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Relation	

Measurement and modeling of solubilities and diffusion coefficients of carbon dioxide in poly(ethylene-co-acrylic acid)

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Abstract

We measured and modeled the solubilities and diffusion coefficients of carbon dioxide (CO_2) in poly(ethylene-co-acrylic acid) (PEAA) over temperatures of 373–473 K and pressures of up to 20 MPa. The measured solubilities of CO_2 in PEAA obeyed Henry's law and decreased with an increase in the acrylic acid content of the copolymer. The Sanchez-Lacombe equation of state could be applied to correlate the measured solubilities. The temperature dependence of the CO_2 solubilities in PEAA was found to be similar to that in polyethylene with analysis using Henry's law. Further, the gas solubility and acrylic acid content were the influential factors for determining the diffusivity of CO_2, which could be modeled based on the free volume theory.

Keywords: poly(ethylene-co-acrylic acid) (PEAA); carbon dioxide; solubility; Sanchez–Lacombe equation of state; diffusion coefficient; free volume theory

1. Introduction

Supercritical fluids (SCF), including supercritical carbon dioxide (CO_2), are attracting considerable attention for use in industrial applications such as polymer processing. In a polymer–gas mixture, the solubility of the gas is the maximum amount of the gas that can be dissolved in the polymer matrix at a specific operating temperature and pressure [1]. Further, the gas diffusivity is the primary factor determining the time required by a polymer−gas mixture to reach a state of dissolution equilibrium [2]. Accordingly, quantitative studies of the solubilities and diffusivities of gases in polymers are essential for designing polymer processing techniques that use SCFs. In fact, the solubilities and diffusivities of CO_2 in different polymers such as polyethylene [3-5], polystyrene [5-8], polypropylene [5, 7, 9], poly(vinyl acetate), [8] polycarbonate [10], and poly(methyl methacrylate) [11-14] have been reported previously.

Poly(ethylene-co-acrylic acid) (PEAA), which is a copolymer composed of ethylene and acrylic acid (AA), is an industrially important material that has wide applicability because of its high tensile strength, moldability, flexibility, impact strength, and gas permeability [15]. Moreover, these properties can be controlled by varying the composition of AA repeat units in the copolymer [15]. In addition, foamed PEAA can be a promising material with good mechanical strength, which is attributable to properties of the polymer mentioned above. To efficiently design foaming processes for polymers such as PEAA, the solubility and diffusivity of CO_2, which is a representative blowing gas used in the polymer foaming process, must be known over a wide range of temperatures and pressures. However, to the best of our knowledge, there have been no previous reports on the solubility and diffusivity of CO_2 in PEAA.

Given this fact, in this study, we measured the solubilities and diffusion coefficients of CO_2 in two types of PEAA polymers having different AA contents at temperatures of 373−473 K and pressures of 5−20 MPa. In addition, the effects of the temperature, pressure, and AA content of the polymer on the solubility were elucidated by comparing the obtained data with those reported previously for the solubility of CO_2 in polyethylene [3, 4] based on the Sanchez-Lacombe equation of state (SL–EoS) [16, 17]. Finally, the diffusion coefficients of CO_2 in the PEAA samples were evaluated in terms of the temperature, gas solubility, and polymer AA content based on the free volume theory.

2. Materials and methods

2.1. Materials

The PEAA samples used, which contained 5 and 20 wt% AA, were labeled as PEAA5 and PEAA20, respectively, and were purchased from Sigma-Aldrich. The weight average molar mass (M_w) of PEAA20 was reported by the supplier to be 17.2 kg/mol. In addition, we assumed the M_w value for PEAA5 to be equal to that for PEAA20 because no data were available for PEAA5. The melting temperatures (T_m) of PEAA5 and PEAA20 were determined to be 373 and 352 K, respectively, using differential scanning calorimetry (DSC7020, Hitachi High-Tech Science, Japan) under nitrogen atmosphere at a heating rate of 10 K/min. Table S1 (supplementary material) shows the DSC curves for each polymer. All the CO_2 solubility and diffusion coefficient measurements were performed at temperatures higher than the melting point of the polymers used. Finally, the CO_2 gas (purity: 99.5 vol%) used was obtained from Iwatani Industrial Gas Co. Ltd., Japan.

2.2 Measurements of solubilities and diffusion coefficients of CO_2 in PEAA

A magnetic suspension balance (MSB) (Rubotherm GmbH) was used to measure the solubilities and diffusivities of CO_2 in PEAA; the details of the experimental procedure can be found elsewhere [10, 11, 18]. The mass of the dissolved gas at time t, $m_g(t)$, was calculated as follows [11]:

$$m_{\mathrm{g}}(t)=W(t)-W_0+\rho_{\mathrm{g}}(P,T)\left[V_{\mathrm{B}}+m_{\mathrm{p}}v_{\mathrm{p0}}(P,T)\left\{S_{\mathrm{w}}(t)+1\right\}\right] \tag{1}$$

where W_0 and $W(t)$ are the MSB readouts at zero pressure and time t, respectively. Further, ρ_g (P, T) is the density of CO_2 at pressure P and temperature T, as calculated based on the Span−Wagner equations of state [19], and V_B is the volume of the sample basket. Finally, m_p is the mass of the pure PEAA sample loaded in the sample basket, and $v_{p0}(P,T)$ is the specific volume of the pure polymer sample. The Tait equation [20] was used to determine v_{p0}:

$$v_{p0}(P,T) = V(0,T)\left\{1 - 0.0894 \ln\left[P/B(T) + 1\right]\right\} \tag{2}$$

$$V(0,T) = a + b(T - 273.15) \tag{3}$$

$$B(T) = B_0 \exp(B_1 T) \tag{4}$$

Table 1 lists the Tait parameters determined based on the previously reported specific volumes of similar PEAA samples [21]. In Eq. (1), S_w is the degree of swelling of the PEAA samples because of the dissolution of CO_2 in them and was determined as follows:

$$S_w(t) = \frac{v_p\left\{S(t) + 1\right\} - v_{p0}}{v_{p0}} \tag{5}$$

where $S(t)$ is the amount of gas dissolved in the PEAA sample per unit mass of the sample, and v_p is the specific volume of the CO_2–PEAA mixture, which was calculated based on the SL–EoS, as described in Section 3.1.

The CO_2 solubility (S_{sat}) was determined from the mass of the dissolved gas ($m_{\mathrm{g,sat}}$) at saturation:

$$S_{\mathrm{sat}} = \frac{m_{\mathrm{g,sat}}}{m_{\mathrm{p}}} \tag{6}$$

Figure 1 shows the sorption curves of CO_2 in PEAA5 and PEAA20 at 423 K as determined while rapidly increasing the pressure from 0 to 5 MPa. As can be seen from the figure, the amount of dissolved CO_2 in the PEAA samples increased gradually, with the solubility values at saturation, S_{sat}, being 0.0361 and 0.0349 g-gas/g-polymer for PEAA5 and PEAA20, respectively.

The diffusivities of CO_2 in the PEAA samples were determined from the sorption curves obtained from the solubility measurements (**Fig. 1**). During the analysis, the following assumptions were made for each diffusion process [10, 18]: (i) the diffusion process obeys Fick's second law; (ii) the gas dissolves from the upper surface of the polymer sample, and the diffusion process is a one-dimensional one and occurs along the thickness direction of the sample; (iii) the thickness of the polymer sample, L, remains constant during the gas dissolution process in consideration of the swelling at the average value between the initial and final solubility. Keeping these assumptions in mind, the diffusion equation was as follows [22]:

$$\frac{m_{\mathrm{g}}(t)-m_{\mathrm{g}}(0)}{m_{\mathrm{g,sat}}-m_{\mathrm{g}}(0)}=1-\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-\frac{(2n+1)^2\pi^2 Dt}{4L^2}\right\} \tag{7}$$

The diffusion coefficients, D, were obtained by adjusting the sorption curves obtained using Eq. (7) to the experimentally determined ones for specific temperature and pressure conditions while using D as the fitting parameter. The solid lines in **Fig. 1** present the fitted curves for CO_2 sorption in PEAA5 and PEAA20 at 423 K for rapid stepwise increases in the pressure from 0 to 5 MPa; the values of D were determined to be 2.9×10^{-9} and 1.6×10^{-9} m^2/s for PEAA5 and PEAA20, respectively.

3. Model used

3.1 Correlation of solubility using Sanchez–Lacombe equation of state

The SL–EoS [16] was used to correlate the data for the solubility of CO_2 in the PEAA samples:

$$\tilde{\rho}^2+\tilde{P}+\left\{\left(1-\frac{1}{r}\right)\tilde{\rho}+\ln(1-\tilde{\rho})\right\}\tilde{T}=0 \tag{8}$$

$$\tilde{\rho}=\frac{\rho}{\rho^*},\ \tilde{P}=\frac{P}{P^*},\ \tilde{T}=\frac{T}{T^*},\ r=\frac{P^*M}{\rho^*RT^*} \tag{9}$$

where ρ*, P*, and T* are the characteristic density, pressure, and temperature, respectively, for each component. Further, r is the number of segments in a molecule, and M is the molar mass. For the mixtures, the mixing rules were used, as follows:

$$P^* = \sum_i \sum_j \phi_i \phi_j \left(1 - k_{ij}\right) \sqrt{P_i^* P_j^*} \tag{10}$$

$$T^* = P^* \sum_i \frac{\phi_i T_i^*}{P_i^*} \tag{11}$$

$$\frac{1}{r} = \sum_i \frac{\phi_i^0}{r_i^0} \tag{12}$$

$$\frac{1}{M} = \sum_i \frac{w_i}{M_i} \tag{13}$$

$$\phi_i^0 = \frac{\phi_i P_i^* / T_i^*}{\sum_j \phi_j P_j^* / T_j^*} \tag{14}$$

$$\phi_i = \frac{w_i / \rho_i^*}{\sum_j w_j / \rho_j^*} \tag{15}$$

where k_{ij} is the parameter for binary interactions between molecules i and j. Further, ϕ_i and w_i are the segment mole fraction and mass fraction of component i, respectively. The pure-component parameters (T_i*, P_i*, and ρ_i*) for each component, i, of the SL–EoS are listed in **Table 2**. In this work, the pure-component parameters for the two PEAA polymers were obtained by fitting the specific volume data for the polymer reported by Zoller and Walsh [21].

