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A new approach for predicting gas separation performances of MOF membranes

Gurdal, Yeliz; Keskin, Seda

Abstract: Metal organic framework (MOF) membranes are widely used for gas separations. Permeability and selectivity of MOF membranes can be accurately calculated using 'the detailed method' which computes transport diffusivities of gases in MOFs' pores. However, this method is computationally demanding therefore not suitable to screen large numbers of MOFs. Another approach is to use 'the approximate method' which uses self-diffusivities of gases to predict gas permeabilities of MOF membranes. The approximate method requires fewer amounts of time compared to the detailed method but significantly underestimates gas permeabilities since mixture correlation effects are ignored in this method. In this work, we first used computationally demanding detailed method to calculate permeabilities and selectivities of 8 different MOF membranes for Xe/Kr and Xe/Ar separations. We then compared these results with the predictions of the approximate method. After observing significant underestimation of the gas permeabilities by the approximate method, we proposed a new computational method to accurately predict gas separation properties of MOF membranes. This new method requires the same computational time and resources with the approximate method but makes much more accurate predictions for gas permeabilities. The new method that we proposed in this work will be very useful for large-scale screening of MOFs to identify the most promising membrane materials prior to extensive computational calculations and experimental efforts.

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Supplementary Material

A New Approach for Predicting Gas Separation Performances of MOF Membranes

Yeliz Gurdal[†,‡] and Seda Keskin[†,*]

[†] Department of Chemical and Biological Engineering, Koç University

Rumelifeneri Yolu, Sariyer, 34450 Istanbul, Turkey

[‡] Current address: Institut für Chemie, Universität Zurich

Winterthurerstrasse 190, CH-8057 Zurich, Switzerland

Proof: Permeability and Selectivity Expressions of New Method

Detailed formula of gas permeability is shown below:

$$P_{i,det} = \left[\frac{k_B T}{c_i} \left(L_{ii}\Gamma^*_{ii} + L_{ij}\Gamma^*_{ji} \right) c_i + \frac{k_B T}{c_j} \left(L_{ii}\Gamma^*_{ij} + L_{ij}\Gamma^*_{jj} \right) c_j \right] \frac{\phi}{fi} \tag{1}$$

Inserting formulas of L_{ii}, L_{jj} and L_{ij} in Eq.(1):

$$P_{i,det} = k_B T \left[\left((a_i c_i + b_i c_i^2)\Gamma^*_{ii} + g_{ij} c_i c_j \Gamma^*_{ji} \right) + \left((a_i c_i + b_i c_i^2)\Gamma^*_{ij} + g_{ij} c_i c_j \Gamma^*_{jj} \right) \right] \frac{\phi}{f_i} \tag{2}$$

$$P_{i,det} = k_B T \left[\left(a_i c_i \Gamma^*_{ii} + b_i c_i^2 \Gamma^*_{ii} + g_{ij} c_i c_j \Gamma^*_{ji} \right) + \left(a_i c_i \Gamma^*_{ij} + b_i c_i^2 \Gamma^*_{ij} + g_{ij} c_i c_j \Gamma^*_{jj} \right) \right] \frac{\phi}{f_i} \tag{3}$$

$$P_{i,det} = k_B T \left[\left((a_i c_i (\Gamma^*_{ii} + \Gamma^*_{ij}) + b_i c_i^2 (\Gamma^*_{ii} + \Gamma^*_{ij}) + g_{ij} c_i c_j (\Gamma^*_{ji} + \Gamma^*_{jj}) \right) \right] \frac{\phi}{f_i} \tag{4}$$

Taking $a_i c_i \, (\Gamma^*_{ii} + \Gamma^*_{ij})$ out of parenthesis,

$$P_{i,det} = k_B T a_i c_i (\Gamma^*_{ii} + \Gamma^*_{ij}) \left(1 + \frac{b_i}{a_i} c_i + \frac{g_{ij}}{a_i} c_j \frac{(\Gamma^*_{ji} + \Gamma^*_{jj})}{(\Gamma^*_{ii} + \Gamma^*_{ij})} \right) \frac{\phi}{f_i} \tag{5}$$

[*] Corresponding author: Email: skeskin@ku.edu.tr

$$P_{i,det} = D_{self,i} c_i (\Gamma^*_{ii} + \Gamma^*_{ij}) \left(1 + k_B T \frac{b_i c_i + g_{ij} c_j \frac{(\Gamma^*_{ji} + \Gamma^*_{jj})}{(\Gamma^*_{ii} + \Gamma^*_{ij})}}{D_{self,i}} \right) \frac{\phi}{f_i} \quad (6)$$

