Supplementary Materials: Modelling Mixed-Gas Sorption in Glassy Polymers for CO_2 Removal: A Sensitivity Analysis of the Dual Mode Sorption Model

Eleonora Ricci , Maria Grazia De Angelis

1. Mixed-Gas Sorption Predictions with Dual Mode Sorption Model Best Fit Parameter Sets Obtained Through Different Parametrization Routes

1.1. Error-Weighted Sum of Squared Errors

Figures S1 to S3 show the comparison between mixed-gas sorption of CO_2 and CH_4 in PTMSP, PIM-1 and TZ-PIM calculated with the Dual Mode Sorption (DMS) model using two different best-fit parameter sets. Solid lines in the figures are obtained with best-fit parameters resulting from the minimization of the sum of squared errors, weighted using the experimental confidence intervals:

$$\chi^2 = \sum_{i=1}^{N} \frac{1}{\sigma_i^2} \left[c_i - \left(k_{D,i} f_i + \frac{C'_{H,i} b_i f_i}{1 + b_i f_i} \right) \right]^2 \quad \text{(S1)}$$

σ_i represents the confidence interval associated with the experimental value of the concentration c_i, N is the total number of experimental points, f_i is the gas fugacity and $k_{D,i}$, $C'_{H,i}$, b_i are the DMS parameters for the polymer-i penetrant couple.

Dashed lines in the figures are obtained with best-fit parameters resulting from minimizing the sum of squared errors, unweighted:

$$\chi^2 = \sum_{i=1}^{N} \left[c_i - \left(k_{D,i} f_i + \frac{C'_{H,i} b_i f_i}{1 + b_i f_i} \right) \right]^2 \quad \text{(S2)}$$

The parameter sets obtained using Equation S1 or Equation S2 are reported in Table 1 and Table 2 in the main text, respectively.

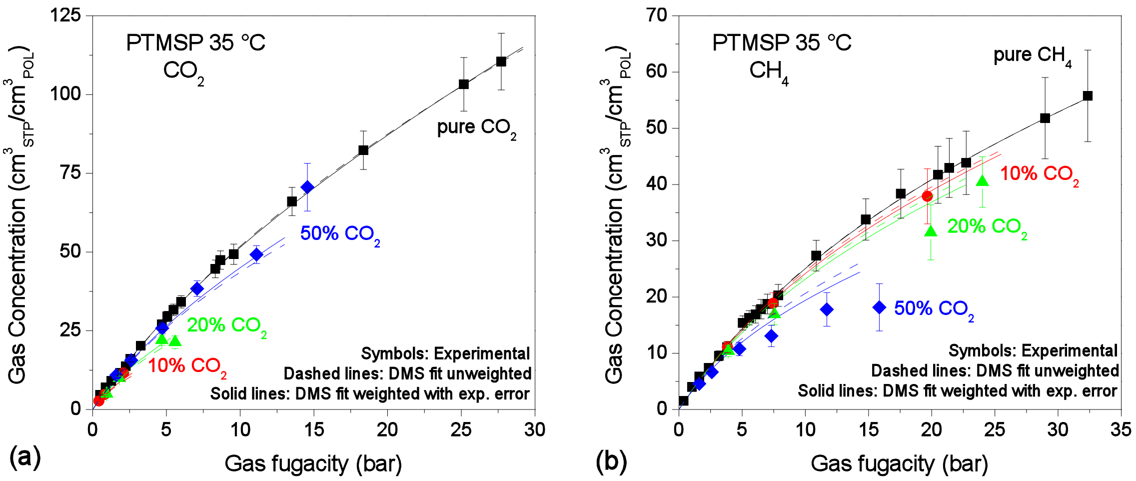

Figure S1. Sorption isotherms of (**a**) CO_2 and (**b**) CH_4 at 35 °C in poly(trimethylsilyl propyne) (PTMSP), in pure and mixed-gas conditions (Black squares: pure gas; Red circles: ~10% CO_2 mixture; Green triangles: ~20% CO_2 mixture; Blue diamonds: ~50% CO_2 mixture). Exp. data from [1]. Solid lines are Dual Mode Sorption (DMS) model predictions obtained using the parameters reported in Table 1 in the main text. Dashed lines are DMS model predictions obtained with parameters reported in Table 2 in the main text.

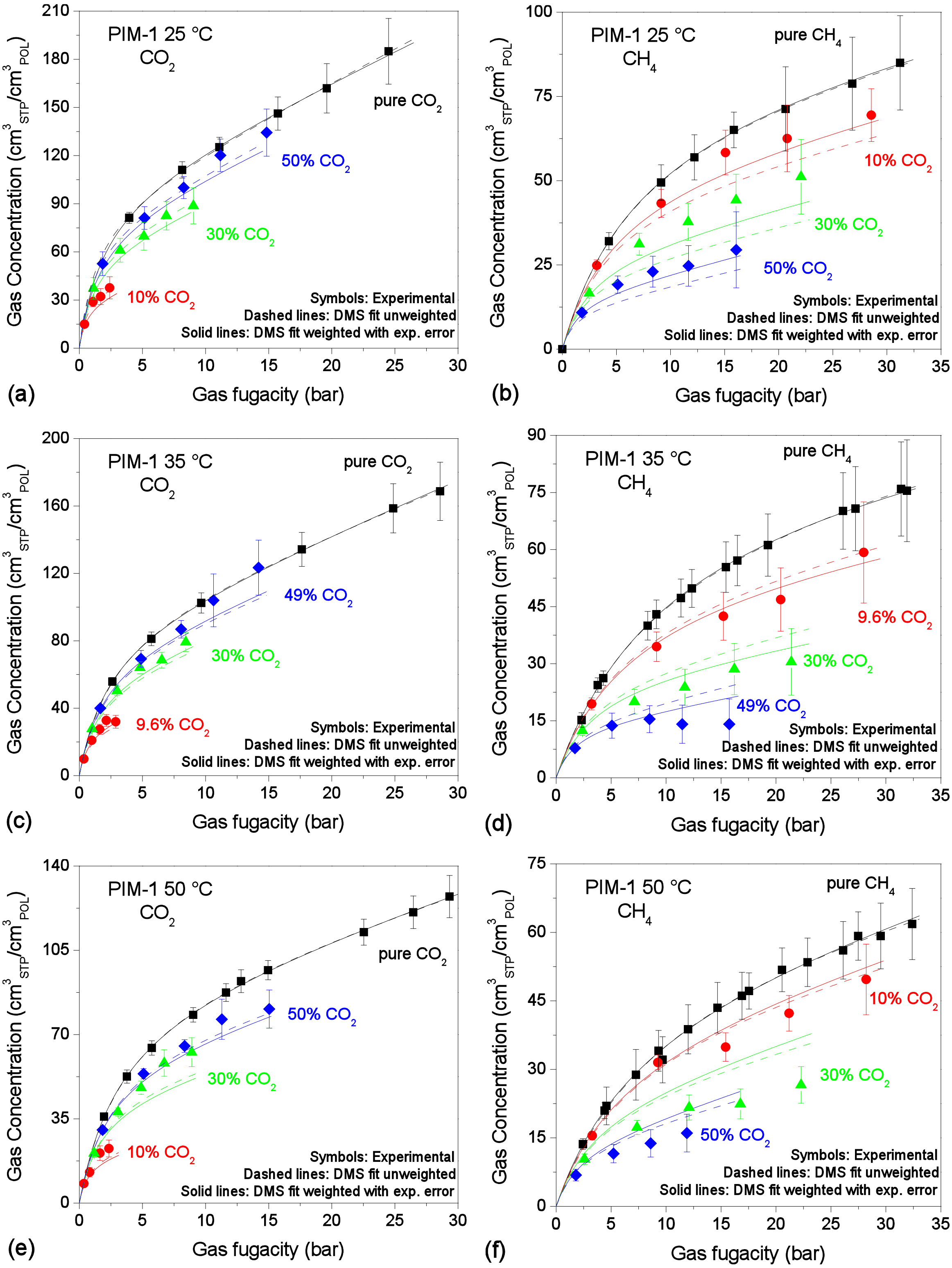

Figure S2. Sorption isotherms of CO_2 and CH_4 at 25 °C (**a**,**b**), 35 °C (**c**,**d**), 50 °C (**e**,**f**) in PIM-1, in pure and mixed-gas conditions (Black squares: pure gas; Red circles: ~10% CO_2 mixture; triangles: ~30% CO_2 mixture; Blue diamonds: ~50% CO_2 mixture). Experimental data from [2,3]. Solid lines represent DMS model predictions obtained using the parameters reported in Table 1 in the main text. Dashed lines are DMS model predictions obtained with parameters reported in Table 2 in the main text.