While calculating the solubilities using the SL–EoS, it was assumed that the polymers did not dissolve into the gas phase and that they were monodispersed. Therefore, the equilibrium relationship for the chemical potentials of CO_2 (1) in the polymer phase (μ_1^{P}) and that in the pure gas phase (μ_1^{G}) at a given T and P could be described as follows [9]:

$$\mu_1^{\mathrm{P}}\left(T, P, \phi_1^{\mathrm{P}}\right) = \mu_1^{\mathrm{G}}\left(T, P\right) \tag{16}$$

The value of the binary interaction parameter, k_{12}, for the CO_2 (1) and polymer (2) mixture in Eq. (10) was determined by minimizing the average relative deviation (ARD), which was defined as follows:

$$\mathrm{ARD}\left[\%\right] = \frac{1}{ND}\sum_{k=1}^{ND}\frac{\left|S_{\mathrm{sat},k}^{\mathrm{exp}} - S_{\mathrm{sat},k}^{\mathrm{corr}}\right|}{S_{\mathrm{sat},k}^{\mathrm{exp}}}\times 100 \tag{17}$$

where ND is the number of data points and $S_{\mathrm{sat}}^{\mathrm{exp}}$ and $S_{\mathrm{sat}}^{\mathrm{corr}}$ are the experimentally determined and calculated solubilities of CO_2 in the polymers, respectively.

3.2 Model for diffusion coefficients of CO₂ in PEAA based on free volume theory

In the present study, the model proposed by Areerat [5], which is based on the free volume theory, was employed to model the diffusion coefficients of CO_2 in the polymers. In this model, the self-diffusion coefficient of a gas can be described as follows [5]:

$$D_{\mathrm{self}} = RTA_{\mathrm{d}} \exp\left(\frac{-B_{\mathrm{d}}}{v_{\mathrm{mix}}^{\mathrm{f}}}\right) \tag{18}$$

$$v_{\mathrm{mix}}^{\mathrm{f}} = v_{\mathrm{mix}}\left(w_1, P, T\right) - v_{\mathrm{mix}}^{0} \tag{19}$$

where A_{d} and B_{d} are the characteristic parameters [5, 23]. Further, $v_{\mathrm{mix}}^{\mathrm{f}}$ is the specific free volume of the CO_2−polymer mixture, which is given by Eq. (19); v_{mix} corresponds to the specific volume of the CO_2−polymer system at a CO_2 mass fraction of w_1 and pressure P and temperature T; this was determined using the S−L EoS. Finally, v_{mix}^{0}, which is the occupied specific volume of the CO_2−polymer mixture, was determined using the following expression [23]:

$$v_{\mathrm{mix}}^{0} = w_1 v_1^0 + \left(1 - w_1\right) v_2^0 \tag{20}$$

In Eq. (20), the value of the occupied specific volume of pure CO_2, v_1^0, was taken to be 0.589 cm^3/g [5, 11, 14, 24] based on its van der Waals volume [25]. The occupied specific volume of the pure polymer, v_2^0, was also determined from its van der Waals volume ($v_{w,2}$), as follows [5]:

$$v_2^0 = 1.3 v_{w,2} \tag{21}$$

The $v_{w,2}$ values for the PEAA polymers ($v_{w,2}^{PEAA}$) were calculated using the following equation:

$$v_{w,2}^{PEAA} = (1 - w_{AA}) v_{w,2}^{PE} + w_{AA} v_{w,2}^{PAA} \tag{22}$$

where $v_{w,2}^{PE}$ (=0.7307 cm^3/g [26]) and $v_{w,2}^{PAA}$ (=0.5032 cm^3/g [26]) are the $v_{w,2}$ values of polyethylene (PE) and poly(acrylic acid)(PAA), respectively, and w_{AA} is the mass fraction of AA in the pure PEAA polymers. The $v_{w,2}^{PEAA}$ values for PEAA5 and PEAA20 calculated using Eq. (22) were 0.719 and 0.685 cm^3/g, respectively.

To allow for a comparison of the measured diffusion coefficients of CO_2 in the PEAA polymers with those calculated, the mutual-diffusion coefficients of CO_2 in the polymer (D_{mutual}) for the gas (1)−polymer (2) mixture were calculated using the self-diffusion coefficients (D_{self}) and the following equation

[5, 27]:

$$D_{\text{mutual}} = \frac{x_2 D_{\text{self}}}{RT} \left[\frac{\partial \mu_1^{\text{P}} \left(T, P, x_1 \right)}{\partial \ln x_1} \right]_{T,P} \tag{23}$$

where μ_1^{P} is the chemical potential of CO_2 in the polymer phase and x_i is the mole fraction of component *i*. The following equation could be derived from Eqs. (18) and (23):

$$D_{\text{mutual}} = x_2 A_{\text{d}} \exp\left(\frac{-B_{\text{d}}}{v_{\text{mix}}^{\text{f}}} \right) \left[\frac{\partial \mu_1^{\text{P}} \left(T, P, x_1 \right)}{\partial \ln x_1} \right]_{T,\,P} \tag{24}$$

The partial differential term in this equation was determined numerically using the S–L EoS.

To correlate the measured diffusion coefficients using Eq. (24), the characteristic parameters, A_{d} and B_{d}, were used as the fitting parameters for the investigated temperature and pressure conditions during the minimization of ARD, as follows:

$$\text{ARD}\left[\%\right] = \frac{1}{ND} \sum_{k=1}^{ND} \frac{\left| D_k^{\text{exp}} - D_k^{\text{corr}} \right|}{D_k^{\text{exp}}} \times 100 \tag{25}$$

where D^{exp} and D^{corr} (=D_{mutual} in Eq. (24)) are the experimentally determined and correlated diffusion coefficients, respectively, and ND is the number of data points.

4. Results and discussion

4.1. Solubility of CO_2 in PEAA

Figures 2 and 3 show the measurement results for the solubilities of CO_2 in PEAA5 and PEAA20, respectively, while **Table 3** lists the experimentally determined values. For all the temperatures investigated, the solubilities increased almost linearly with an increase in the pressure, obeying Henry's law in the investigated pressure range in a manner similar to other CO_2–polymer systems [6, 8, 11, 28, 29]. Further, the solubilities of CO_2 increased with a decrease in the temperature; similar temperature dependences have been reported previously during the dissolution of condensable gases such as CO_2 [6, 8, 28, 29] and ethylene [30] in other polymers.

Figure 4 compares the measured solubilities of CO_2 in low-density polyethylene [3] (acrylic acid: 0 wt%), PEAA5 (acrylic acid: 5 wt%), and PEAA20 (acrylic acid: 20 wt%) at 423 K; these polymers contain AA in different mass fractions. As shown in the figure, the solubilities of CO_2 in the polymers decreased with an increase in the AA content; this result can mainly be attributed to low affinity of CO_2 for AA resulting from the possible self-association between the AA groups.

The solid lines in **Figs. 2 and 3** correspond to the fitted solubilities of CO_2 in PEAA determined using the S–L EoS. As shown in **Table 4**, the S–L EoS allowed the solubility data to be adjusted to within 2.8% of the ARD. **Figure 5** and **Table 4** show the k_{12} values (Eq. (10)) for CO_2 and PEAA used as the fitting parameters. The k_{12} values decreased linearly with an increase in the temperature; this was true for all the polymers investigated. Further, this temperature dependence of k_{ij} was similar to that for polyethylene, as shown in **Fig. 5**, and can be expressed using the following approximated curves based on the least-squares method.

For CO_2 in PEAA5: $k_{12} = -1.302\times10^{-3}T + 4.468\times10^{-1}$ (26)

For CO_2 in PEAA20 : $k_{12} = -1.284\times10^{-3}T + 4.282\times10^{-1}$ (27)

These approximated curves can be useful for interpolating and even extrapolating the solubilities of CO at other temperatures.

4.1.2. Henry's constant for dissolution of CO_2 in PEAA

The value of Henry's constant, K_p for the solubilities of CO_2 in the PEAA polymers was determined based on the S–L EoS. The linear relationship between $(T_c/T)^2$ and $\ln(1/K_p)$, which was originally proposed by Stern *et al.* [31], was used to analyze the data; here, T_c (=304.12 K [32]) is the critical temperature of CO_2. **Figure 6** compares the values of Henry's constant corresponding to the CO_2 solubilities in the PEAA polymers with those reported in the literature for the solubilities of CO_2 in low-density polyethylene [3, 4]. As can be seen from the figure, the curves for the $1/K_p$ values for CO_2 in PEAA and polyethylene exhibit similar slopes and hence represent similar temperature dependences. Further, the values of $1/K_p$ for CO_2 in the copolymers decreased with an increase in the AA mass fraction and could be arranged in the following order: polyethylene > PEAA5 > PEAA20. This was probably because of a decrease in the extent of interactions between CO_2 and AA, since the latter contains the acrylic group, in contrast to the ethylene structure.