If cross correlations between same species and different species are assumed to be negligible ($b_i \to 0, g_{ij} \to 0$), then permeability equation of the new method becomes;

$$P_{i,new} = \frac{D_{self,i} c_i \left(\Gamma^*_{ii} + \Gamma^*_{ij}\right)\phi}{f_i} \quad (7)$$

Permeation selectivity, $S_{permeation(i,j)}$, is relative permeabilities of gas species in nanoporous materials which is shown below;

$$S_{permeation(i,j),new} = \frac{P_{i,new}}{P_{j,new}} = \frac{\frac{D_{self,i} c_i \left(\Gamma^*_{ii} + \Gamma^*_{ij}\right)\phi}{f_i}}{\frac{D_{self,j} c_j \left(\Gamma^*_{ji} + \Gamma^*_{jj}\right)\phi}{f_j}} = \frac{D_{self,i}}{D_{self,j}} \frac{c_i}{c_j} \frac{\left(\Gamma^*_{ii} + \Gamma^*_{ij}\right)}{\left(\Gamma^*_{ji} + \Gamma^*_{jj}\right)} \frac{f_j}{f_i} \quad (8)$$

Table S1. Fit Constants for Xe/Kr:20/80 Mixture

Coefficients	Cu-BTC	CPO-Co	CPO-Ni	IRMOF-1	ZIF-2	ZIF-3	ZIF-10	$Zn(bdc)(ted)_{0.5}$
h1	0.92	1.15	1.16	1.29	1.63	4.17	16.62	17.64
h2	0.01	0.05	0.05	0.01	0.08	0.04	0.21	0.85
h3	0	0.01	0.01	0	0.01	0.01	0.03	0.08
h4	0.01	0.06	0.05	0.06	0.02	0.08	0.58	0.26
h5	-2.72	0.01	0.01	0	-2.73	-125.14	1.85	-0.02
h6	-2.75	-0.45	-0.45	-0.49	-0.33	1.97	7.17	7.07
h7	-3.39	0.42	0.42	0.3	-1.12	0.18	0.96	2.74
h8	-11.74	-0.27	-0.27	-0.2	-12.95	4.4	19.57	19.7
s1	1.07	0.28	0.3	0.61	1.22	6.01	4.57	5.43
s2	-0.02	-0.04	-0.03	0.01	0.16	1.4	0.31	2.94
s3	0.02	0.05	0.03	0	0.09	0.19	0.04	0.25
s4	2.1	2.79	2.79	0.16	3.8	1.45	1.07	1.08
s5	4.97	2.41	2.4	0.81	6.26	0.87	0.35	1.41
s6	0.24	0.62	0.76	0.09	3.56	0.02	-0.46	0.21
s7	0.03	0.08	0.09	0.1	0.27	-0.04	-0.04	0.12
s8	0.56	1	0.92	1.76	1.17	14.77	14.71	14.68

Table S2. Fit Constants for Xe/Ar:20/80 Mixture

Coefficients	Cu-BTC	CPO-Co	CPO-Ni	IRMOF-1	ZIF-2	ZIF-3	ZIF-10	$Zn(bdc)(ted)_{0.5}$
h1	1	1.2	1.21	174.84	1.17	1.44	3.87	0.03
h2	0.01	0.05	0.05	0.2	0.06	0.05	0.05	-0.15
h3	0	0	0	0	0	0	0	-0.32
h4	0.02	0.07	0.05	0.49	0.02	0.05	0.13	8.82
h5	13.95	0.04	0	-8773.06	0	0.02	-0.04	5
h6	0.64	-2.47	-0.43	11.83	-0.19	-0.68	2.21	0.24
h7	0.01	2.07	0.4	0.2	0.19	0.62	-0.28	0.01
h8	1	-0.98	-0.2	24.75	-0.09	-0.26	0.53	0.08
s1	0.13	0.22	0.21	3.05	0.49	0.09	0.2	0.24
s2	0	0	-0.01	0.18	0.13	-0.01	-0.07	0.21
s3	0	0.03	0.01	0	0.03	0.01	0.02	0.01
s4	0.46	3.37	3.54	1.76	3.34	3.42	3.55	4.02

s5	4.44	0.65	0.48	0.64	0.35	0.68	2.81	0.55
s6	0.72	0.69	0.61	0.24	0.85	0.61	0.6	1.4
s7	0.02	0.02	0.01	0.3	0.01	0.02	0.02	0.02
s8	1.57	0.84	0.6	3.18	0.26	0.59	1.79	0.42

Table S3. Comparison of Xe and Kr (Ar) permeabilities for Xe/Kr (Xe/Ar) mixture calculated by detailed method at 298 K with varying feed pressures.

