual sorption model. In this model, the populations in each of the sorptions can be assigned separate diffusion coefficients D_D and D_H , and the permeability coefficient of pure gas can be written as:

$$P = k_D D_D \left[1 + \frac{FK}{(1+bp_1)(1+bp_2)} \right] \quad (2)$$

where, $K = C_H b / k_D$ and $F = D_H / D_D$.

The diffusion coefficients, D_D and D_H , are calculated from the slope and intercept of the plot of experimental permeability coefficient versus $1/(1+bp_1)(1+bp_2)$. The diffusion coefficients obtained by this analysis are also listed in Table 3. The solid curves in Fig. 3, which are calculated by Eq. (2) using param-

Table 4. Transport properties^a of CO₂ and CH₄ for modified polysulfones at 30 °C and 10 atm

| Polymer | P_{CO_2} | P_{CH_4} | α_{CO_2/CH_4} | S_{CO_2} | S_{CO_2/CH_4} | D_{CO_2} | D_{CO_2/CH_4} |
|---------------------|------------|------------|----------------------|------------|-----------------|------------|-----------------|
| PSf ^b | 4.6 | 0.21 | 22 | 2.4 | 2.8 | 1.9 | 7.8 |
| TMSPSF ^b | 15.1 | 0.94 | 16 | 2.1 | 2.7 | 7.2 | 5.5 |
| BPSf ^c | 3.2 | 0.12 | 27 | 1.7 | 3.4 | 1.9 | 7.9 |
| BTMSPSF | 8.0 | 0.42 | 19 | 2.4 | 2.8 | 3.2 | 6.5 |

^aUnits: $P \times 10^{10} [\text{cm}^3(\text{STP})\text{cm/s cm}^2 \text{cmHg}]$; $D \times 10^8 (\text{cm}^2/\text{s})$; $S \times 10^2 [\text{cm}^3(\text{STP})/\text{cm}^3 \text{cmHg}]$.

^bData from Kim and Hong, 1997b.

^cData from Kim and Hong, 1999.

ters given in Table 1, show that the permeability coefficient is well fitted to the dual mobility model over the entire pressure range.

The comparison of the permeability coefficients and ideal separation factors for modified polysulfones at 10 atm is shown in Table 4. The ideal separation factor was calculated from the ratio of the pure component permeability coefficients. The ideal separation factor is the product of diffusivity selectivity (D_{CO_2/CH_4}) and solubility selectivity (S_{CO_2/CH_4}), and the high diffusivity selectivity in this study results in a high ideal separation factor as listed in Table 4. In Table 4, the data for PSf, TMSPSF [Kim and Hong, 1997b] and BPSf [Kim and Hong, 1999] in our laboratory are also included to compare with BTMSPSF synthesized in this study. The permeability coefficients of CO₂ and CH₄ for four polysulfones rank in the following order, TMSPSF > BTMSPSF > PSf > BPSf, and ideal separation factors are in the opposite order. The ideal separation factor for BTMSPSF is reduced by about 10% than that for PSf, but BTMSPSF is about two times more permeable than PSf.

Fractional free volume (FFV) and d-spacing have been representative of average intermolecular packing distance or free spaces. Fractional free volume, given in Table 2, is calculated Eq. (3). The group contribution method of Bondi [1964; Van Krevelen, 1990] is used to calculate V_∞ , hypothetical specific volume of the polymer at 0 K, and V_f , specific volume of the polymer at T, is determined from the polymer density.

$$FFV = \frac{V - V_\infty}{V} \quad (3)$$

As shown in Tables 2 and 4, the substitutions of bulky trimethylsilyl groups are responsible for the higher FFV of TMSPSF and BTMSPSF. BPSf, however, shows a lower value of both permeability coefficient and FFV than PSf. As mentioned in a previous paper [Kim and Hong, 1999], it can be explained that the interchain interaction increased by an induced dipole. The higher ideal separation factor BTMSPSF than TMSPSF may be due to the above reason. Addition of bromo substituents to TMSPSF is also found to decrease the permeability coefficients for BTMSPSF, suggesting that the potential increase in FFV due to chain packing-disrupting bulky trimethylsilyl groups is overridden by the increase in interchain interaction. The dipole-induced dipole attraction attributed to the substitution of bromine may act to reduce the chain packing inhibiting ability. Fig. 4 represents the correlation of permeability coefficients with $1/$