As shown in **Fig. 6**, the $\ln(1/K_p)$ and $(T_c/T)^2$ values for the PEAA polymers were linearly related. Hence, we could obtain the following approximate curves using with the least-squares method:

For CO_2 in PEAA5: $$\ln\left(1/K_p\right) = 1.523\left(T_c/T\right)^2 + 7.365 \qquad (28)$$

For CO_2 in PEAA20 : $\ln\left(1/K_{\mathrm{p}}\right) = 1.770\left(T_{\mathrm{c}}/T\right)^2 + 7.145$ (29)

4.2. Diffusivities of CO_2 in PEAA

4.2.1. Results of measurements of diffusion coefficients of CO_2 in PEAA

Figures 7 and 8 show the diffusion coefficients of CO_2 in PEAA5 and PEAA20, respectively, as functions of the average solubilities during the sorption process while **Table 5** lists the experimental values. The diffusion coefficients of CO_2 in the two PEAA polymers increased with an increase in the temperature; this was true for all the conditions investigated. A similar temperature dependence of the diffusion coefficient has also been reported in the case of the CO_2−low-density polyethylene system [3], as shown in **Figure 9**. In fact, this is a typical phenomenon for the diffusivity of gases in polymers [2, 8, 10, 11, 14, 18].

In addition, for all the temperatures investigated, the diffusion coefficients of CO_2 in the PEAA polymers increased with an increase in the average solubility of the gas, especially at lower temperatures. This solubility dependence of the diffusion coefficients is mainly attributable to the plasticization effect arising from the solvation of the gas; the mobility of CO_2 is promoted by the plasticization of the copolymers, especially at lower temperatures. The effect of plasticization on the diffusion coefficient of CO_2 has also been observed in the cases of polystyrene [8] and poly(methyl methacrylate) [11] for the same temperature range.

Further, for all the temperature conditions, the diffusion coefficients of CO_2 in PEAA 5 (**Fig. 7**) were larger than those in PEAA20 (**Fig. 8**). This was probably because the mobility of CO_2 in the PEAA polymers decreased with an increase in their AA content. In fact, as shown in **Figs. 7, 8, and 9**, the diffusion coefficients of CO_2 at 423 K in the polymers decreased in the order of their mass fractions of AA: polyethylene [3](**Fig. 9**, AA: 0 wt%) > PEAA5 (**Fig. 7**, AA: 5 wt%)> PEAA20 (**Fig. 8**, AA: 20 wt%). Consequently, a higher AA content reduced the diffusivity of CO_2 in PEAA; this can be attributable to an increase in the diffusion resistance of the gas with an increase in the interaction between the AA unit in the polymers resulting from the self-association in the AA groups.

4.2.2. Modeling of diffusion coefficients based on free volume theory

The dashed lines in **Figs. 7, 8, and 9** show the diffusion coefficients of CO_2 in the polymers as calculated based on the free volume theory (Eq. (24)). For the correlations represented by the dashed lines, the characteristic parameters, A_d and B_d, in Eq. (24) were used as the universal fitting parameters for the investigated polymers (PEAA5: **Fig. 7**, PEAA20: **Fig. 8**, and polyethylene (M_w=133 kg/mol [3]): **Fig. 9**), based on the free volume theory [5, 23]. The fitting results are listed in **Table 6**. We confirmed that the molecular weight of the polymers has little effect on the calculation results. As can be seen from the figures, the model could describe the effects of the temperature, solubility, and AA mass fraction in the PEAA polymers on the diffusivities of CO_2 to within 25.8% of the ARD, which is in keeping with the discussion in Section 4.2.1.

Further, to improve the correlation accuracy of the diffusion coefficients of CO_2 in the polymers, the characteristic parameter A_d in Eq. (24) was used as the polymer-dependent fitting parameter while parameter B_d was used as the universal parameter; the solid lines in **Figs. 7, 8, and 9** show the correlation results, while **Table 7** lists the determined parameters and ARD values. As can be seen from the figures, the free volume theory and the polymer-dependent parameter, A_d, could describe the diffusion coefficients to within 5.7 % of the ARD. **Figure 10** shows the values of the polymer-dependent parameter, A_d, as a function of the AA mass fraction in the polymers (w_AA); this relationship can be represented by the following curve, which is shown as the solid line in **Fig. 10**.

$$A_\mathrm{d}(w_\mathrm{AA}) = A_\mathrm{d}^\mathrm{PE} \exp\left[-\alpha\left(w_\mathrm{AA}\right)^{\beta}\right] \tag{30}$$

where A_d^PE is the A_d value for polyethylene (**Table 7**); α (=0.1071) and β (=0.4392) are the fitting parameters determined based on the correlations of the

A_d values in **Table 7** and **Fig.10**. Eq. (30) can be used to predict the diffusion coefficients of CO_2 in other PEAA polymers with the different AA contents.

5. Conclusions

We measured and modeled the solubilities and diffusion coefficients of carbon dioxide (CO_2) in poly(ethylene-co-acrylic acid) (PEAA) for temperatures of 373−473 K and pressures of up to 20 MPa. The measured solubilities of CO_2 in the PEAA polymers obeyed Henry's law and decreased with an increase in the AA mass fraction in the polymers. The SL–EoS was used to correlate the measured solubilities. The analysis using Henry's law revealed that temperature dependence of the solubilities of CO_2 in PEAA was similar to that in polyethylene. The CO_2 solubility and acrylic acid content were the crucial factors for affecting the diffusion coefficient of CO_2 in the PEAA polymers. In addition, the effects of these parameters on the diffusion coefficient could be described quantitatively based on the free volume theory.

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Tables

Table 1. Tait parameters for PEAA samples used in this study

Polymer	a [cm^3/g]	b [cm^3/(g·K)]	B_0 [MPa]	B_1 [K^{-1}]	T range [K]	P range [MPa]
PEAA5	1.107	9.82×10^{-4}	203.2	-4.93×10^{-3}	373 to 473	0 to 20
PEAA20	1.045	8.49×10^{-4}	209.7	-4.47×10^{-3}	373 to 473	0 to 20

Table 2. Characteristic parameters for each component for S–L EoS

Component	w_{AA} [%] [a]	P^* [MPa]	ρ^* [kg/m^3]	T^* [K]	Reference
CO_2	-	720.3	1580.0	$208.9 + 0.459\,T - 0.756\times10^{-4}\,T^2$	[33]
Polyethylene	0	382.1	889.3	685.0	[3]
PEAA5	5	434.5	906.9	674.8	This work
PEAA20	20	438.3	957.4	711.7	This work

a: Mass fraction of acrylic acid (AA) in PEAA polymers

Table 3. Measured solubilities of CO_2 in PEAA polymers [a]

Polymer	T [K]	P [MPa]	S_{sat} [g-gas/g-polymer]	S_w [-] [b]
PEAA5	373.15	5.04	0.0436	0.0412
		9.94	0.0839	0.0791
		14.9	0.125	0.118
		19.8	0.148	0.138
	398.15	5.42	0.0409	0.0407
		10.1	0.0778	0.0773
		15.1	0.115	0.114
		19.6	0.142	0.140
	423.15	5.08	0.0361	0.0380
		10.1	0.0727	0.0763
		15.0	0.106	0.111
		19.9	0.140	0.145
	448.15	5.27	0.0336	0.0375
		10.3	0.0676	0.0751
		15.3	0.101	0.111
		20.0	0.133	0.146
	473.15	5.01	0.0313	0.0372
		10.1	0.0625	0.0736
		15.3	0.0958	0.112
		20.1	0.130	0.151
PEAA20	373.15	5.15	0.0419	0.0409
		9.96	0.0801	0.0783
		15.1	0.112	0.110
		20.0	0.141	0.137
	398.15	5.01	0.0365	0.0376
		10.1	0.0745	0.0766
		15.2	0.107	0.110
		20.1	0.132	0.135
	423.15	5.4	0.0349	0.0379
		10.1	0.0676	0.0733
		15.2	0.0990	0.107
		20.1	0.125	0.134
	448.15	5.08	0.0293	0.0338
		10.2	0.0600	0.0688
		15.3	0.0904	0.103
		20.1	0.116	0.131
	473.15	5.33	0.0280	0.0342
		10.2	0.0544	0.0661
		15.4	0.0840	0.101
		20.2	0.111	0.134

a: Standard uncertainties u are $u(T)$= 0.05 K, $u(P)$= 0.01 MPa, and the combined relative expanded uncertainty U_r is estimated to be less than $U_r(S_{sat})$ = 0.05 (0.95 level of confidence).

b: Degree of swelling as estimated using S−L EoS

Table 4. Binary interaction parameter, k_{12}, in Sanchez–Lacombe equation and ARD values obtained by fitting data for solubility of CO_2 in PEAA

Polymer	T [K]	k_{12} [-]	ARD [%] [a]
PEAA5	373.15	-0.0424	1.6
	398.15	-0.0694	1.3
	423.15	-0.1015	1.5
	448.15	-0.1345	0.7
	473.15	-0.1726	1.7
PEAA20	373.15	-0.0522	1.5
	398.15	-0.0825	2.8
	423.15	-0.1138	2.4
	448.15	-0.1453	1.6
	473.15	-0.1812	0.8

a: Average relative deviation between experimental and calculated values as determined using Eq. (17).