	Xe Permeability (/10^2 Barrers) in Xe/Kr:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	28598.6	22439.3	6352.2	18024.7	19930.0	7244.2	3254.2	2661.9
5	20477.1	18065.2	6492.1	25168.1	19868.3	11128.0	3217.5	4043.5
10	12480.3	14886.1	6650.8	19643.3	18815.0	9557.6	5918.3	3714.7
15	11634.1	11520.9	7151.1	17535.8	19320.5	8343.9	4933.1	3187.4
20	11884.9	8951.2	6271.8	14973.4	14570.0	6626.3	4617.0	4610.8
25	8804.2	9968.2	6378.3	15456.6	12807.1	7116.4	4736.3	3778.2

	Kr Permeability (/10^2 Barrers) in Xe/Kr:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	3635.4	3374.1	1620.2	4771.6	3922.2	2142.5	1503.4	971.2
5	3528.0	3162.8	1252.8	7585.5	5452.3	2280.2	1594.1	1113.8
10	2493.7	3759.7	1572.2	4374.5	4211.5	1844.0	2358.2	1124.1
15	2813.3	2181.9	1586.7	4361.4	4431.6	1854.1	1762.2	1142.7
20	2335.2	1798.7	1516.8	4419.3	3924.2	1688.5	2063.6	1082.7
25	2063.3	2056.7	1649.6	4678.3	4458.8	1660.1	2067.5	1241.4

	Xe Permeability (/10^2 Barrers) in Xe/Ar:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	21420.4	22788.6	5561.4	13782.4	22222.1	8096.3	2223.8	2325.3
5	18076.5	18367.0	6726.0	23449.0	18082.4	8058.6	2771.7	3273.4
10	15145.6	9825.4	6208.6	19893.1	15317.8	8316.2	3185.7	3599.5
15	12575.3	11059.5	4976.5	13554.4	17101.1	8348.9	4914.1	3628.9

20	10146.2	9408.4	4355.3	14169.1	12949.0	7094.2	4749.2	3559.4
25	12899.1	5831.6	3765.7	14200.2	12070.7	6599.7	5466.3	3231.5
	Ar Permeability (/10^2 Barrers) in Xe/Ar:20/80							
Pressure	ZIF-2	Zn(bdc)(ted)$_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	1501.8	1608.2	785.5	2826.5	2890.6	1624.9	1044.8	773.5
5	1355.0	753.1	707.3	2838.1	1847.6	1126.1	1242.6	847.4
10	1215.7	1133.4	773.0	3279.0	1874.3	1039.2	1441.0	675.2
15	1116.9	736.4	389.9	2639.6	2146.1	1091.6	1199.4	663.1
20	894.0	483.3	351.8	1550.0	1843.9	914.7	1688.9	666.7
25	1168.5	323.2	314.4	2412.1	2190.4	866.8	1475.1	815.3

Table S4. Comparison of Xe and Kr (Ar) permeabilities for Xe/Kr (Xe/Ar) mixture calculated by new method at 298 K with varying feed pressures.

	Xe Permeability (/10^2 Barrers) in Xe/Kr:20/80							
Pressure	ZIF-2	Zn(bdc)(ted)$_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	9393.5	6234.9	2441.5	10880.5	14460.4	4555.4	1575.4	1586.7
5	9693.5	5894.2	2518.9	16175.6	14958.4	4874.0	1967.8	2085.4
10	7051.3	4723.8	2667.9	15777.9	14335.9	3829.1	2664.4	1942.8
15	5151.7	3888.4	2579.3	11563.2	11902.2	2811.0	2823.1	1856.4
20	5392.8	3505.2	2486.5	10988.7	10913.4	2361.9	3008.9	1793.9
25	4599.2	2989.9	2260.3	9419.9	9698.2	1961.5	2898.2	1537.5

	Kr Permeability (/10^2 Barrers) in Xe/Kr:20/80							
Pressure	ZIF-2	Zn(bdc)(ted)$_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	1201.3	1324.9	713.3	3011.3	3310.8	1447.5	950.1	642.2
5	1582.8	1234.1	705.6	4257.7	3231.3	1140.3	1053.4	691.8
10	1236.0	998.9	697.6	4189.1	3229.8	876.5	1318.4	638.2
15	1016.5	890.7	664.6	3063.7	2838.1	701.8	1332.3	641.2

20	1124.5	823.6	629.9	3161.4	3135.0	607.5	1285.7	543.6
25	1031.5	685.3	593.8	3069.1	2772.0	574.2	1257.0	533.8
	Xe Permeability (/10^2 Barrers) in Xe/Ar:20/80							
Pressure	ZIF-2	Zn(bdc)(ted)$_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	9108.5	6408.8	2378.4	11378.1	11701.3	4469.2	964.4	1570.4
5	8588.2	2765.2	2011.7	7605.1	7527.5	4970.9	1392.9	1950.9
10	6383.3	2719.9	2130.3	13626.2	7700.8	4107.0	1792.5	2000.9
15	5773.3	1635.5	1314.5	8805.4	8695.4	3216.4	2330.4	1905.8
20	5196.9	1422.3	1123.0	7277.7	7743.9	2739.5	2636.9	1789.6
25	4716.2	1151.9	1037.2	6931.0	7190.5	2401.2	2743.6	1659.9