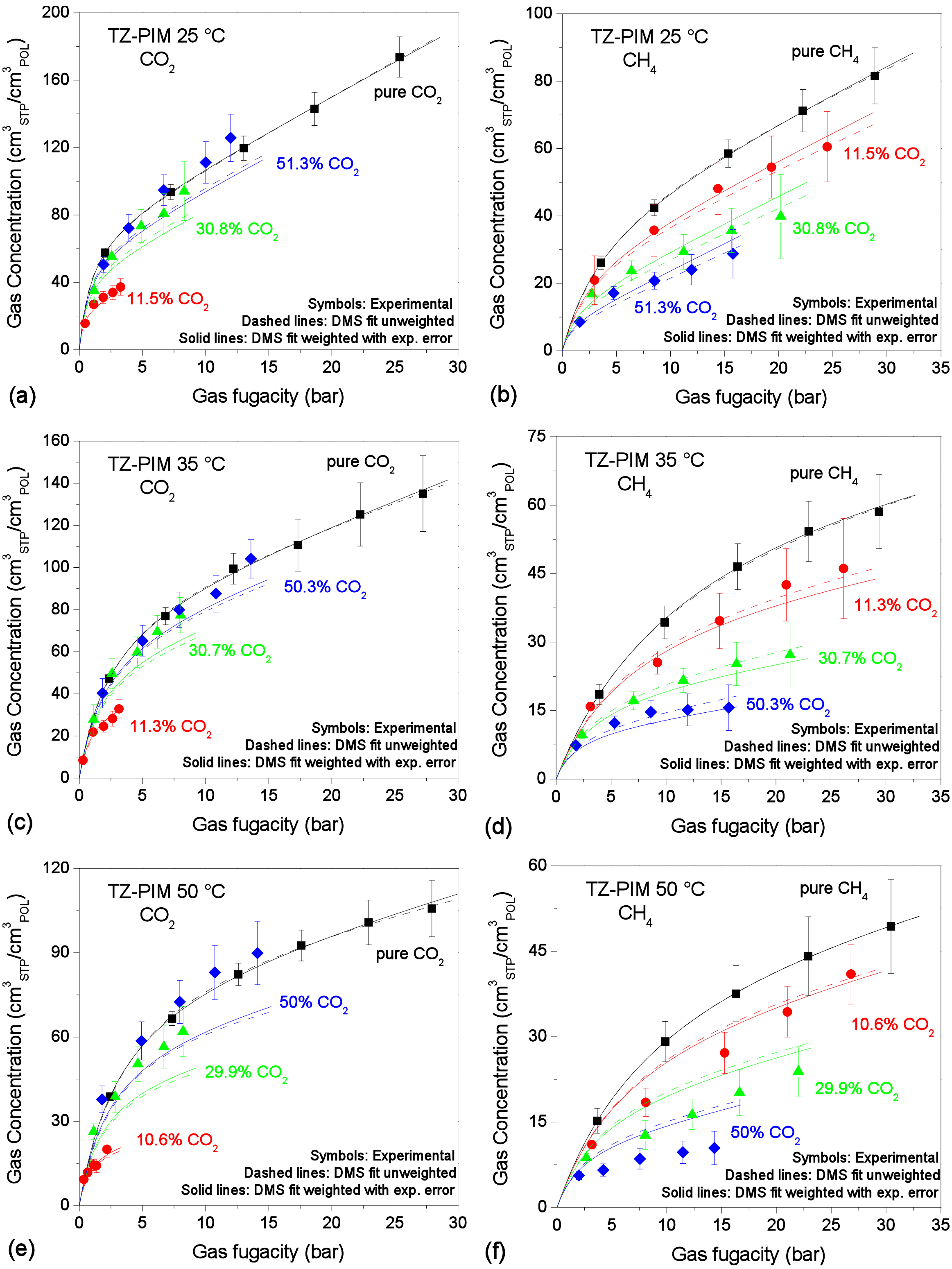

Figure S3. Sorption isotherms of CO_2 and CH_4 at 25 °C (**a**,**b**), 35 °C (**c**,**d**), 50 °C (**e**,**f**) in TZ-PIM, in pure and mixed-gas conditions (Black squares: pure gas; Red circles: ~10% CO_2 mixture; Green triangles: ~30% CO_2 mixture; Blue diamonds: ~50% CO_2 mixture). Experimental data from [4]. Solid lines represent DMS model predictions obtained using the parameters reported in Table 1 in the main text. Dashed lines are DMS model predictions obtained with parameters reported in Table 2 in the main text.

1.2. Constrained Temperature Dependence

Figures S4 and S5 show the comparison between mixed-gas sorption of CO_2 and CH_4 in PIM-1 and TZ-PIM calculated with the Dual Mode Sorption (DMS) model using two different best-fit parameter sets.

Dashed lines in the figures are obtained with best-fit parameters reported in Table 1 in the main text, resulting from minimizing the sum of squared errors, unweighted (Equation S2).

Solid lines in the figures are obtained with best-fit parameters reported in Table 2 in the main text, resulting from the simultaneous minimization of the sum of squared errors at three temperatures, imposing a van't Hof temperature dependence to b and k_D, and constraining C'_H to decrease as temperature increases.

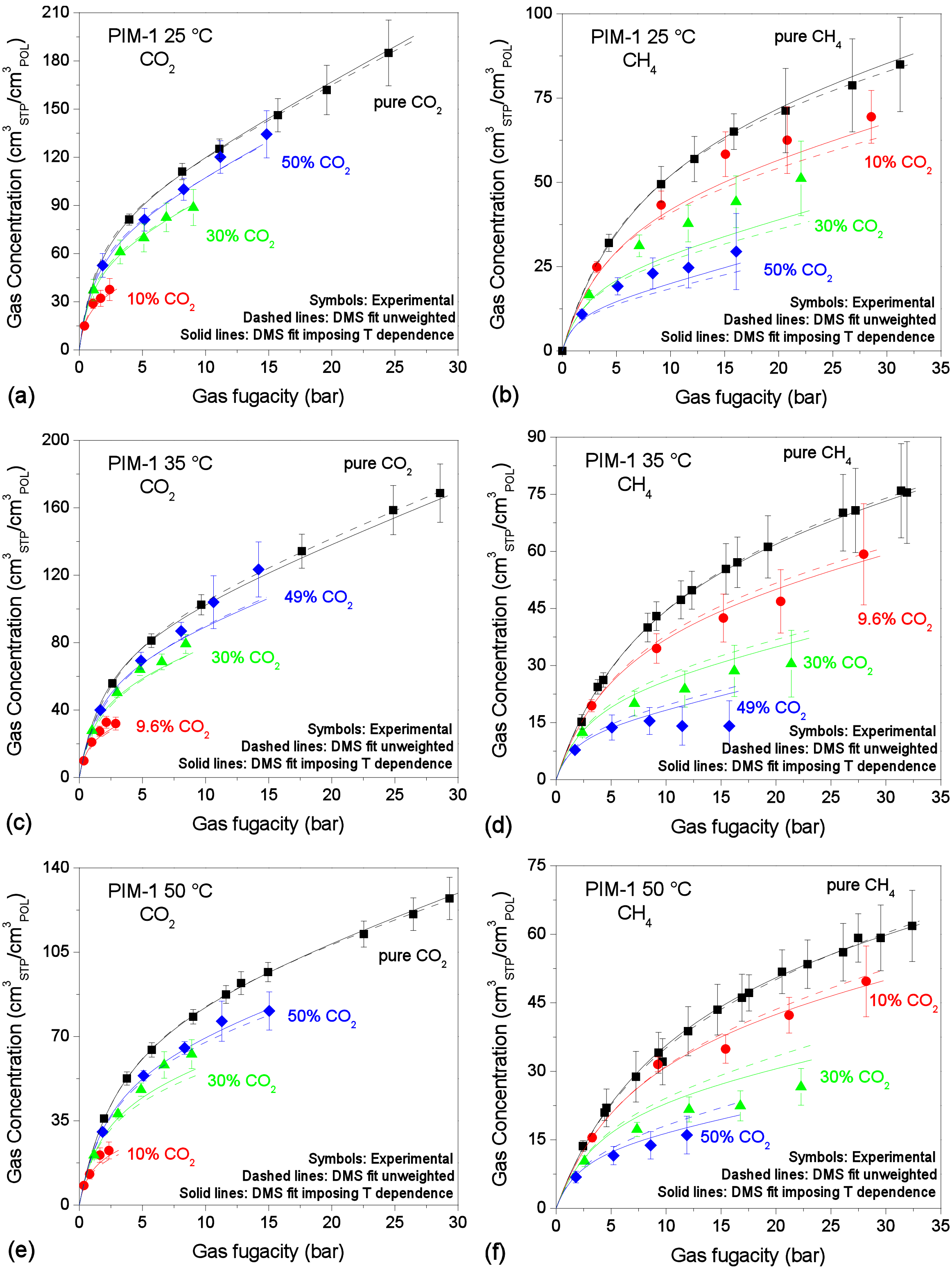

Figure S4. Sorption isotherms of CO_2 and CH_4 at 25 °C (**a**,**b**), 35 °C (**c**,**d**), 50 °C (**e**,**f**) in PIM-1, in pure and mixed-gas conditions (Black squares: pure gas; Red circles: ~10% CO_2 mixture; Green triangles: ~30% CO_2 mixture; Blue diamonds: ~50% CO_2 mixture). Experimental data from [2,3]. Solid lines represent DMS model predictions obtained using the parameters reported in Table 3 in the main text. Dashed lines are DMS model predictions obtained with parameters reported in Table 1 in the main text.

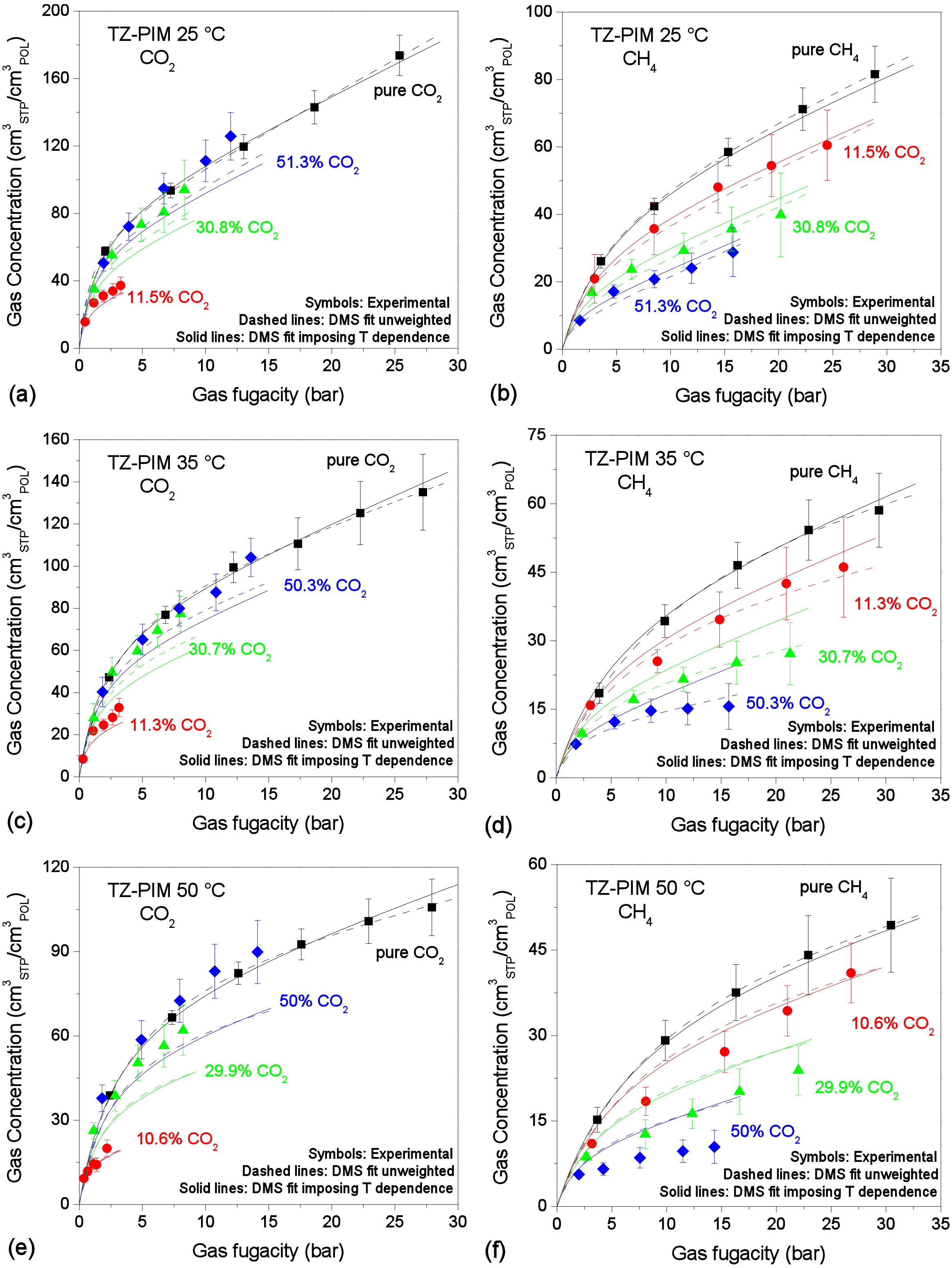

Figure S5. Sorption isotherms of CO_2 and CH_4 at 25 °C (**a**,**b**), 35 °C (**c**,**d**), 50 °C (**e**,**f**) in TZ-PIM, in pure and mixed-gas conditions (Black squares: pure gas; Red circles: ~10% CO_2 mixture; Green triangles: ~30% CO_2 mixture; Blue diamonds: ~50% CO_2 mixture). Experimental data from [4]. Solid lines represent DMS model predictions obtained using the parameters reported in Table 3 in the main text. Dashed lines are DMS model predictions obtained with parameters reported in Table 1 in the main text.