Table 5. Diffusion coefficients (D) of CO_2 in PEAA [a]

Polymer	T [K]	P range [MPa]		Average solubility [g-gas/g-polymer]	$D\times10^9$ [m^2/s]
		min	max		
PEAA5	373.15	0	5.04	0.0218	1.5
		5.04	9.94	0.0638	1.8
		9.94	14.9	0.104	2.1
		14.9	19.8	0.137	2.1
	398.15	0	5.42	0.0205	2.1
		5.42	10.1	0.0594	2.5
		10.1	15.1	0.0964	2.6
		15.1	19.6	0.129	2.8
	423.15	0	5.08	0.0181	2.9
		5.08	10.1	0.0544	3.2
		10.1	15.0	0.0894	3.6
		15.0	19.9	0.123	3.7
	448.15	0	5.27	0.0168	3.9
		5.27	10.3	0.0506	4.1
		10.3	15.3	0.0843	4.3
		15.3	20.0	0.117	4.6
	473.15	0	5.01	0.0157	5.1
		5.01	10.1	0.0469	5.5
		10.1	15.3	0.0792	5.8
		15.3	20.1	0.113	6.0
PEAA20	373.15	0	5.15	0.0210	0.6
		5.15	9.96	0.0610	0.8
		9.96	15.1	0.0961	1.0
		15.1	20.0	0.127	1.0
	398.15	0	5.01	0.0183	1.0
		5.01	10.1	0.0555	1.2
		10.1	15.2	0.0908	1.4
		15.2	20.1	0.120	1.4
	423.15	0	5.4	0.0175	1.6
		5.4	10.1	0.0513	1.8
		10.1	15.2	0.0833	1.9
		15.2	20.1	0.112	1.9
	448.15	0	5.08	0.0147	2.3
		5.08	10.2	0.0447	2.4
		10.2	15.3	0.0752	2.7
		15.3	20.1	0.103	2.7
	473.15	0	5.33	0.0140	3.0
		5.33	10.2	0.0412	3.3
		10.2	15.4	0.0692	3.4
		15.4	20.2	0.0975	3.6

a: Standard uncertainties u are $u(T)$= 0.05 K, $u(P)$= 0.01 MPa, and the combined relative expanded uncertainty U_r is estimated to be less than $U_r(D)$ = 0.2 (0.95 level of confidence).

Table 6. Diffusion coefficients of CO_2 in polymers calculated based on free volume theory (Eq. (24)) using A_d and B_d used as universal fitting parameters

Polymer	w_{AA} [%] [a]	A_d ×10^{11} [m^2·mol/(J·s)] [b]	B_d [cm^3/g] [b]	ARD [%] [c]
Polyethylene	0	1.848	1.004	25.8
PEAA5	5			8.3
PEAA20	20			13.6

a: Mass fraction of acrylic acid (AA) in PEAA polymers

b: Fitting parameters of Eq. (24)

c: Average relative deviation between experimental and calculated values of diffusion coefficients defined in Eq. (25)

Table 7. Diffusion coefficients of CO_2 in polymers calculated based on free volume theory (Eq. (24)) where fitting parameter A_d was determined for each polymer and same B_d value was used every polymer

Polymer	w_{AA} [%] [a]	A_d ×10^{11} [m^2·mol/(J·s)] [b]	B_d [cm^3/g] [b]	ARD [%] [c]
Polyethylene	0	2.487	1.004	3.4
PEAA5	5	2.004		4.6
PEAA20	20	1.668		5.7

a: Mass fraction of acrylic acid (AA) in PEAA polymers

b: Fitting parameters of Eq. (24)

c: Average relative deviation between experimental and calculated values of diffusion coefficients defined in Eq. (25)

Figures

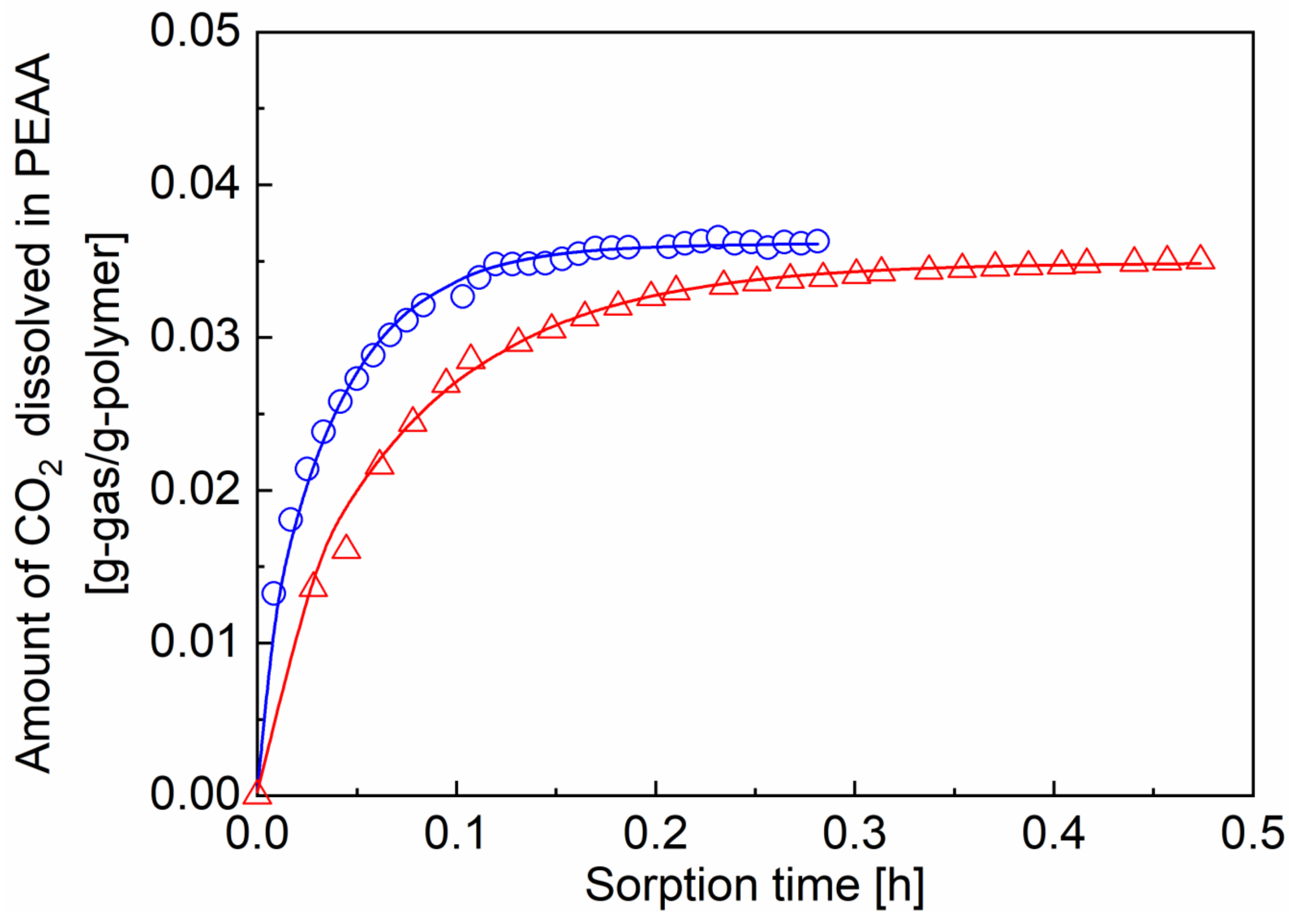

Fig. 1 Sorption curves of CO_2 in PEAA5 (○) and PEAA20 (△) at 423 K for pressures of 0–5 MPa. Saturated solubility, S_{sat}, values were determined to be 0.0361 and 0.0349 g-gas/g-polymer, respectively, while diffusion coefficient, D, values were determined to be 2.9×10^{-9} and 1.6×10^{-9} m^2/s, respectively, for PEAA5 and PEAA20 (solid lines are fits obtained using Eq. (7)).