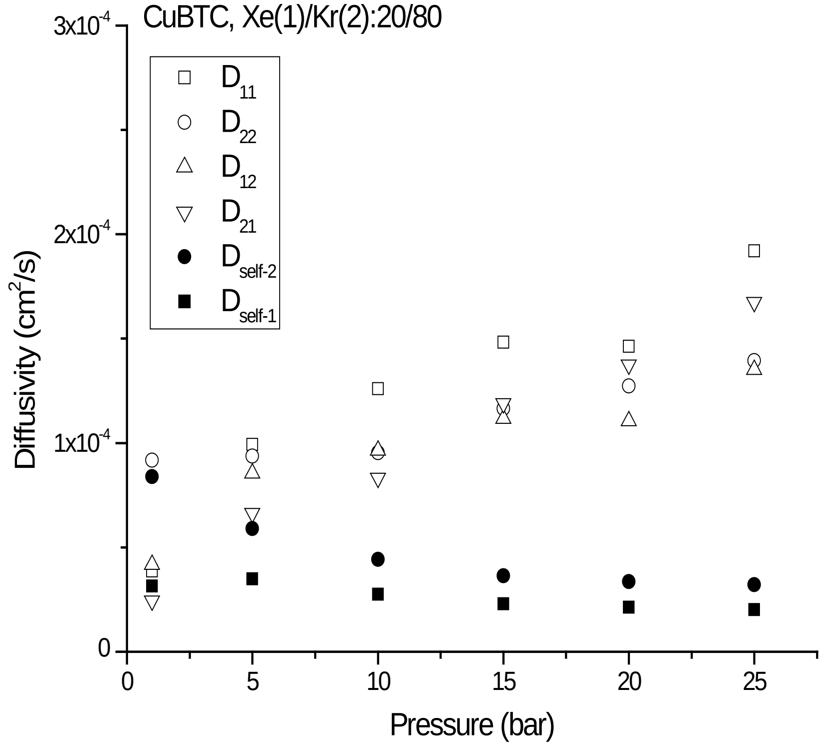
	Ar Permeability (/10^2 Barrers) in Xe/Ar:20/80							
Pressure	ZIF-2	Zn(bdc)(ted)$_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	536.1	743.8	485.7	2109.6	1800.0	991.6	916.3	519.7
5	505.9	310.9	278.1	885.6	785.3	711.3	984.8	525.2
10	424.4	350.6	298.0	1807.9	845.5	500.1	1051.2	465.7
15	387.0	186.7	145.4	1220.8	1010.2	397.8	1060.2	410.9
20	362.8	161.1	121.0	1017.0	986.7	345.6	1101.1	395.6
25	332.8	136.4	102.8	985.4	898.5	306.6	1101.4	358.4

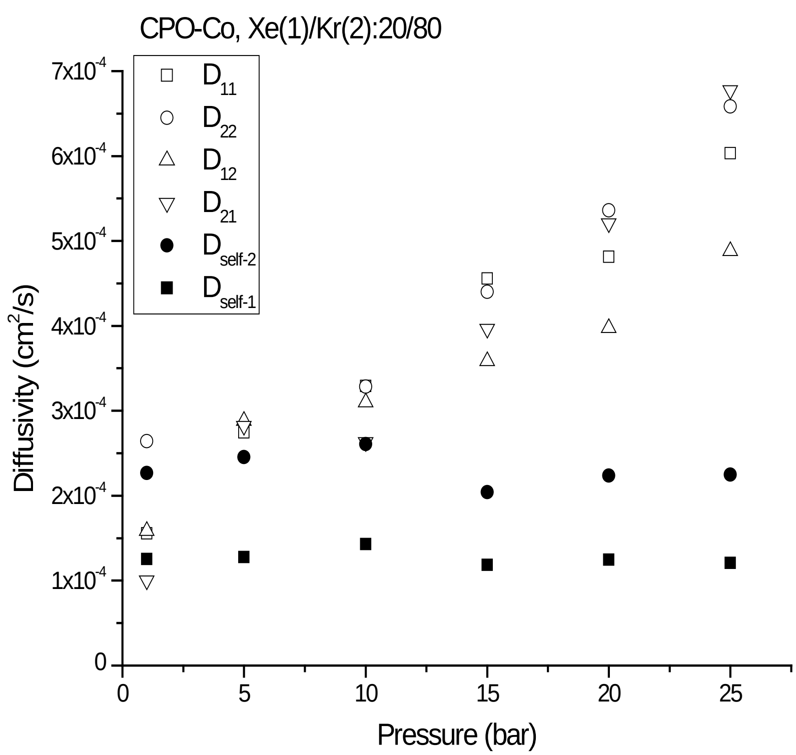
Table S5. Comparison of Xe and Kr (Ar) permeabilities for Xe/Kr (Xe/Ar) mixture calculated by approximate method at 298 K with varying feed pressures.