2. Sensitivity Analysis of the Dual Mode Sorption Model Predictions of CO_2 and CH_4 Sorption in PIM-1 in Multicomponent Conditions

2.1. Effect of b_{CO_2} on the Calculated Mixed-Gas Sorption of CH_4 in PIM-1

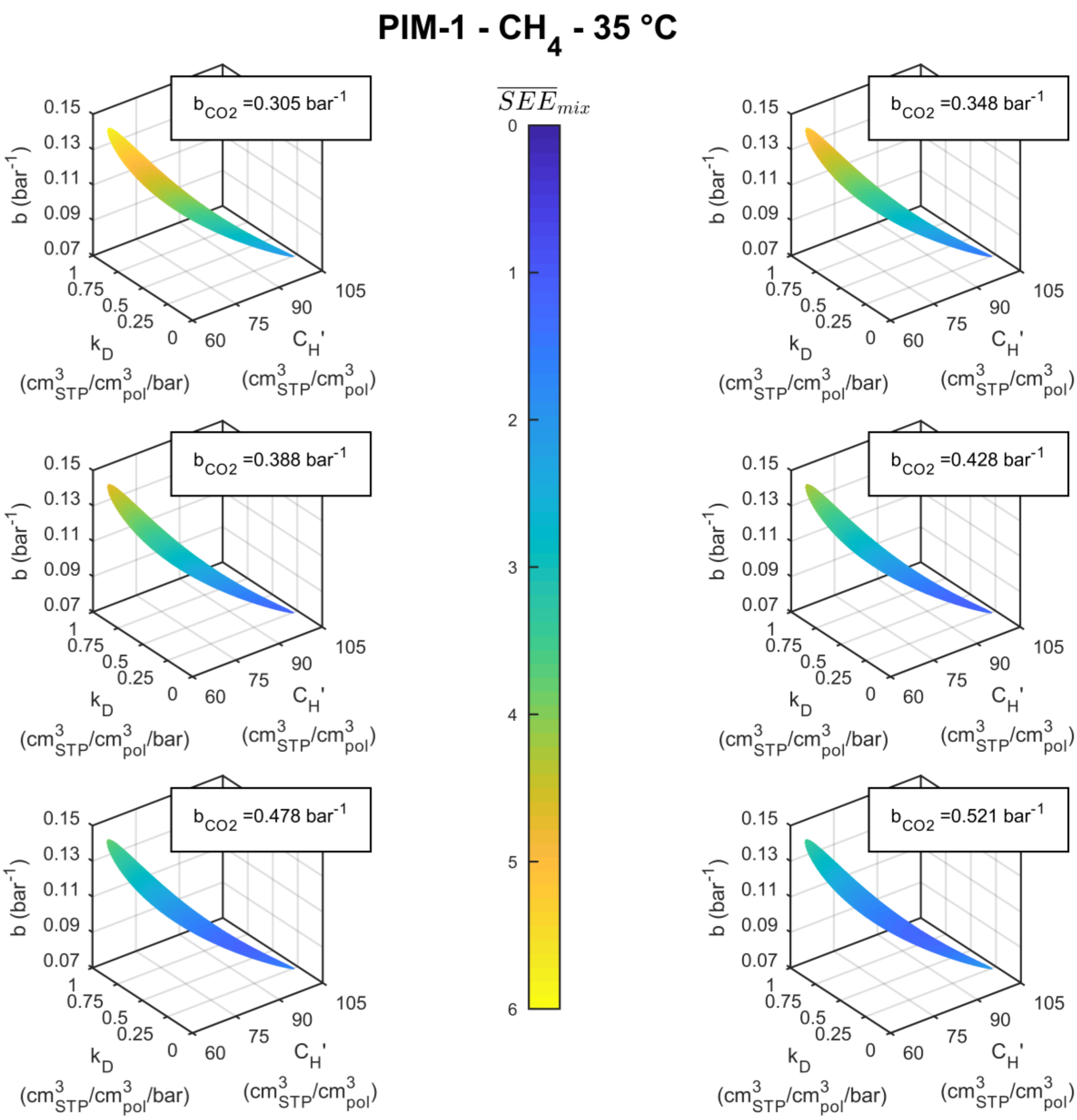

Figure S6. Isosurfaces the DMS model parameter space for CH_4 sorption in PIM-1 at 35 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CO_2}.

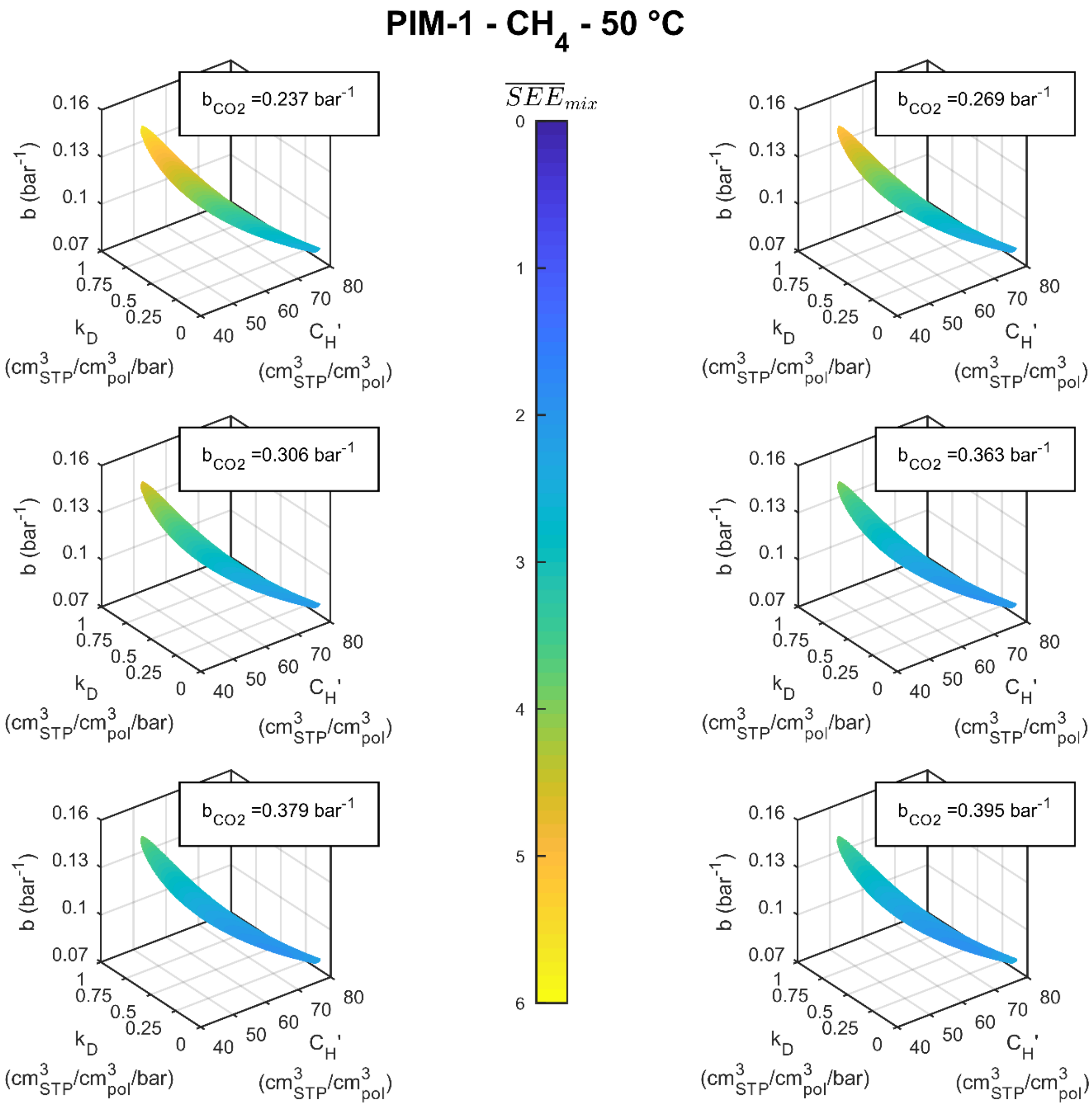

Figure S7. Isosurfaces the DMS model parameter space for CH_4 sorption in PIM-1 at 50 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CO_2}.

2.2. Confidence Intervals of CO_2/PIM-1 DMS Model Parameters

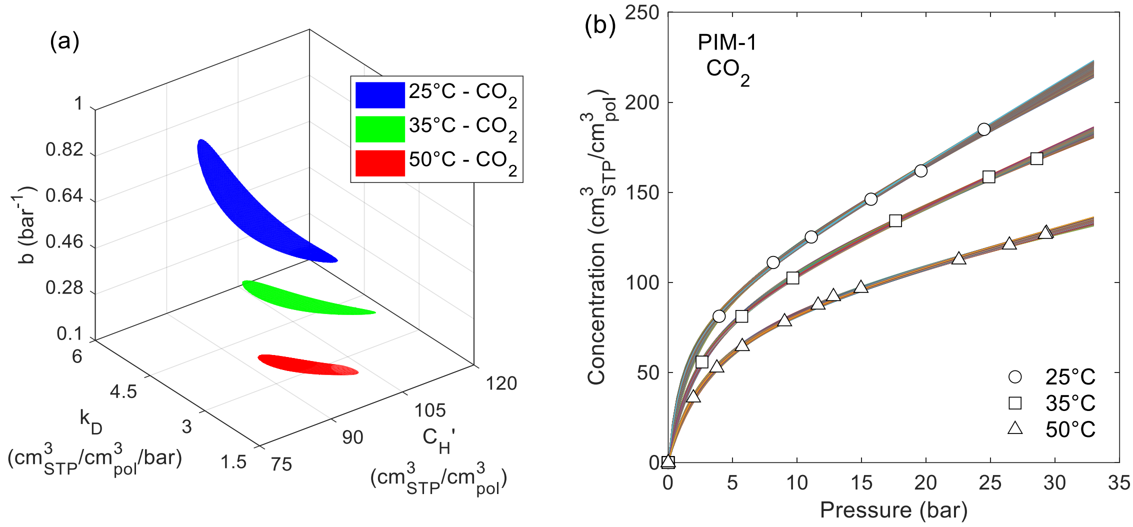

Figure S8. (**a**) Surfaces enclosing the range where DMS parameter sets yield *SEE* < *SEE*$_{max}$ in the prediction of CO_2 sorption in PIM-1 at three different temperatures; (**b**) CO_2 sorption isotherms in PIM-1 at 25, 35 and 50 °C, calculated with all the parameter sets enclosed by the corresponding coloured regions in the plot on the left.