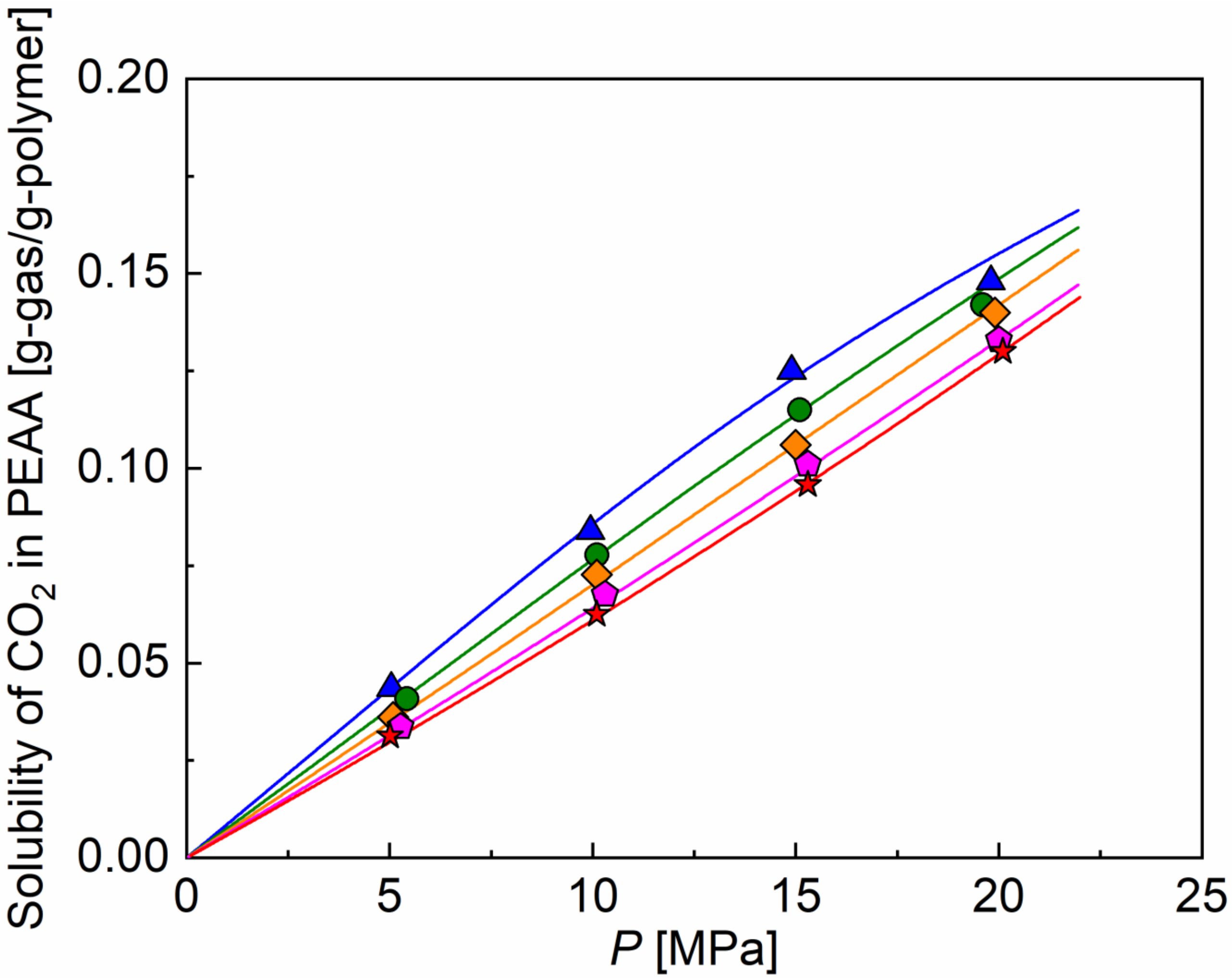

Fig. 2. Measured solubilities of CO_2 in PEAA5 at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★) and fits obtained using Sanchez–Lacombe equation of state (solid lines).

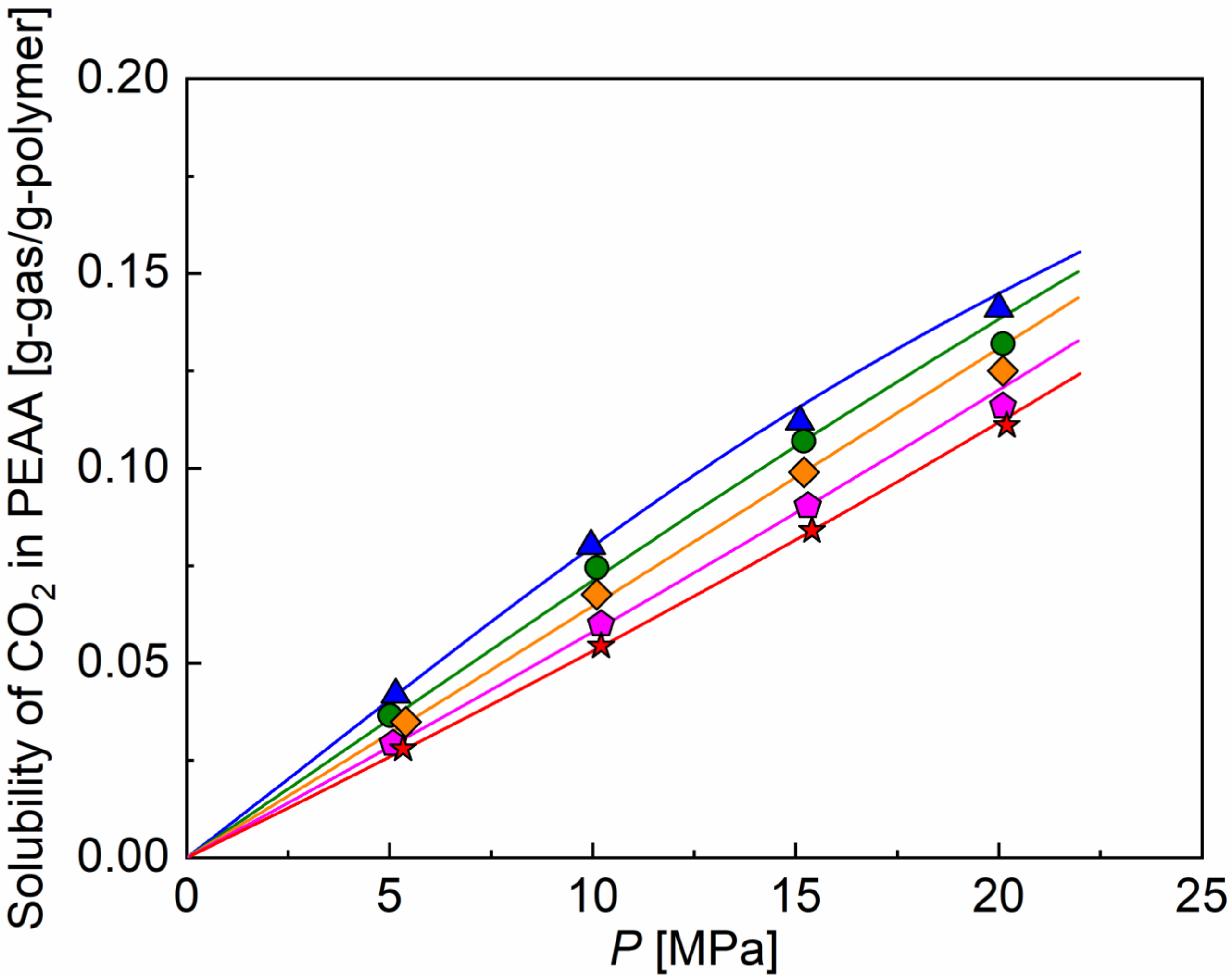

Fig. 3. Measured solubilities of CO_2 in PEAA20 at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★) and fits obtained using Sanchez–Lacombe equation of state (solid lines).

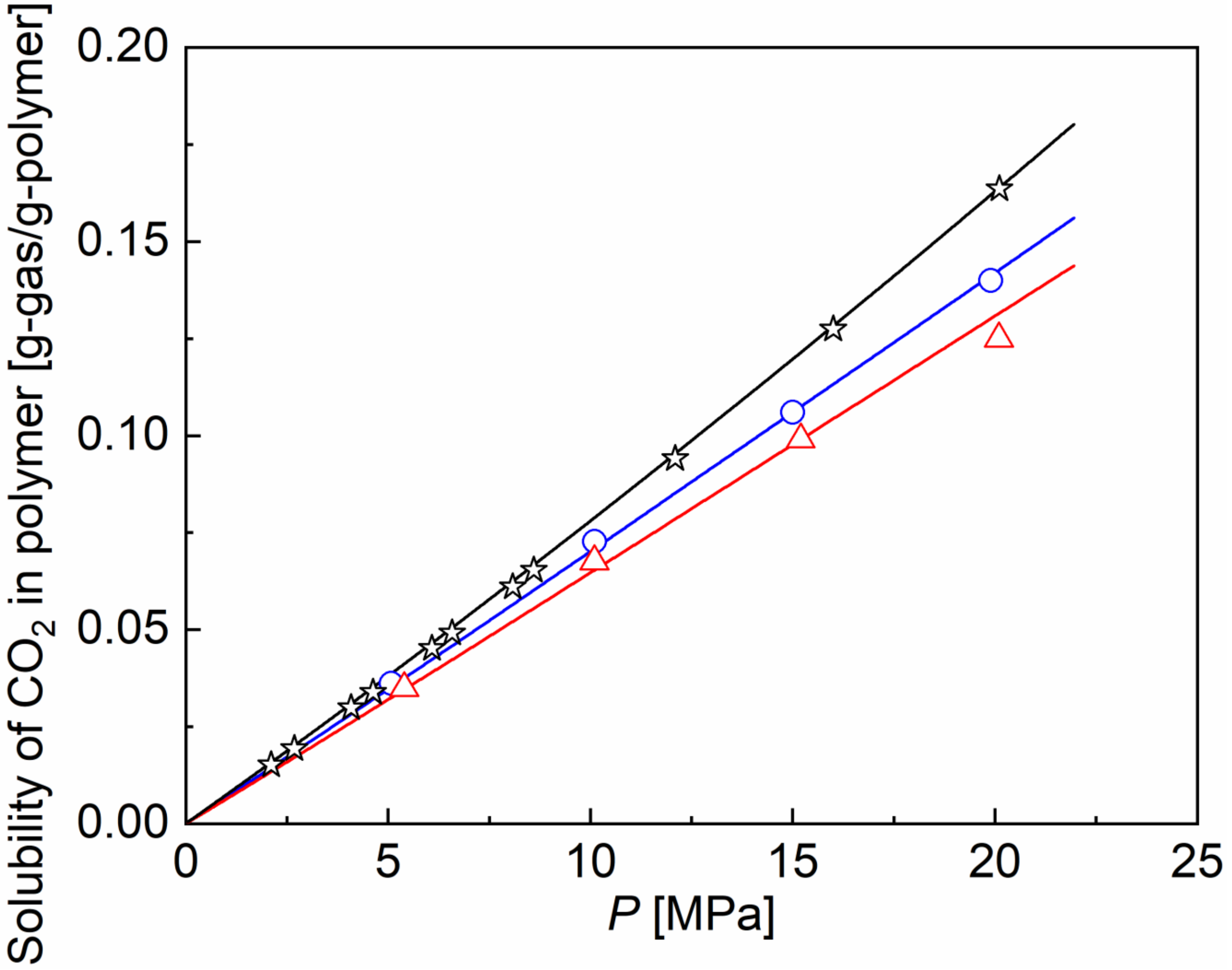

Fig. 4. Comparison of measured solubilities of CO_2 in polyethylene (☆)[3] , PEAA5 (○), and PEAA20 (△) at 423 K.