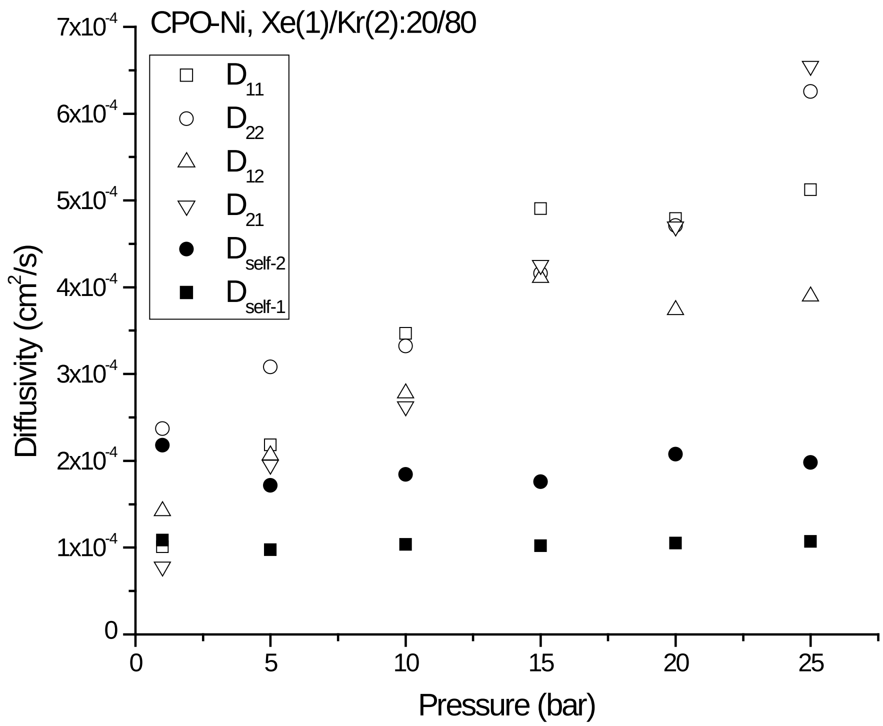
	Xe Permeability (/10^2 Barrers) in Xe/Kr:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	4831.1	3678.0	1996.8	8604.5	10320.4	3823.9	1536.9	1457.0
5	1959.5	1323.0	1074.6	7184.8	5871.4	2536.2	1673.3	1341.6
10	1055.5	688.1	671.9	5518.2	3855.5	1380.4	1852.0	906.4
15	671.3	451.2	474.1	2954.7	2620.4	825.5	1693.6	708.2
20	642.6	337.9	363.4	2427.4	2089.9	605.3	1600.1	579.2
25	514.7	279.5	290.1	1887.6	1739.5	459.5	1418.1	441.1
	Kr Permeability (/10^2 Barrers) in Xe/Kr:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	677.4	805.1	562.0	2618.9	2712.2	1282.2	931.2	599.9
5	381.8	314.8	299.8	2063.4	1400.4	677.2	936.3	471.6
10	231.0	177.7	185.4	1459.8	981.7	370.4	993.7	320.2
15	168.8	132.1	133.6	874.9	717.9	244.8	879.7	262.2
20	172.5	105.6	103.7	785.3	699.9	186.9	757.4	188.3
25	148.8	86.3	87.7	693.2	568.5	162.6	682.7	164.4