Table S1. Confidence intervals of the fugacity-based DMS parameters yielding and average relative deviation < 1.5% in the calculation of CO_2 sorption in PIM-1 at three different temperatures.

T (°C)	k_{D,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	C'_{H,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}}\right)$	b_{CO_2} (bar^{-1})
25	$4.046^{+0.253}_{-0.552}$	$90.04^{+16.57}_{-6.50}$	$0.710^{+0.272}_{-0.291}$
35	$2.890^{+0.311}_{-0.308}$	$94.83^{+12.53}_{-10.15}$	$0.388^{+0.133}_{-0.083}$
50	$1.596^{+0.325}_{-0.096}$	$89.30^{+6.47}_{-10.88}$	$0.290^{+0.105}_{-0.053}$

2.3. Uncertainty in Mixed-Gas Sorption of CO_2 in PIM-1

Set 1 and Set 2 reported in Table S2 correspond, respectively, to the highest and lowest accuracy in the prediction of mixed-gas sorption of CO_2 in PIM-1, among all the parameter sets belonging to the confidence regions displayed in Figure S8.

Table S2. DMS model fugacity-based parameter sets used in the calculation of mixed-gas sorption of CO_2 in PIM-1 reported in Figure S9.

	T (°C)	k_{D,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	C'_{H,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}}\right)$	b_{CO_2} (bar^{-1})	SEE_{pure} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	$\overline{SEE}_{mix}$ $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$
Set 1	25	4.284	84.93	0.822	1.998	2.41
	35	3.156	85.69	0.518	1.791	2.28
	50	1.906	78.01	0.395	1.498	1.92
Set 2	25	3.532	105.85	0.413	1.999	6.00
	35	2.599	105.40	0.299	1.797	4.93
	50	1.500	94.87	0.238	1.482	2.77

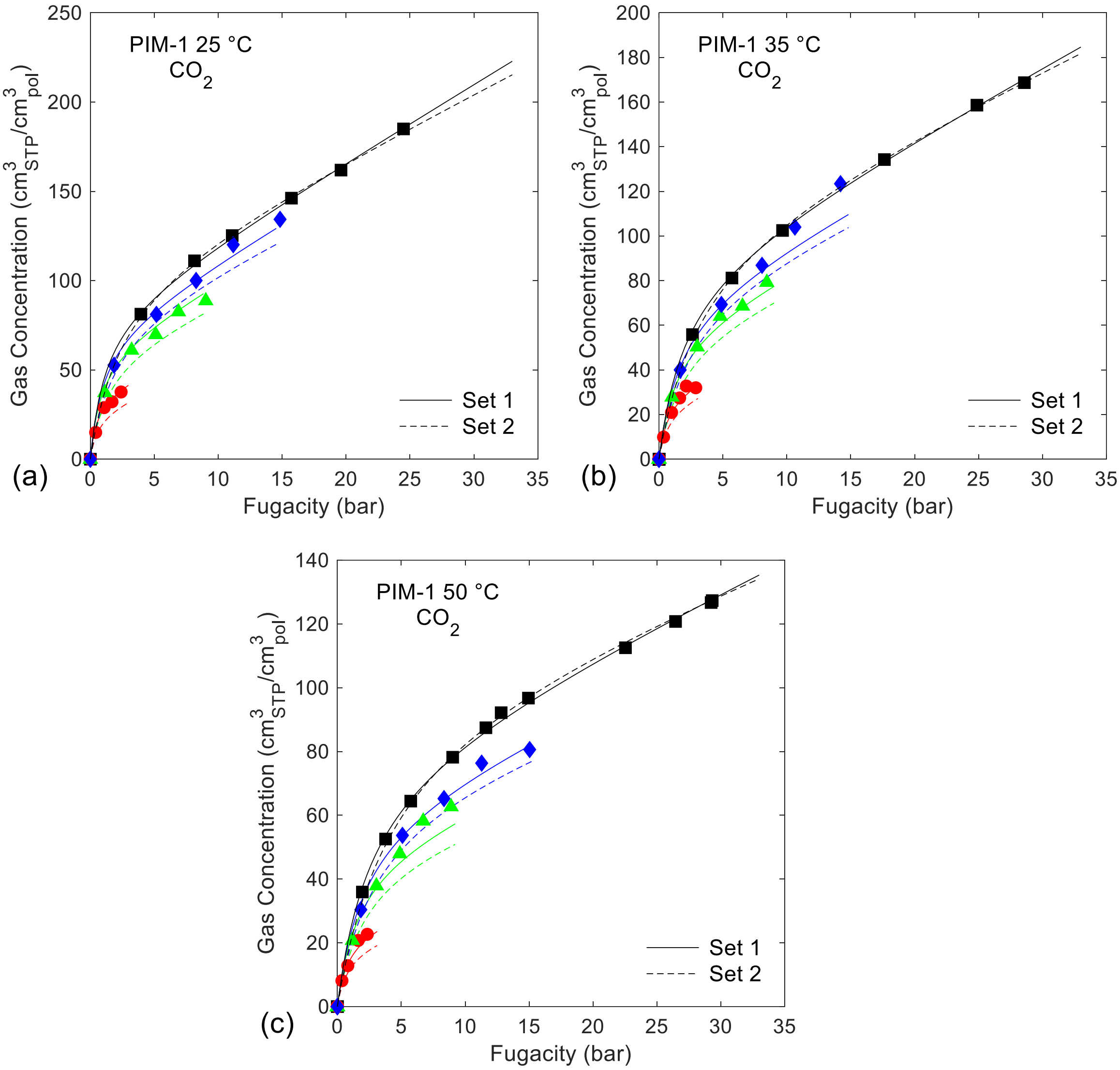

Figure S9. Dual Mode Sorption model mixed-gas predictions of CO_2 sorption in PIM-1 at 25 °C (**a**), 35 °C (**b**), 50 °C (**c**) obtained with the two parameter sets reported in Table S2.

2.4. Effect of b_{CH_4} *on the Calculated Mixed-Gas Sorption of CO2 in PIM-1*

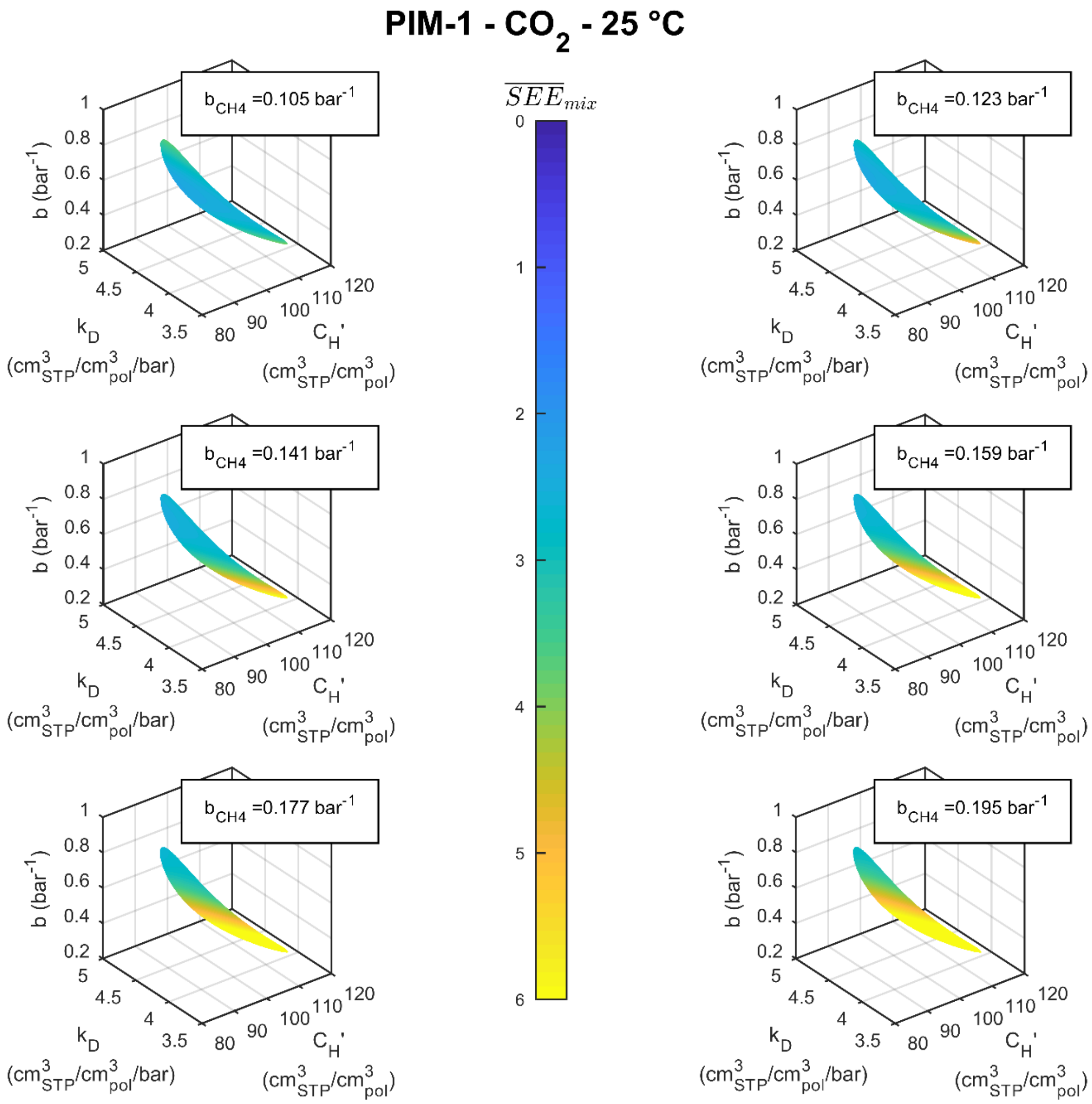

Figure S10. Isosurfaces the DMS model parameter space for CO_2 sorption in PIM-1 at 25 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CH_4}.