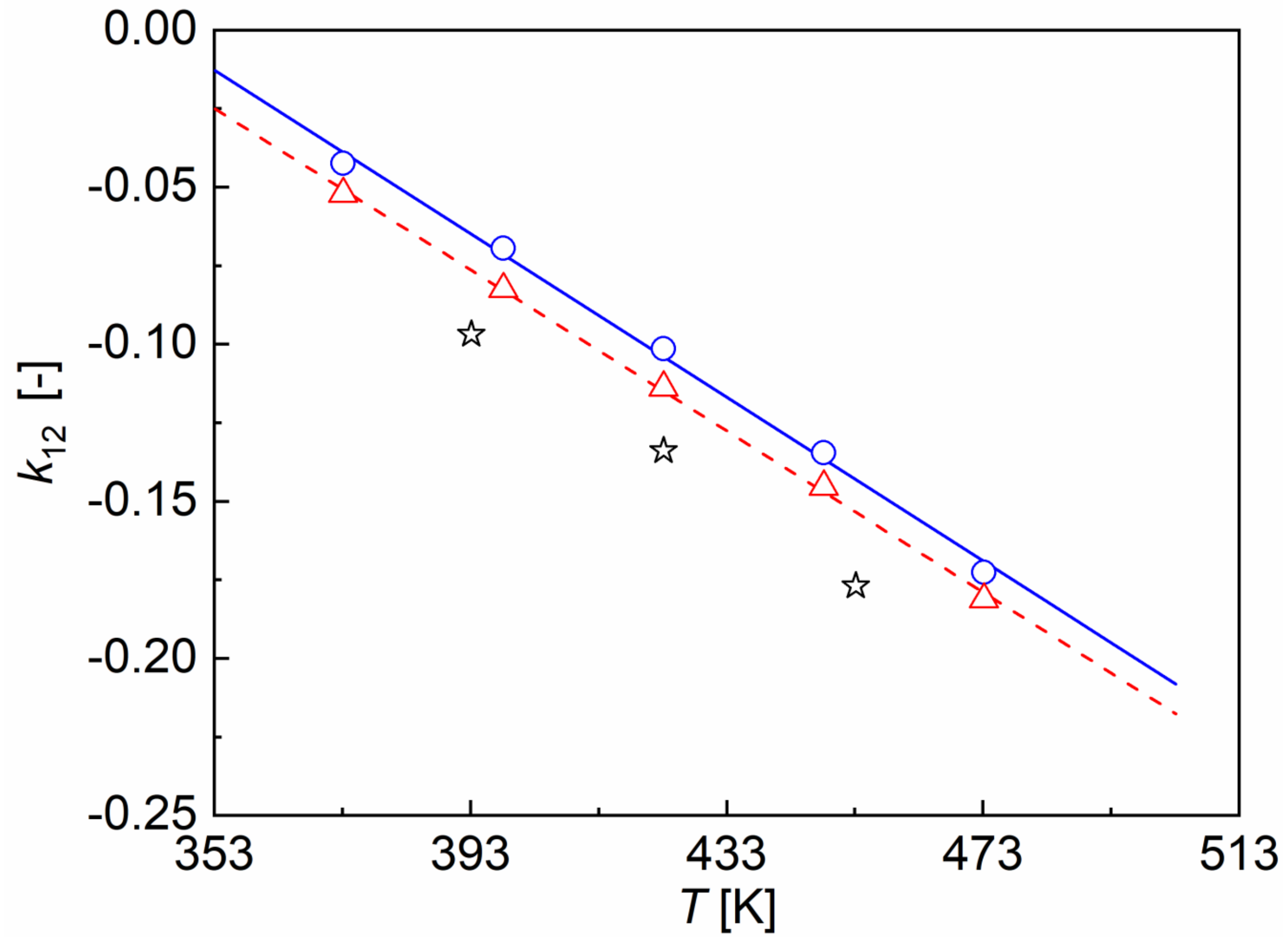

Fig. 5. Binary interaction parameter, k_{ij}, in Sanchez–Lacombe equation as determined by fitting solubilities of CO_2 in polyethylene (☆)[3] , PEAA5 (○), and PEAA20 (△). Solid (PEAA5) and dashed (PEAA20) lines are fitted curves for data obtained in this work using Eqs. (26) and (27), respectively.

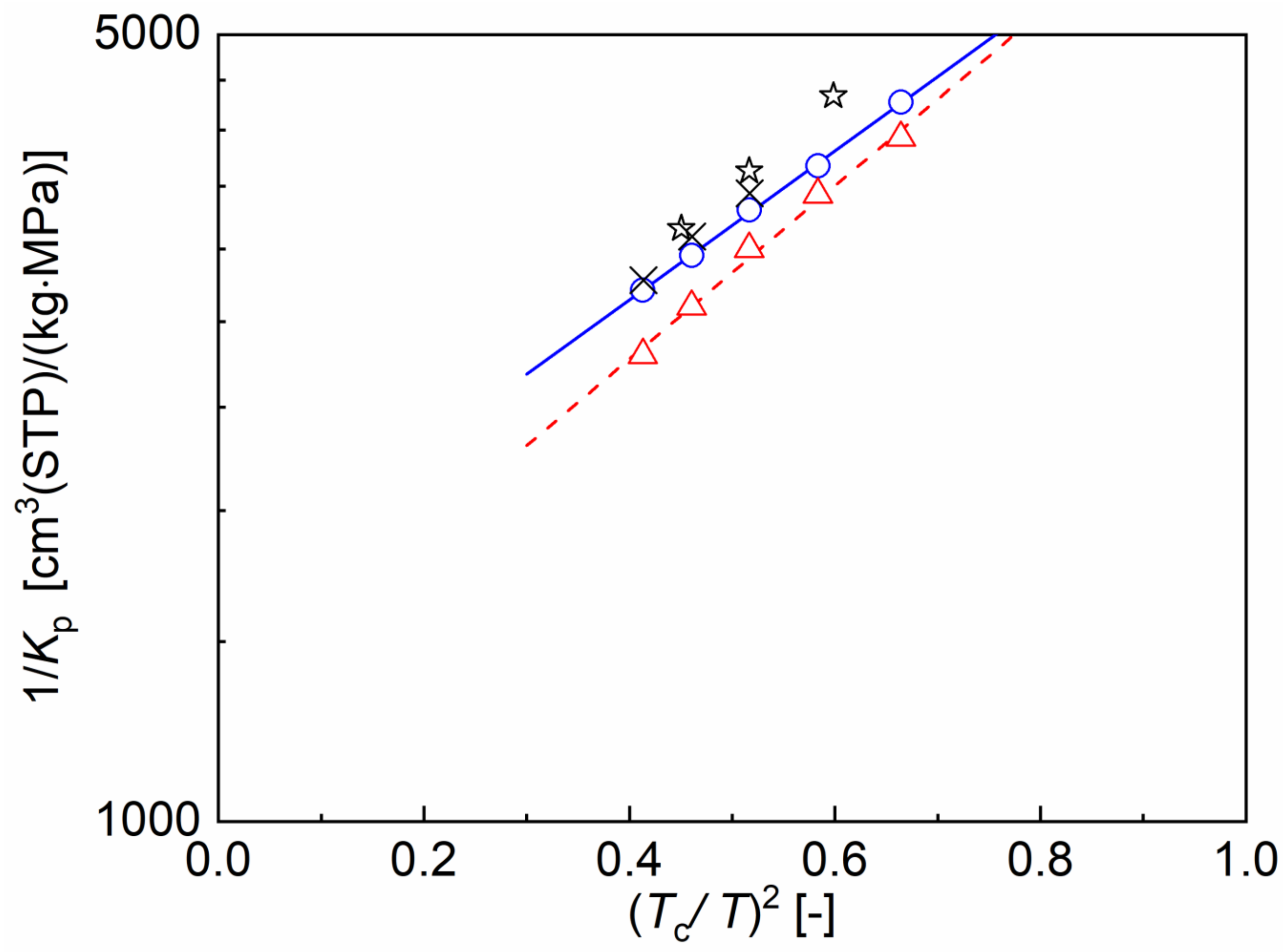

Fig. 6. Henry's constant for dissolution of CO_2 in polyethylene (☆[3], ×[4]), PEAA5 (○), and PEAA20 (△). Solid (PEAA5) and dashed (PEAA20) lines are fitted curves for data obtained in this work using Eqs. (28) and (29), respectively.