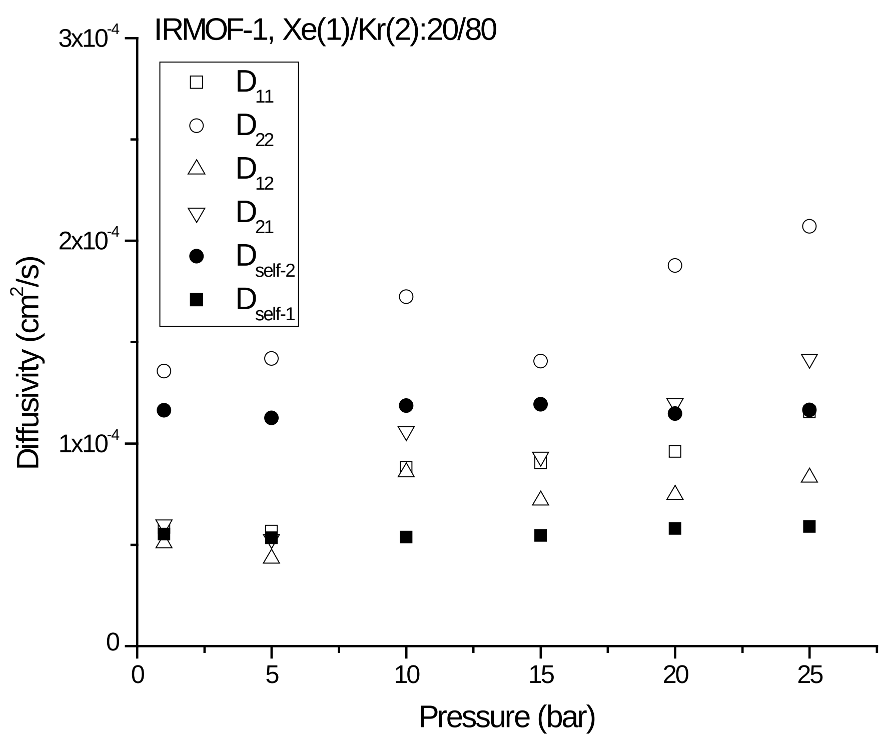
	Xe Permeability (/10^2 Barrers) in Xe/Ar:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	5328.2	3775.3	1935.3	9080.3	9952.5	3882.2	1427.5	1478.3
5	2072.3	619.4	981.1	3863.8	3374.1	2966.9	1729.5	1399.3
10	1006.1	864.9	676.6	4862.6	2347.1	1700.6	1752.1	1066.0
15	729.0	190.3	321.4	2557.5	2172.3	1049.7	1835.3	825.3
20	556.9	137.9	230.7	1859.0	1656.1	768.6	1732.2	668.9
25	442.6	107.2	180.6	1566.8	1368.2	593.2	1561.6	546.6

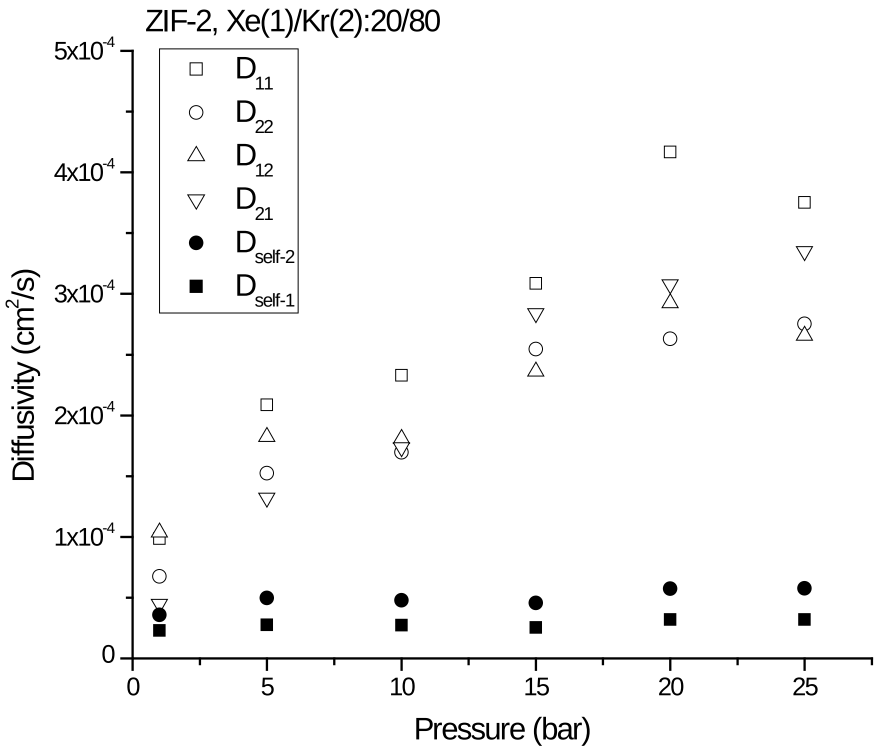
	Ar Permeability (/10^2 Barrers) in Xe/Ar:20/80							
Pressure	ZIF-2	$Zn(bdc)(ted)_{0.5}$	ZIF-3	CPO-Co	CPO-Ni	CuBTC	IRMOF-1	ZIF-10
1	334.3	442.4	399.8	1874.6	1549.1	898.8	892.7	492.6
5	155.2	79.8	135.7	473.4	381.0	478.7	894.3	388.6
10	96.1	105.7	97.5	713.3	296.6	245.5	868.9	261.1
15	75.3	27.4	37.6	405.4	302.2	158.8	786.2	189.8
20	62.9	20.0	26.8	303.0	262.2	121.1	730.1	159.4
25	52.1	16.9	19.8	265.4	219.1	96.6	659.7	128.5