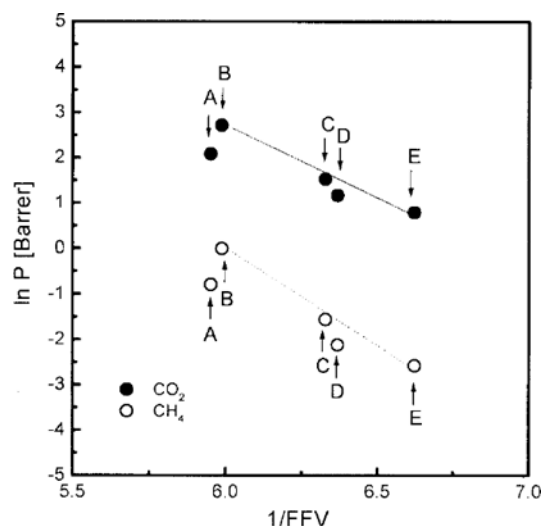


Fig. 4. Correlation of permeability coefficients at 10 atm and 30 °C with inverse fractional free volume of modified polysulfones; A: BTMSPSF, B: TMSPSF, C: PSf, D: BPSf and E: MPSf. The results of PSf, MPSf, TMSPSF and BPSf represent the previous studies [Kim and Hong, 1997a, b, 1999].

FFV for CO₂ and CH₄. In Fig. 4 MPSf (bisphenol A methylated polysulfone) synthesized in our laboratory is also included for reasonable correlation [Kim and Hong, 1997a]. MPSf is the polymer in which ortho sites of sulfone units in PSf have been replaced with methyl groups. The correlation between permeability coefficients and 1/FFV is not so clear. For BTMSPSF and BPSf, the deviation may be due to the errors in the estimation of Van der Waals volume, V_w . According to Bondi [1964], Van der Waals volumes of the structural elements are estimated with some errors in a situation where bonds may be distorted by dipoles or H-bonding. Other workers reported that small errors in the estimation of V_w have been found to lead to large differences in calculated FFV [Ghosal et al., 1995]. In addition, McHattie et al. [1991] and Puleo et al. [1989] suggested that the increase in intermolecular forces caused by the presence of the polar groups such as halogen results in a lower permeability than would be predicted by estimated FFV. In some polymers, gas permeability coefficient has been correlated with d-spacing [O'Brien et al., 1988; Hellums et al., 1989; Charati et al., 1991]. The variation of d-spacing in this work is reasonably consistent with the permeability coefficient. For example, TMSPSF has the highest d-spacing and permeability coefficient, and BPSf the lowest values. BPSf and BTMSPSF have additional peaks corresponding to 9.5 Å and 10.4 Å, respectively, as shown in Table 2. Aguilar-Vega and Paul [1993] and Jacobson [1991] reported that the appearance of the second peak might stem from the intrachain interaction. A more careful study of this result is needed to elucidate the intrachain interaction corresponding to the second peak.

It is generally known that the glass transition temperature is a pragmatic measure of the chain stiffness of polymer backbone, and chain stiffening leads to high permselectivity [McHattie et al., 1991b, 1992]. In our study, the values of T_g of silylated

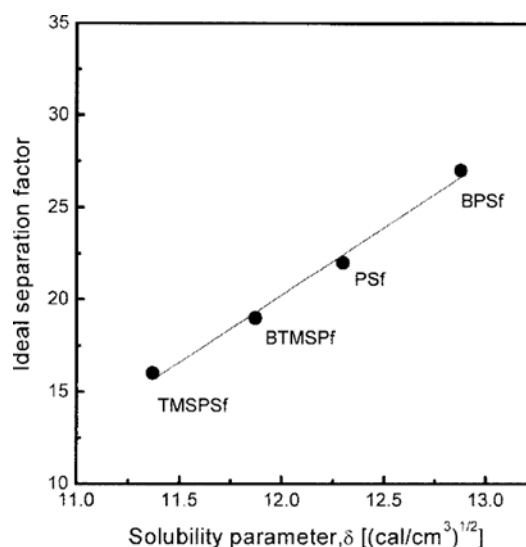


Fig. 5. Correlation of ideal separation factors at 10 atm and 30 °C with solubility parameters of modified polysulfones. The results of PSf, TMSPSF and BPSf represent the previous studies [Kim and Hong, 1997b, 1999].

polysulfones are about 20 °C lower than that of PSf. This result may be due to the flexible C-Si bond and increase of free volume. The lower ideal separation factors of these polysulfones may be attributed, at least in part, to the lower T_g of these polymers.