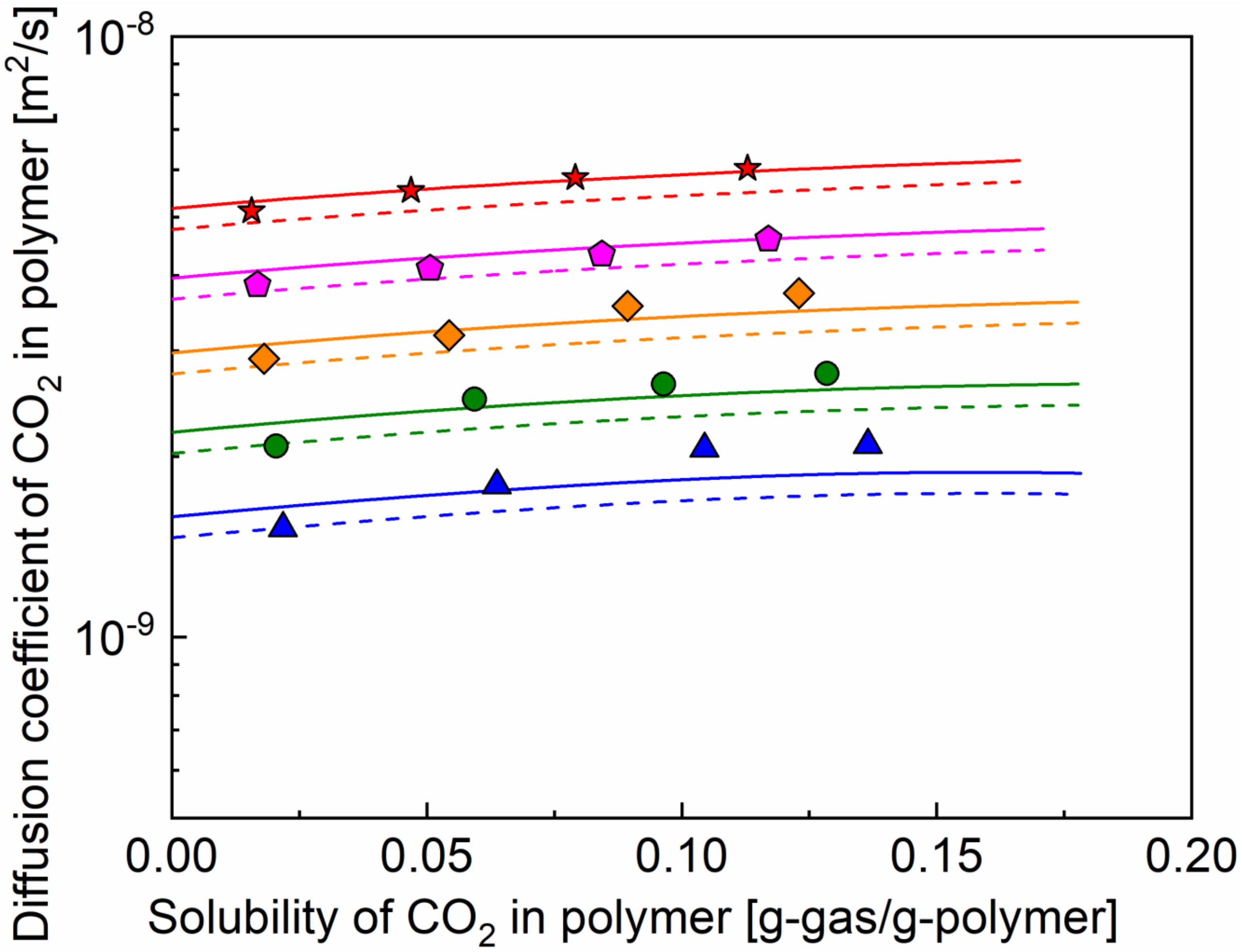

Fig. 7. Measured and calculated diffusion coefficients of CO_2 in PEAA 5 as functions of average solubility of CO_2 in polymers during sorption step at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★). Lines correspond to correlation results obtained using Eq. (24) where values of fitting parameters A_d and B_d in **Table 6** (dashed lines) and **Table 7** (solid lines) were used.

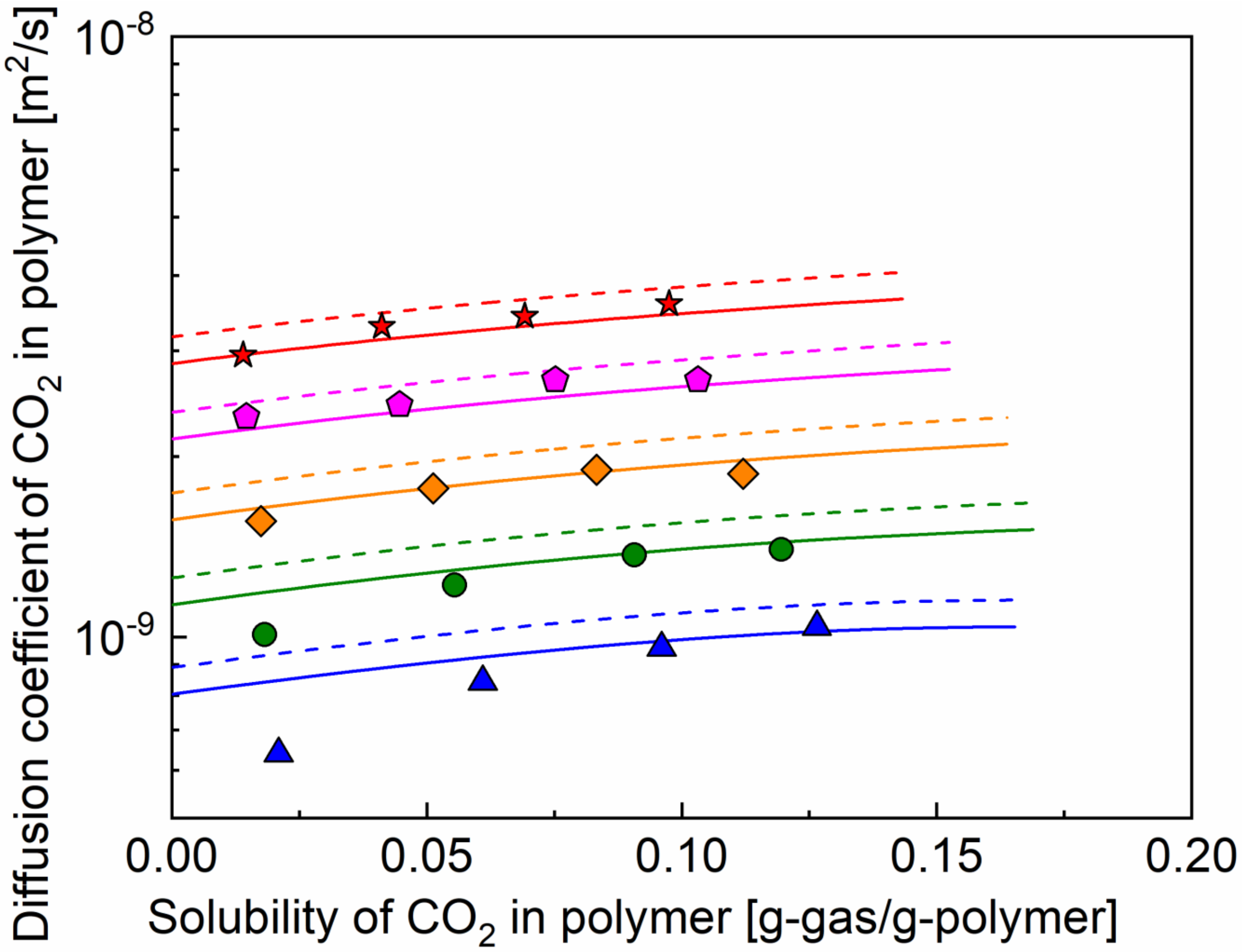

Fig. 8. Measured and calculated diffusion coefficients of CO_2 in PEAA 20 as functions of average solubility of CO_2 in polymers during sorption step at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★). Solid lines correspond to correlation results obtained using Eq. (24) where values of fitting parameters A_d and B_d in **Table 6** (dashed lines) and **Table 7** (solid lines) were used.