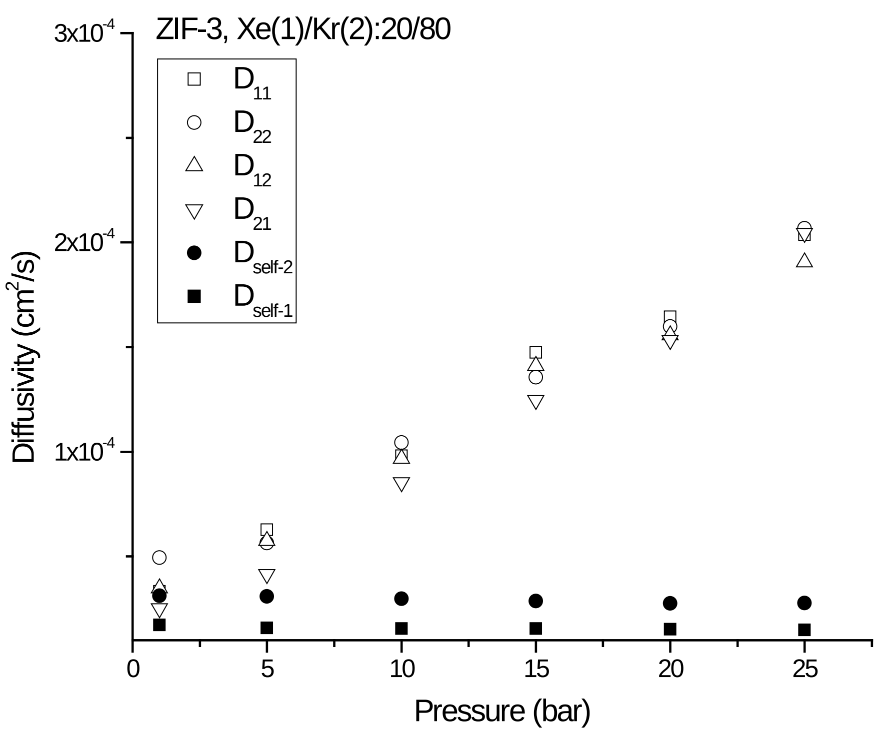

CuBTC, Xe(1)/Kr(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
3x10-4
2x10-4
1x10-4
0
0
5
10
15
20
25

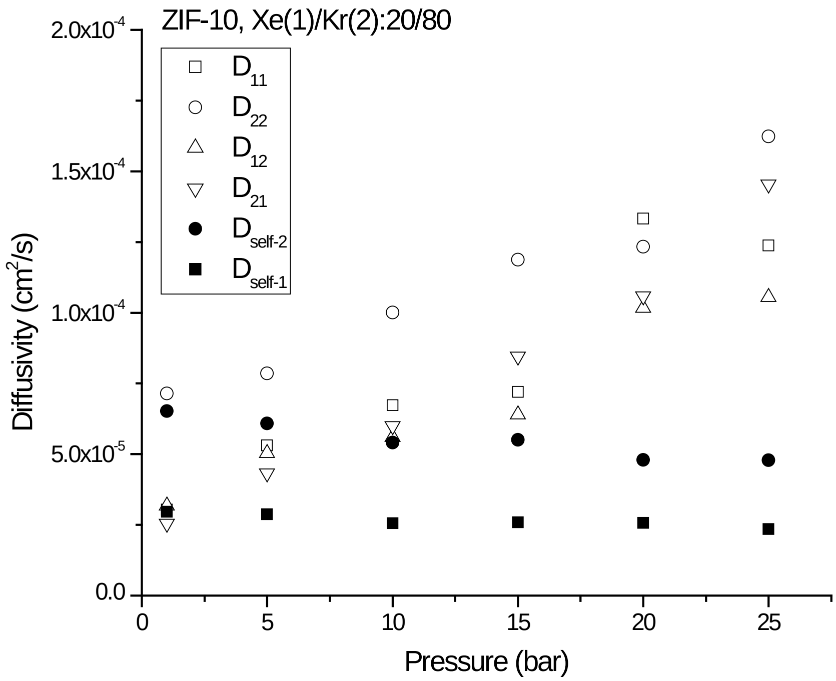

CPO-Co, Xe(1)/Kr(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
7x10-4
6x10-4
5x10-4
4x10-4
3x10-4
2x10-4
1x10-4
0
0
5
10
15
20
25


CPO-Ni, Xe(1)/Kr(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
0
1x10-4
2x10-4
3x10-4
4x10-4
5x10-4
6x10-4
7x10-4
0
5
10
15
20
25