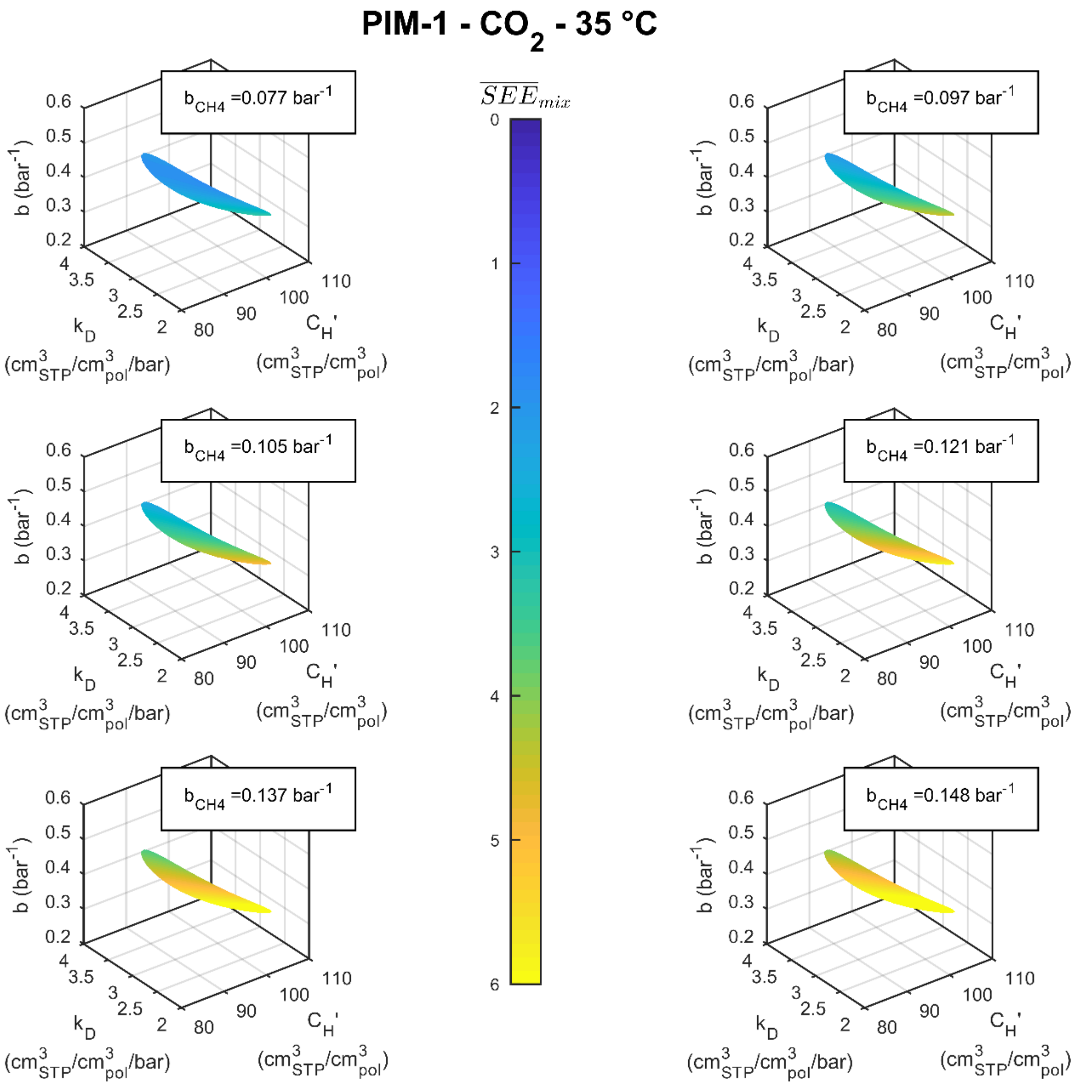

Figure S11. Isosurfaces the DMS model parameter space for CO_2 sorption in PIM-1 at 35 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CH_4}.

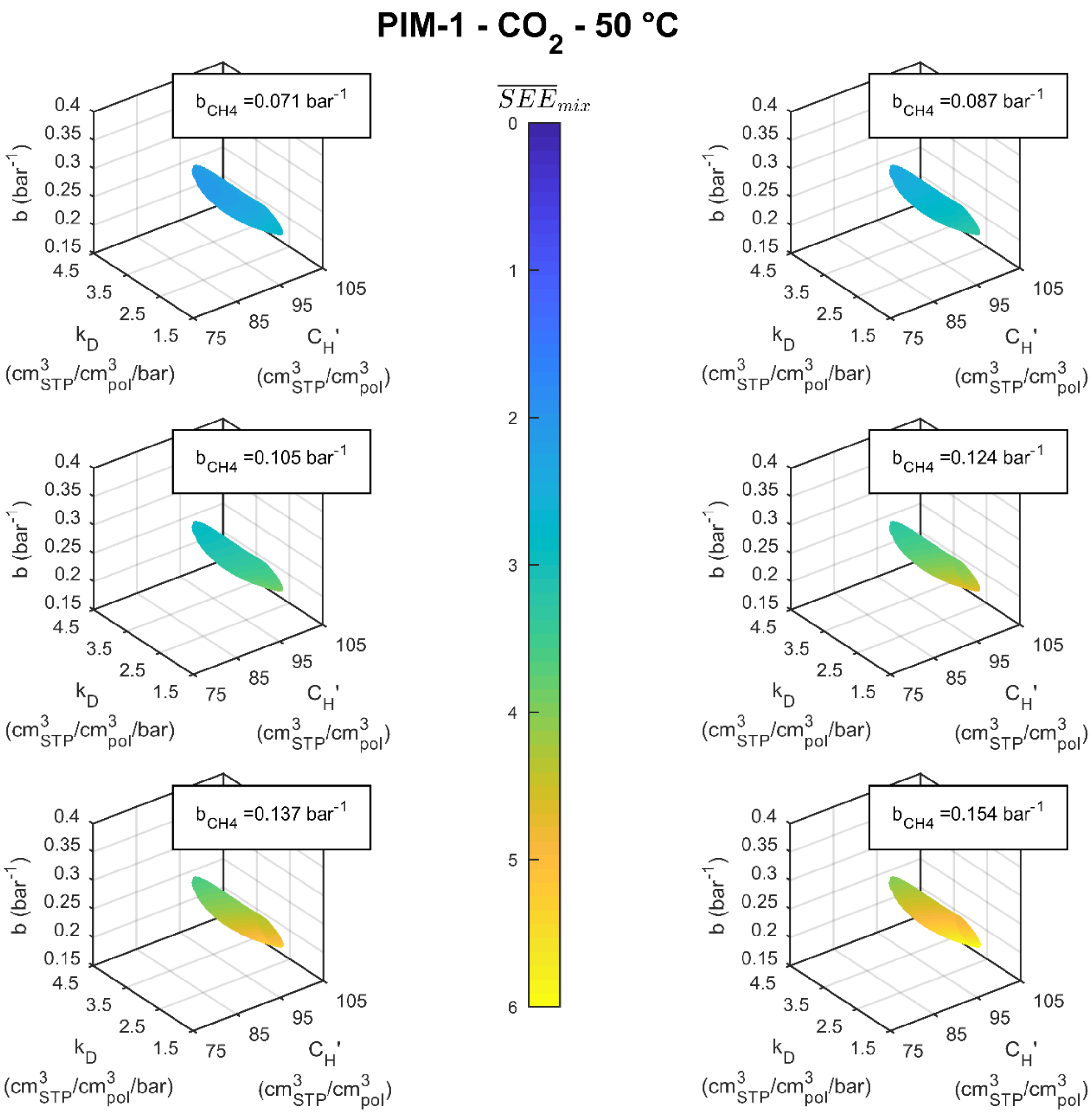

Figure S12. Isosurfaces in the DMS model parameter space for CO_2 sorption in PIM-1 at 50 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CH_4}.

3. Sensitivity Analysis of the Dual Mode Sorption Model Predictions of CO_2 and CH_4 Sorption in TZ-PIM in Multicomponent Conditions

3.1. Confidence Intervals of CO_2/TZ-PIM and CH_4/TZ-PIM DMS Model Parameters

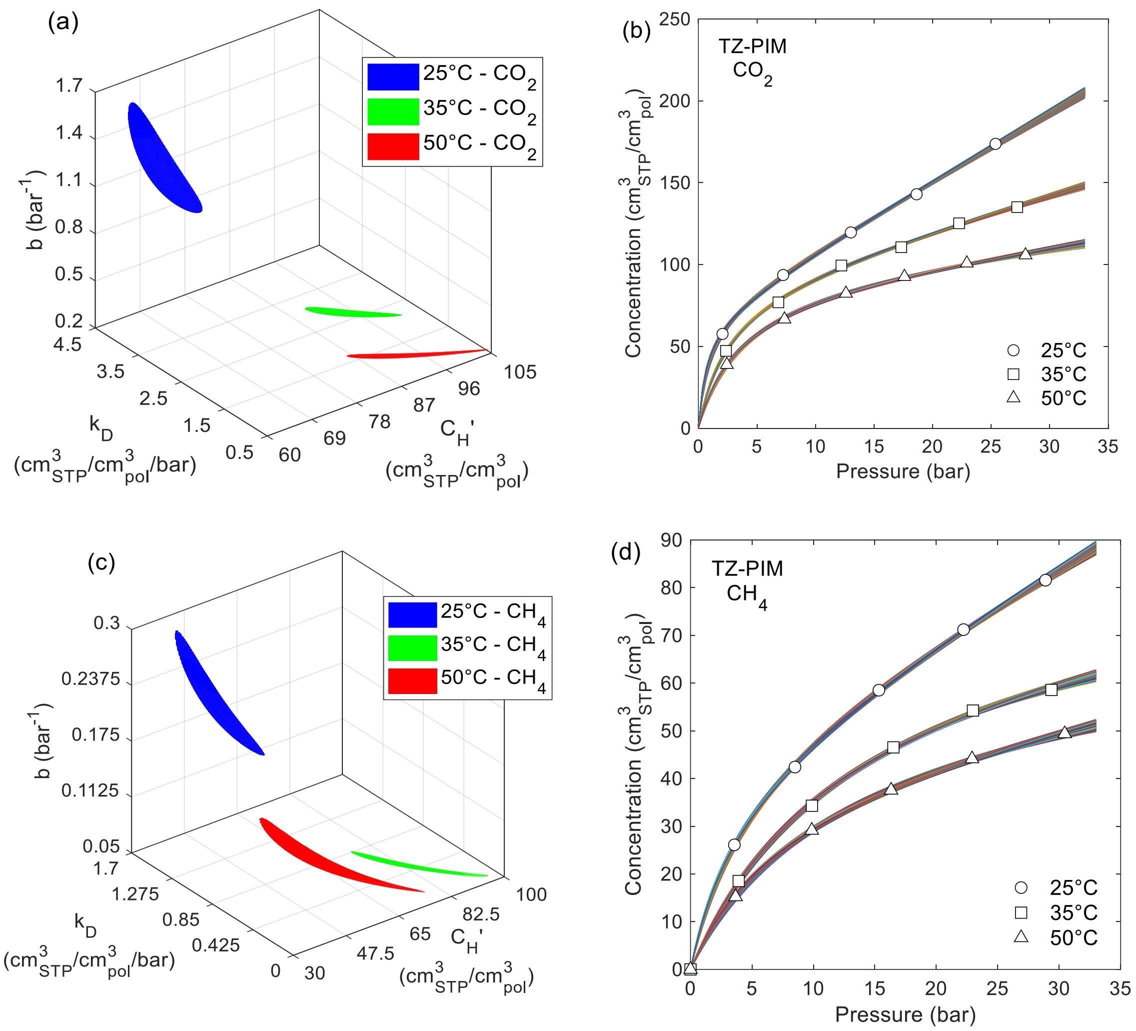

Figure S13. Surfaces enclosing the range where DMS parameter sets yield *SEE* < *SEE$_{max}$* in the prediction of (**a**) CO_2 and (**c**) CH_4 sorption in TZ-PIM at three different temperatures; (**b**) CO_2 and (**d**) CH_4 sorption isotherms in TZ-PIM calculated with all the parameter sets enclosed by the corresponding coloured region in the plot on the left.