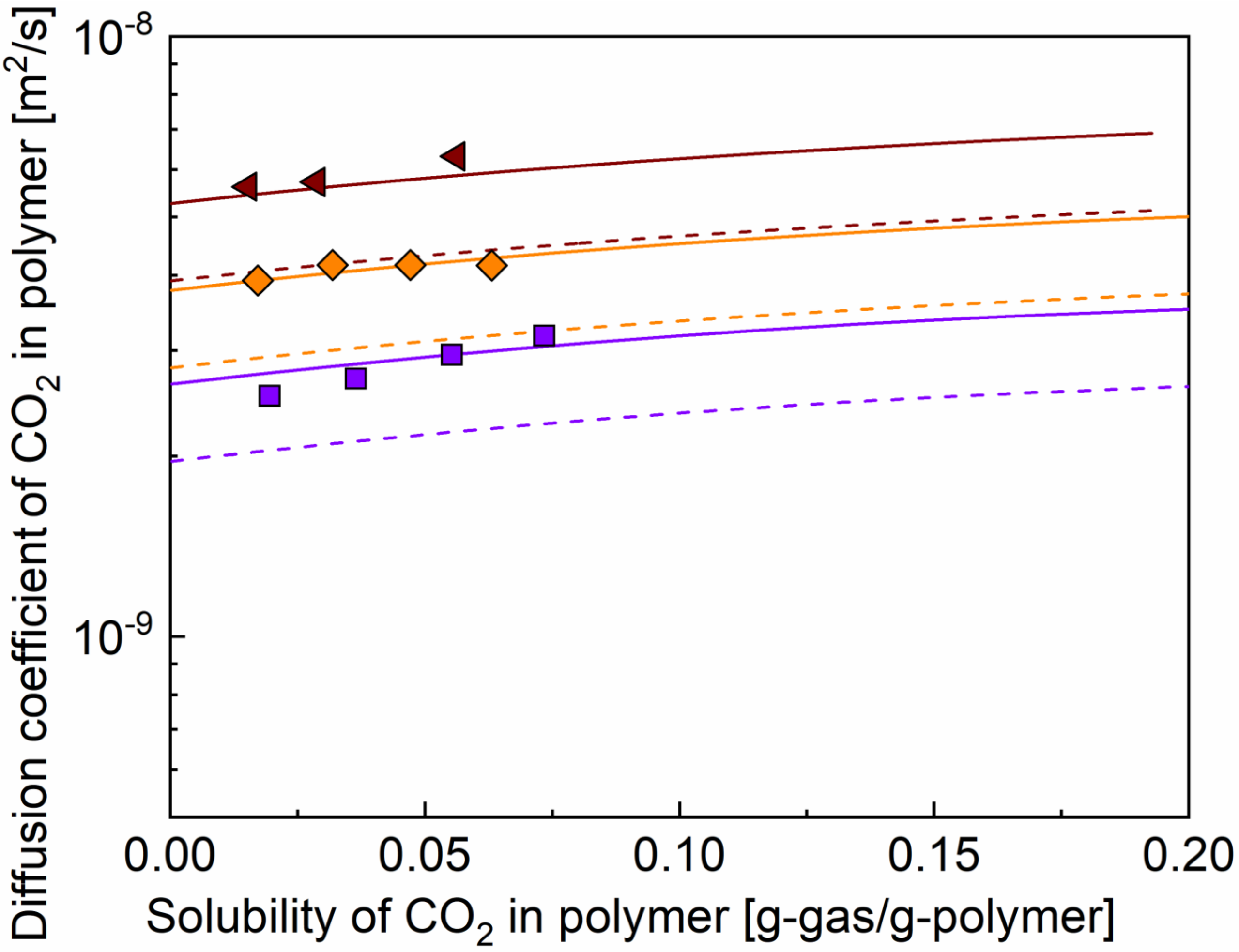

Fig. 9. Calculated diffusion coefficients of CO_2 in polyethylene [3] as functions of average solubility of CO_2 in polymers during sorption step at 393 K (◀) 423 K (◆), and 453 K (■). Solid lines correspond to correlation results obtained using Eq. (24) where values of fitting parameters A_d and B_d in **Table 6** (dashed lines) and **Table 7** (solid lines) were used.

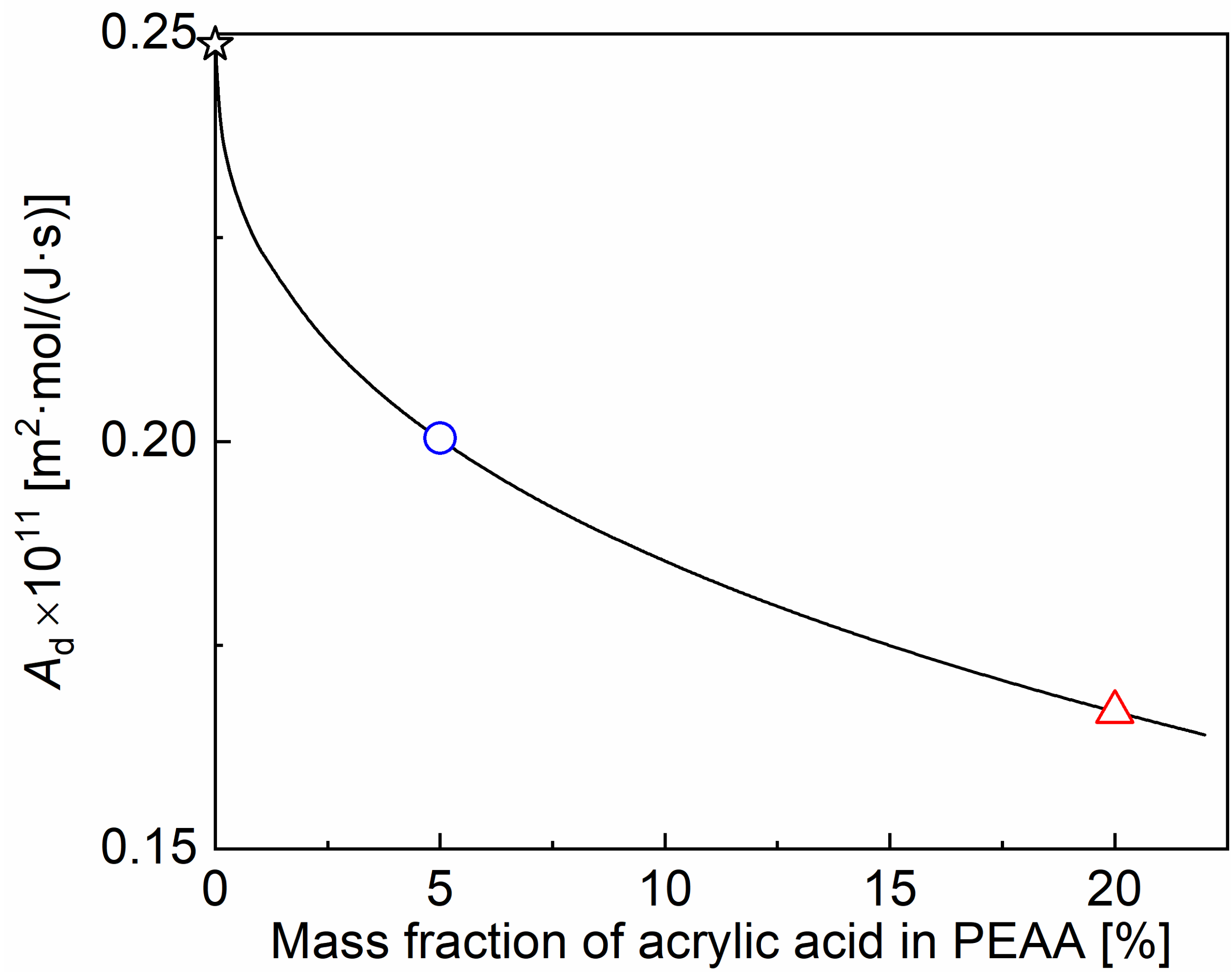

Fig. 10. Parameter A_{d} in Eq. (24) (as listed in **Table 7**) as function of mass fraction of acrylic acid in polymers (☆, polyethylene; ○, PEAA5; △, PEAA20, solid line: curve approximated using Eq. (30)).

Figure captions

Fig. 1 Sorption curves of CO_2 in PEAA5 (○) and PEAA20 (△) at 423 K for pressures of 0–5 MPa. Saturated solubility, S_{sat}, values were determined to be 0.0361 and 0.0349 g-gas/g-polymer, respectively, while diffusion coefficient, D, values were determined to be 2.9×10^{-9} and 1.6×10^{-9} m^2/s, respectively, for PEAA5 and PEAA20 (solid lines are fits obtained using Eq. (7)).

Fig. 2. Measured solubilities of CO_2 in PEAA5 at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★) and fits obtained using Sanchez–Lacombe equation of state (solid lines).

Fig. 3. Measured solubilities of CO_2 in PEAA20 at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★) and fits obtained using Sanchez–Lacombe equation of state (solid lines).

Fig. 4. Comparison of measured solubilities of CO_2 in polyethylene (☆)[3] , PEAA5 (○), and PEAA20 (△) at 423 K.

Fig. 5. Binary interaction parameter, k_{ij}, in Sanchez–Lacombe equation as determined by fitting solubilities of CO_2 in polyethylene (☆)[3] , PEAA5 (○), and PEAA20 (△). Solid (PEAA5) and dashed (PEAA20) lines are fitted curves for data obtained in this work using Eqs. (26) and (27), respectively.

Fig. 6. Henry's constant for dissolution of CO_2 in polyethylene (☆[3], ×[4]), PEAA5 (○), and PEAA20 (△). Solid (PEAA5) and dashed (PEAA20) lines are fitted curves for data obtained in this work using Eqs. (28) and (29), respectively.

Fig. 7. Measured and calculated diffusion coefficients of CO_2 in PEAA 5 as functions of average solubility of CO_2 in polymers during sorption step at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★). Lines correspond to correlation results obtained using Eq. (24) where values of fitting parameters A_d and B_d in **Table 6** (dashed lines) and **Table 7** (solid lines) were used.

Fig. 8. Measured and calculated diffusion coefficients of CO_2 in PEAA 20 as functions of average solubility of CO_2 in polymers during sorption step at 373 K (▲), 398 K (●), 423 K (◆), 448 K (⬟), and 473 K (★). Solid lines correspond to correlation results obtained using Eq. (24) where values of fitting parameters A_d and B_d in **Table 6** (dashed lines) and **Table 7** (solid lines) were used.

Fig. 9. Calculated diffusion coefficients of CO_2 in polyethylene [3] as functions of average solubility of CO_2 in polymers during sorption step at 393 K (◀) 423 K (◆), and 453 K (■). Solid lines correspond to correlation results obtained using Eq. (24) where values of fitting parameters A_d and B_d in **Table 6** (dashed lines) and **Table 7** (solid lines) were used.

Fig. 10. Parameter A_d in Eq. (24) (as listed in **Table 7**) as function of mass fraction of acrylic acid in polymers (☆, polyethylene; ○, PEAA5; △, PEAA20, solid line: curve approximated using Eq. (30)).