Cohesive energy density (CED) is also an important factor for prediction of structure-selectivity relationships. The higher the CED, the higher the attractive forces between polymer chains. This means that the permselectivity will tend to be higher for polar polymers than nonpolar polymers. CED is usually expressed in terms of solubility parameter δ [(cal/cm³)^{1/2}], where $\delta = (\text{CED})^{1/2}$, and the values of solubility parameter are listed in Table 2. Fig. 5 represents correlation of ideal separation factors at 10 atm with solubility parameters of polysulfones in this study. The polysulfone with higher δ has the higher ideal separation factor. The higher ideal separation factors of BPSf and BTMSPSF in comparison with PSf and TMSPSF, respectively, are due to the polarity of bromine as discussed above.

CONCLUSIONS

BTMSPSF (bromobisphenol A trimethylsilylated polysulfone), in which phenyl rings of bisphenol and sulfone units of polysulfone are substituted with bromo and trimethylsilyl groups, respectively, is synthesized, and the transport properties of CO₂ and CH₄ are measured. The effects of molecular structure of polysulfones on transport properties are studied using chemically modified polysulfones, including TMSPSF (bisphenol A trimethylsilylated polysulfone), BPSf (bromobisphenol A polysulfone) and BTMSPSF (bromobisphenol A trimethylsilylated polysulfone). The substitution of very bulky trimethylsilyl groups shows the strong effect on chain packing and stiffness. The replacement of phenylene hydrogens of PSf with trimethylsilyl groups results in increases in interchain distance and decreases in chain stiffness. Silylated polysulfones are several times more perme-

able than PSf. The higher values of permeability coefficient for BTMSPSf are due to higher chain packing distance by addition of bulky substituents. The substitution of bromines results in higher chain interactions, judged by the value of cohesive energy density, and lower interchain distance. The increase of polar interchain attraction reduces the chain packing-inhibiting ability. Substitution of bromines to TMSPSf is found to decrease the permeability coefficients for BTMSPSf, suggesting that the potential increase in FFV and d-spacing due to bulky trimethylsilyl groups is overridden by the increase in interchain interaction.

NOMENCLATURE

| | |
|--------|----------------------------------------------------------------------------------------------|
| b | : Langmuir affinity constant [atm^{-1}] |
| C | : equilibrium concentration of the sorbed gas [$\text{cm}^3(\text{STP})/\text{cm}^3$] |
| C'_H | : Langmuir capacity constant [$\text{cm}^3(\text{STP})/\text{cm}^3$] |
| D | : diffusion coefficient [cm^2/s] |
| k_D | : Henry's law solubility constant [$\text{cm}^3(\text{STP})/\text{cm}^3 \text{atm}$] |
| P | : permeability coefficient [$\text{cm}^3(\text{STP}) \text{cm}/\text{cm}^2 \text{s cmHg}$] |
| p | : pressure [cmHg] |
| S | : solubility coefficient [$\text{cm}^3(\text{STP})/\text{cm}^3 \text{cmHg}$] |
| V | : specific volume of the polymer |
| V_o | : hypothetical specific volume of the polymer at 0 K |
| x | : mole fraction of upstream of the membrane |
| y | : mole fraction of downstream of the membrane |

Greek Letter

| | |
|----------|-------------------------------------------------------------|
| δ | : solubility parameter [$(\text{cal}/\text{cm}^3)^{1/2}$] |
|----------|-------------------------------------------------------------|

Subscripts

| | |
|---|------------------------------|
| A | : component A |
| B | : component B |
| D | : Henry's law mode |
| H | : Langmuir mode |
| 1 | : upstream of the membrane |
| 2 | : downstream of the membrane |

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