Table S3. Confidence intervals of the fugacity-based DMS parameters (average relative deviation < 1.5%) for CO_2 and CH_4 sorption in TZ-PIM at three different temperatures.

T (°C)	k_{D,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	C'_{H,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}}\right)$	b_{CO_2} (bar^{-1})	k_{D,CH_4} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	C'_{H,CH_4} $\left(\frac{cm^3_{STP}}{cm^3_{pol}}\right)$	b_{CH_4} (bar^{-1})
25	$4.127^{+0.224}_{-0.234}$	$70.58^{+5.75}_{-5.28}$	$1.127^{+0.474}_{-0.278}$	$1.400^{+0.191}_{-0.226}$	$48.09^{+9.50}_{-7.13}$	$0.214^{+0.080}_{-0.055}$
35	$1.982^{+0.226}_{-0.255}$	$89.53^{+8.15}_{-7.18}$	$0.378^{+0.084}_{-0.062}$	$0.378^{+0.066}_{-0.378}$	$67.12^{+27.58}_{-3.99}$	$0.087^{+0.012}_{-0.029}$
50	$0.903^{+0.307}_{-0.346}$	$92.42^{+12.85}_{-10.35}$	$0.263^{+0.070}_{-0.055}$	$0.350^{+0.244}_{-0.292}$	$51.41^{+22.33}_{-13.26}$	$0.101^{+0.047}_{-0.035}$

3.2. Uncertainty in Mixed-Gas Sorption of CO_2 and CH_4 in TZ-PIM

Set 1 and Set 2 reported in Table S3 correspond, respectively, to the highest and lowest accuracy in the prediction of mixed-gas sorption of CO_2 and CH_4 in TZ-PIM, among all the parameter sets belonging to the confidence regions displayed in Figure S13.

Table S4. DMS model fugacity-based parameter sets used in the calculation of mixed-gas sorption of CO_2 and CH_4 in TZ-PIM reported in Figure S14.

	T (°C)	k_{D,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	C'_{H,CO_2} $\left(\frac{cm^3_{STP}}{cm^3_{pol}}\right)$	b_{CO_2} (bar^{-1})	SEE_{pure} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	$\overline{SEE}_{mix}$ $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$
Set 1	25	4.179	70.03	1.270	1.993	7.62
	35	2.150	84.07	0.454	1.898	5.16
	50	1.153	83.35	0.333	1.591	7.60
Set 2	25	3.961	75.19	0.849	1.995	9.35
	35	1.807	95.82	0.316	1.896	7.50
	50	0.626	103.55	0.209	1.597	11.07
	T (°C)	k_{D,CH_4} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	C'_{H,CH_4} $\left(\frac{cm^3_{STP}}{cm^3_{pol}}\right)$	b_{CH_4} (bar^{-1})	SEE_{pure} $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$	$\overline{SEE}_{mix}$ $\left(\frac{cm^3_{STP}}{cm^3_{pol}bar}\right)$
Set 1	25	1.393	47.23	0.239	1.049	1.83
	35	0.280	73.01	0.081	0.947	1.14
	50	0.010	71.73	0.067	0.798	2.17
Set 2	25	1.174	57.59	0.160	1.068	3.73
	35	0.071	93.98	0.058	0.949	3.34
	50	0.594	30.715	0.152	0.799	5.63

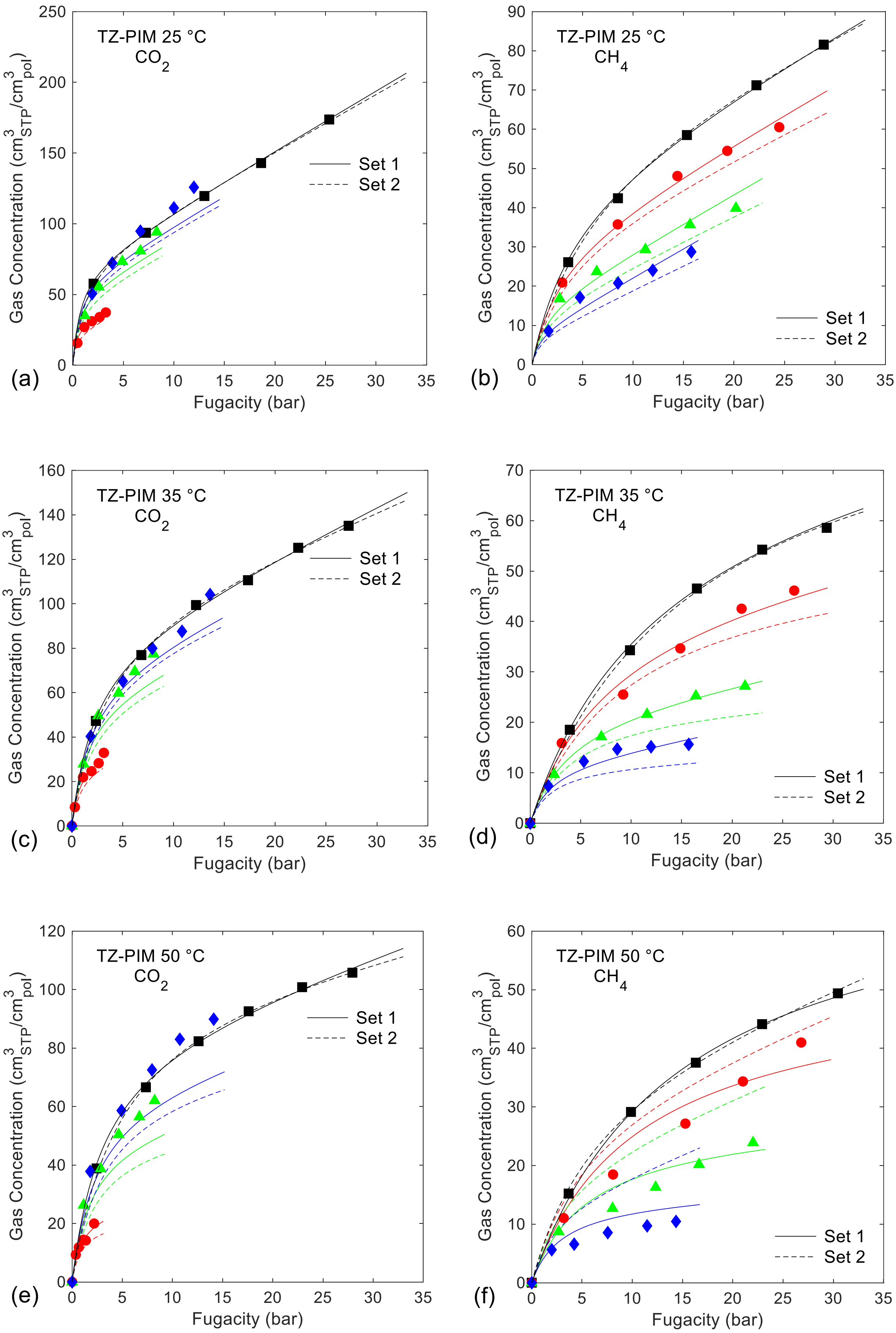

Figure S14. Dual Mode Sorption model mixed-gas predictions of CO_2 and CH_4 at 25 °C (**a**,**b**), 35 °C (**c**,**d**), 50 °C (**e**,**f**) in TZ-PIM, obtained with the two parameter sets reported in in Table S3. Solid lines are obtained with Set 1, dashed ones with Set 2.

3.3. Effect of b_{CO_2} on the Calculated Mixed-Gas Sorption of CH_4 in TZ-PIM

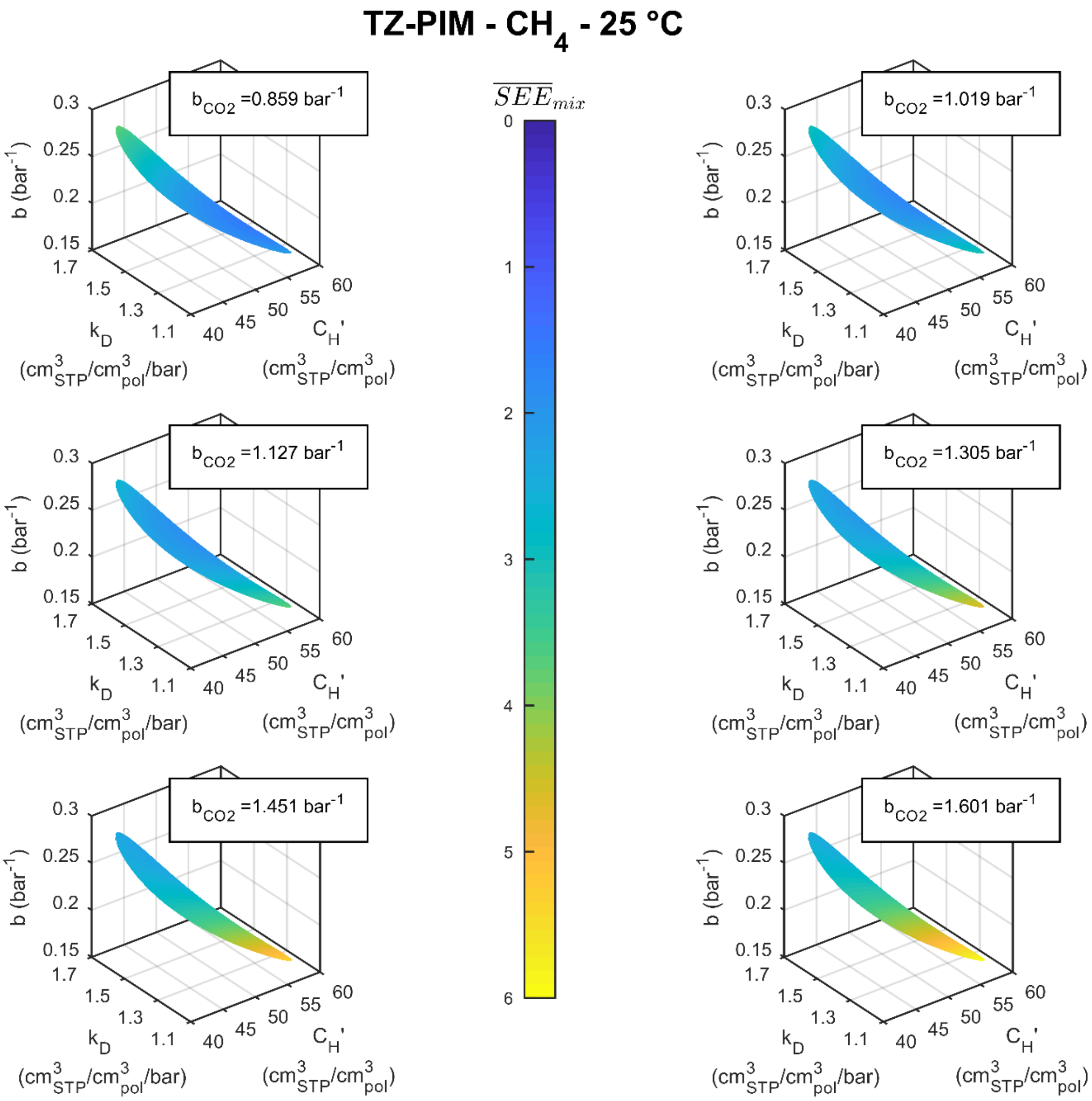

Figure S15. Isosurfaces in the DMS model parameter space for CH_4 sorption in TZ-PIM at 25 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CO_2}.

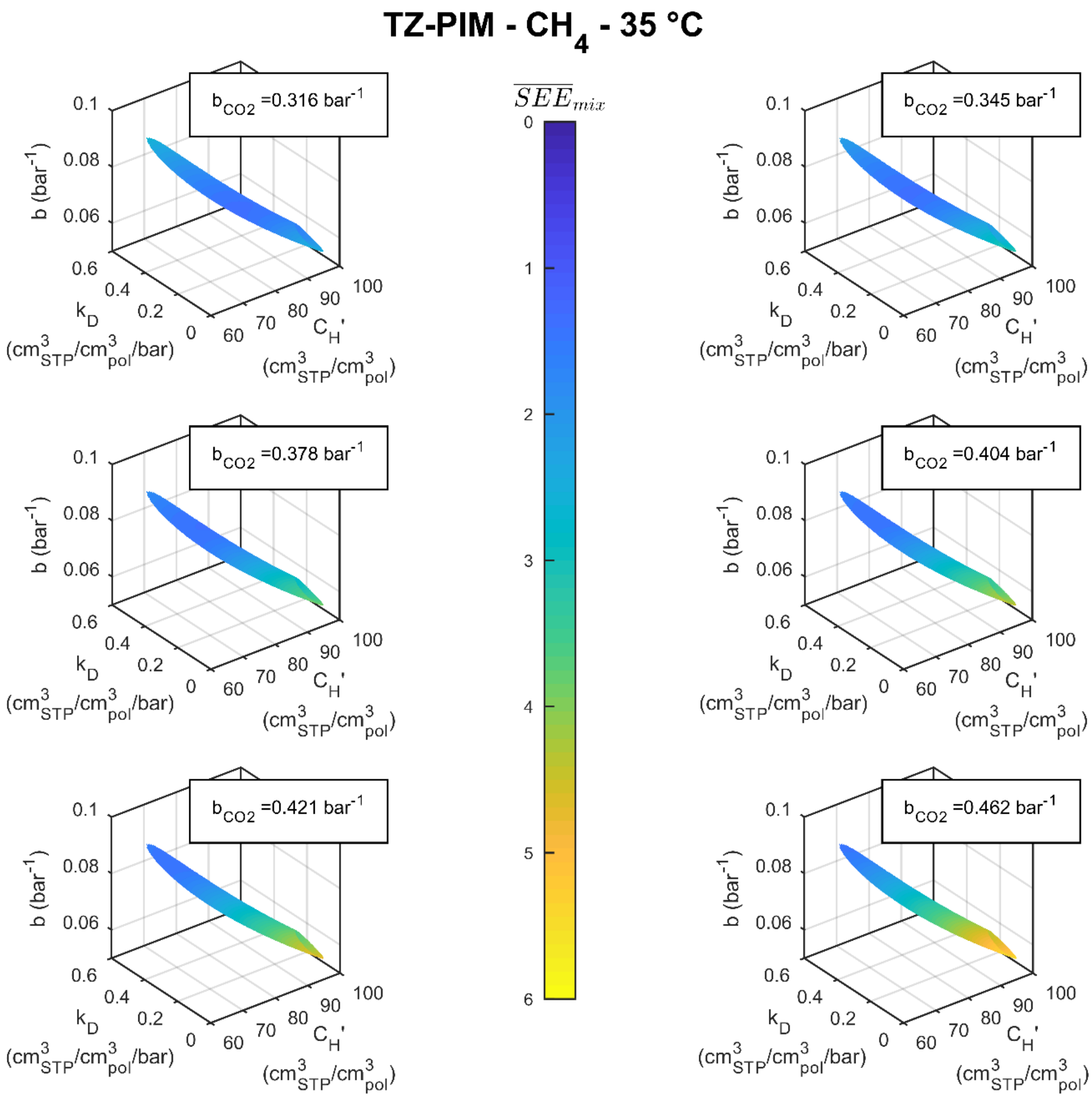

Figure S16. Isosurfaces in the DMS model parameter space for CH_4 sorption in TZ-PIM at 35 °C corresponding to *SEE*$_{pure}$ < *SEE*$_{max}$, coloured according to the average *SEE*$_{mix}$ obtained with different values within the confidence interval of b_{CO_2}.

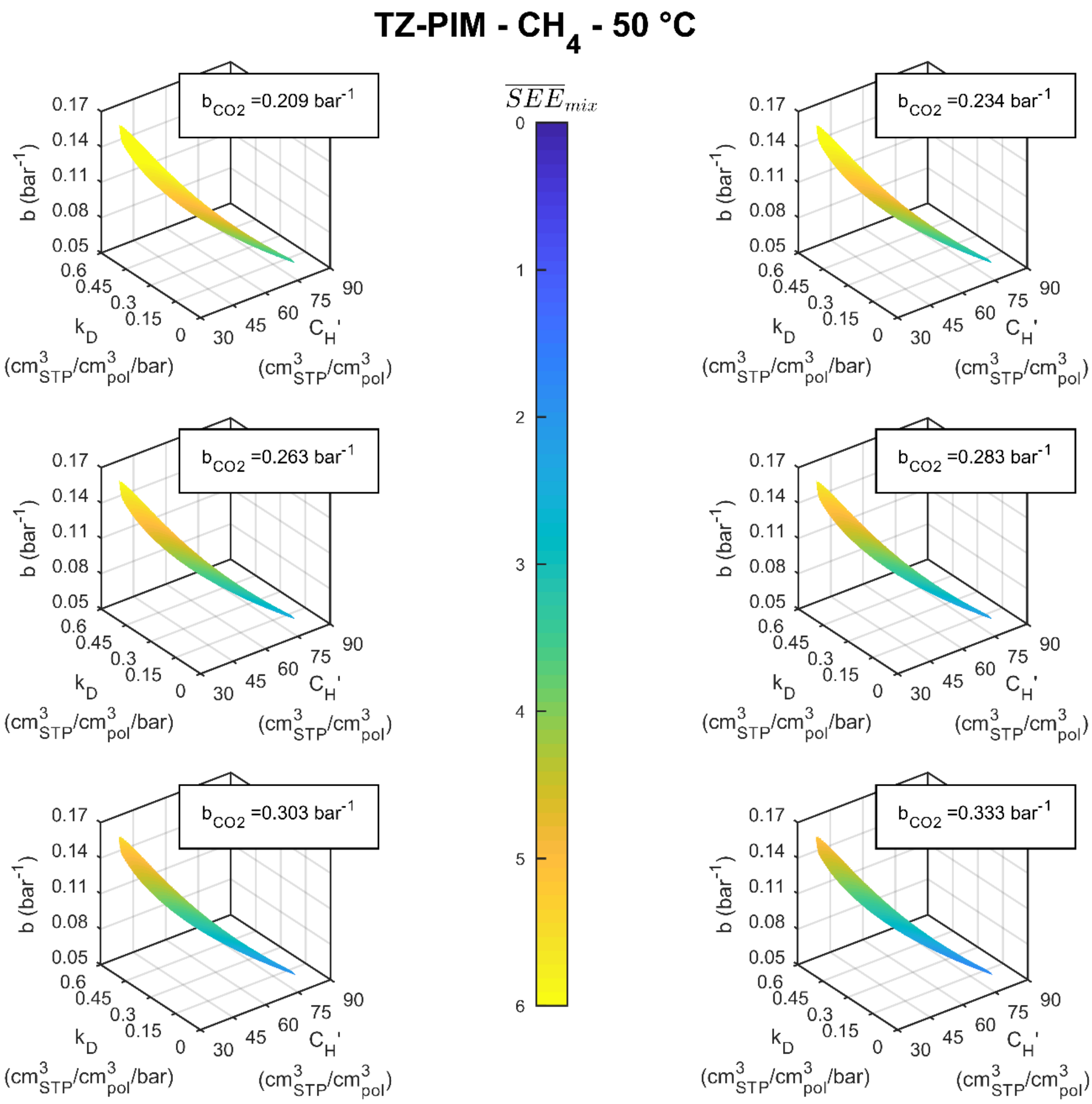

Figure S17. Isosurfaces in the DMS model parameter space for CH_4 sorption in TZ-PIM at 50 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CO_2}.

3.4. Effect of b_{CH_4} on the Calculated Mixed-Gas Sorption of CO_2 in PIM-1

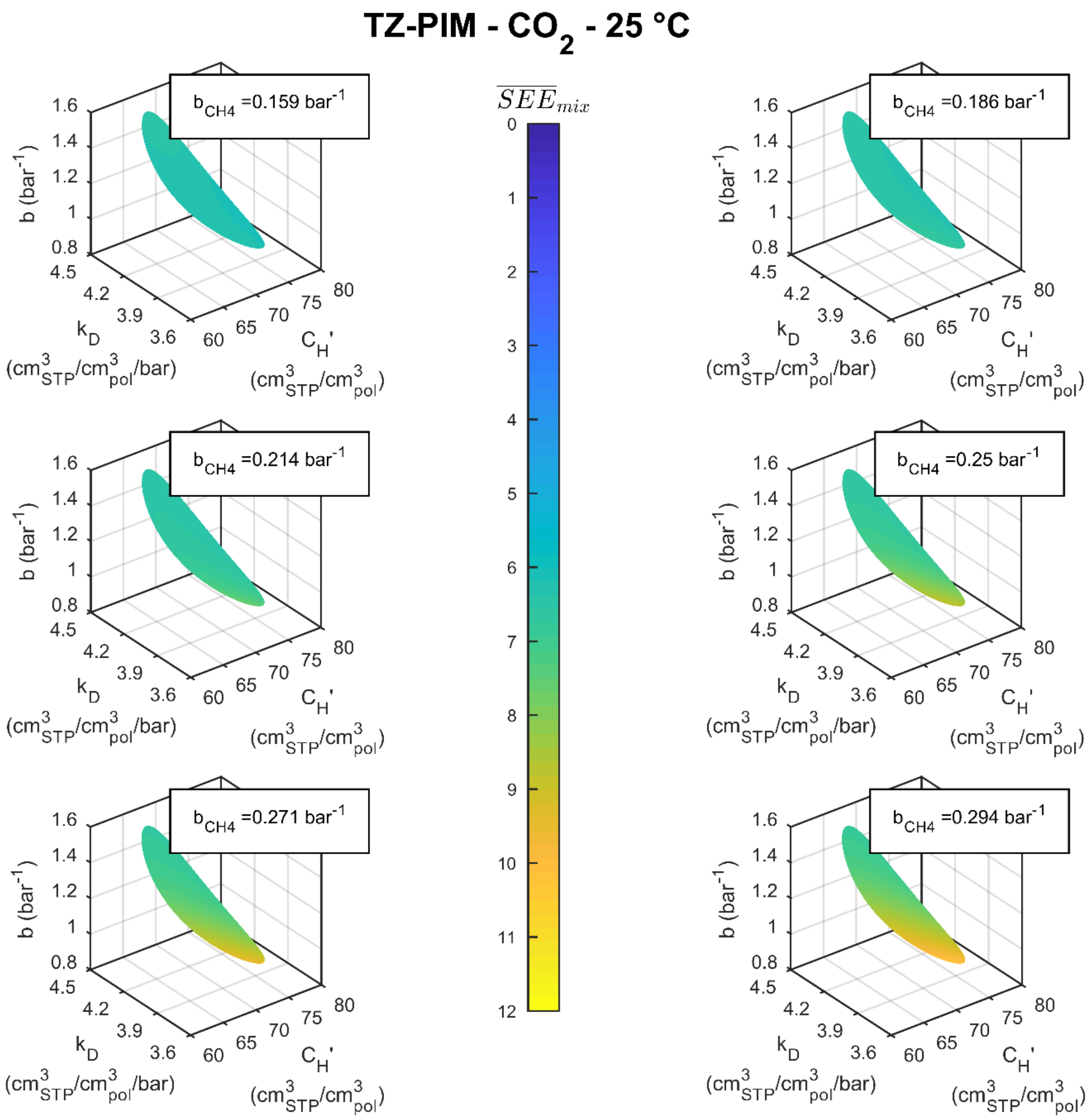

Figure S18. Isosurfaces in the DMS model parameter space for CO_2 sorption in TZ-PIM at 25 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CH_4}.

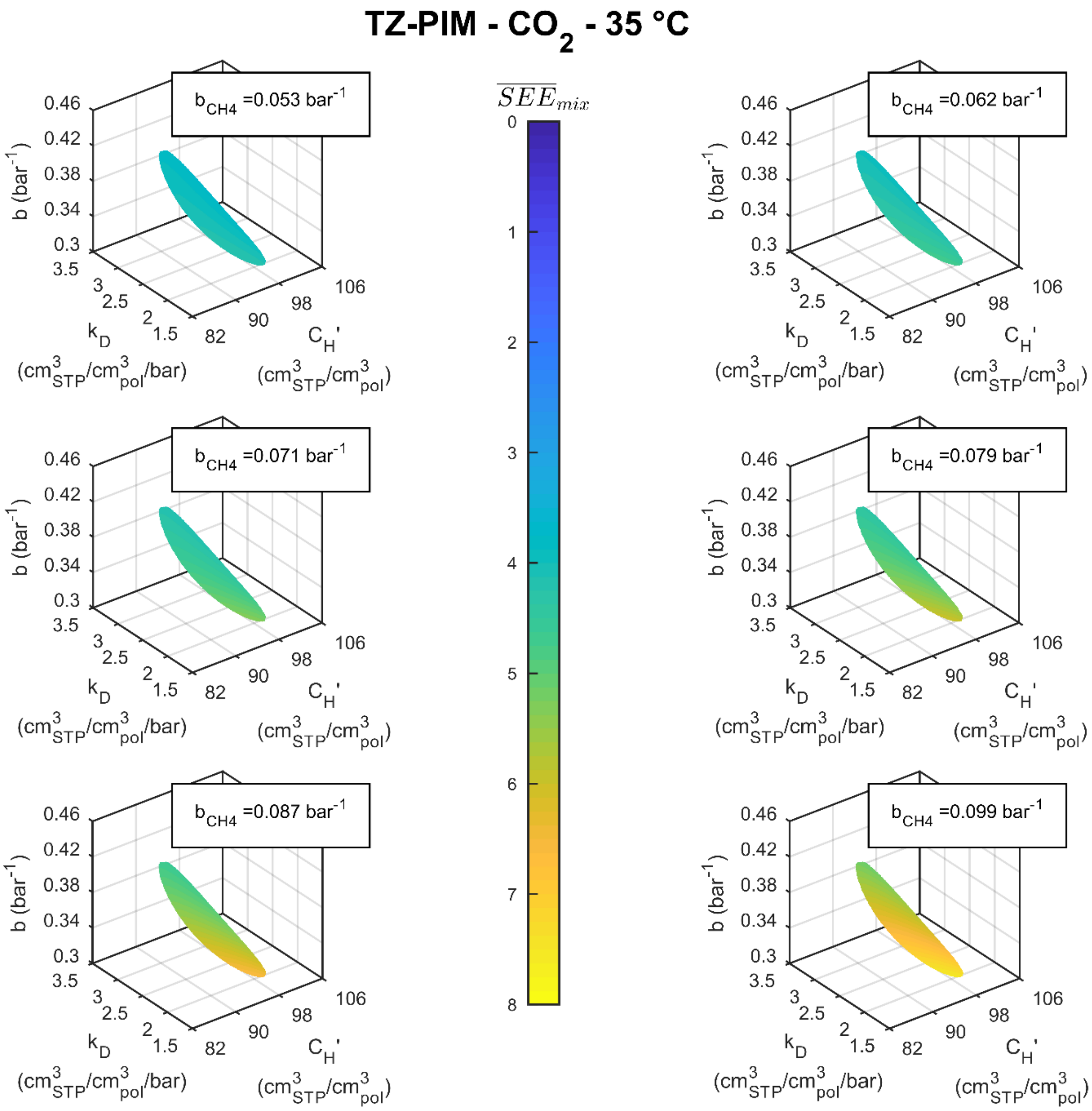

Figure S19. Isosurfaces in the DMS model parameter space for CO_2 sorption in TZ-PIM at 35 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CH_4}.

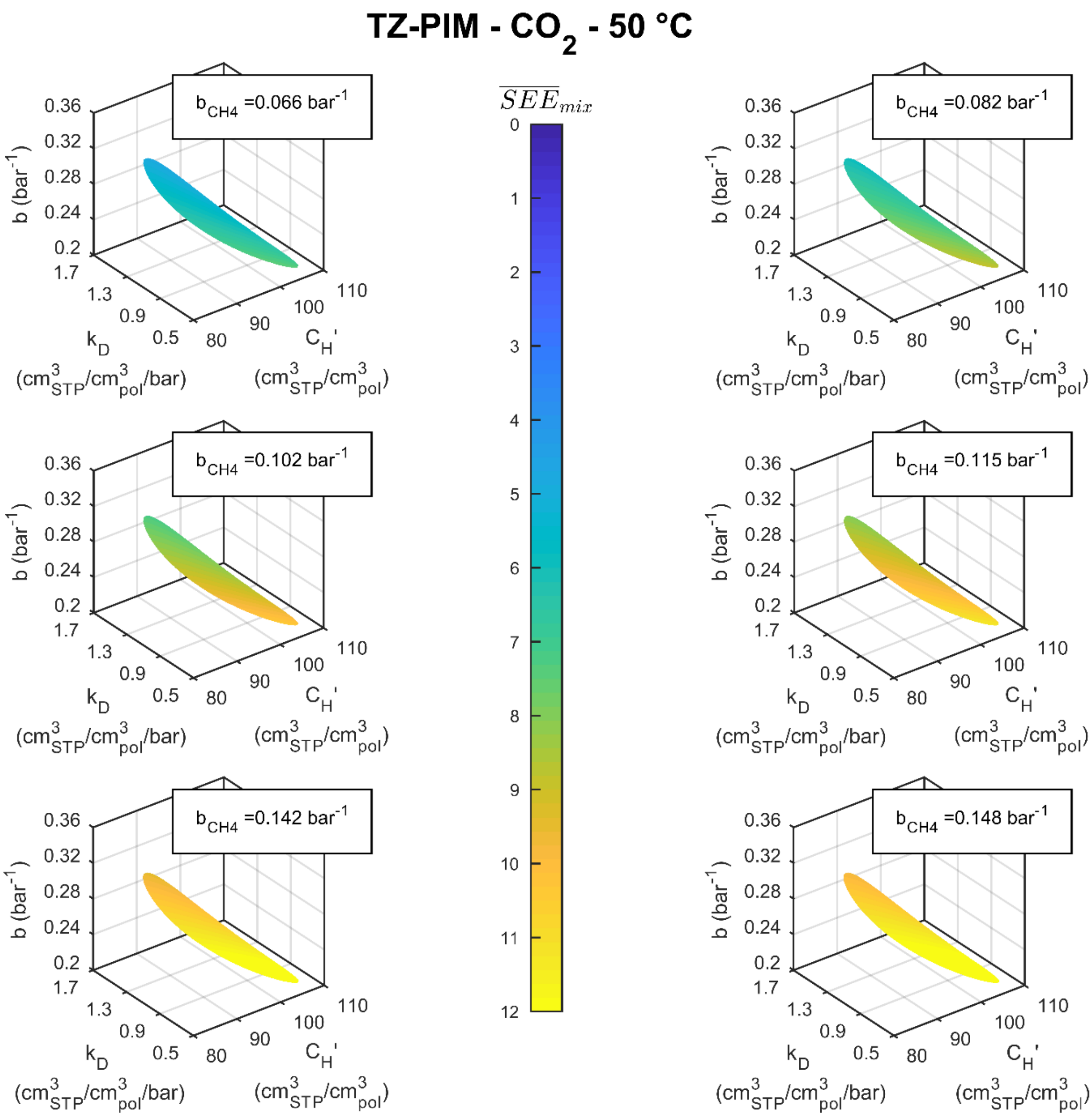

Figure S20. Isosurfaces in the DMS model parameter space for CO_2 sorption in TZ-PIM at 50 °C corresponding to $SEE_{pure} < SEE_{max}$, coloured according to the average SEE_{mix} obtained with different values within the confidence interval of b_{CH_4}.

References

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