IRMOF-1, Xe(1)/Kr(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
0
1x10-4
2x10-4
3x10-4
0
5
10
15
20
25


ZIF-2, Xe(1)/Kr(2):20/80
Diffusivity (cm2/s)
Pressure (bar)
D11
D22
D12
D21
Dself-2
Dself-1
0
1x10-4
2x10-4
3x10-4
4x10-4
5x10-4
0
5
10
15
20
25


ZIF-3, Xe(1)/Kr(2):20/80
Diffusivity (cm2/s)
Pressure (bar)
D11
D22
D12
D21
Dself-2
Dself-1
1x10-4
2x10-4
3x10-4
0
5
10
15
20
25



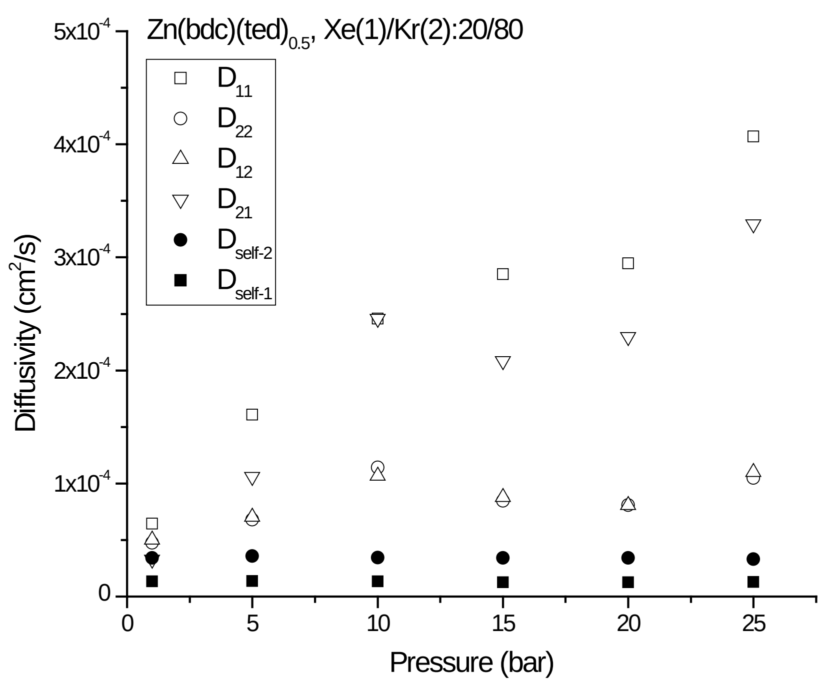
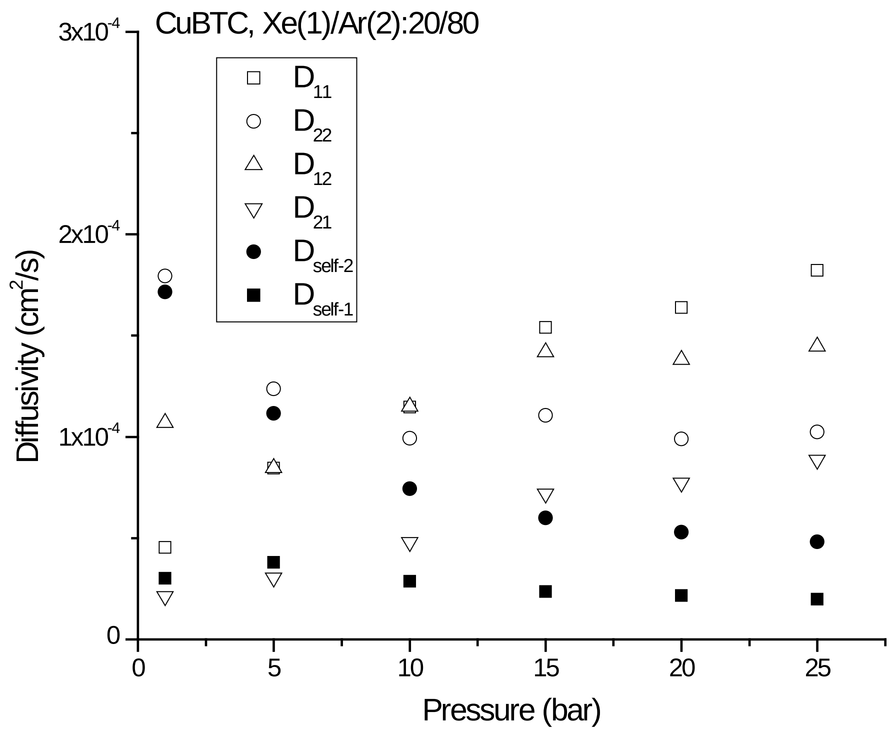
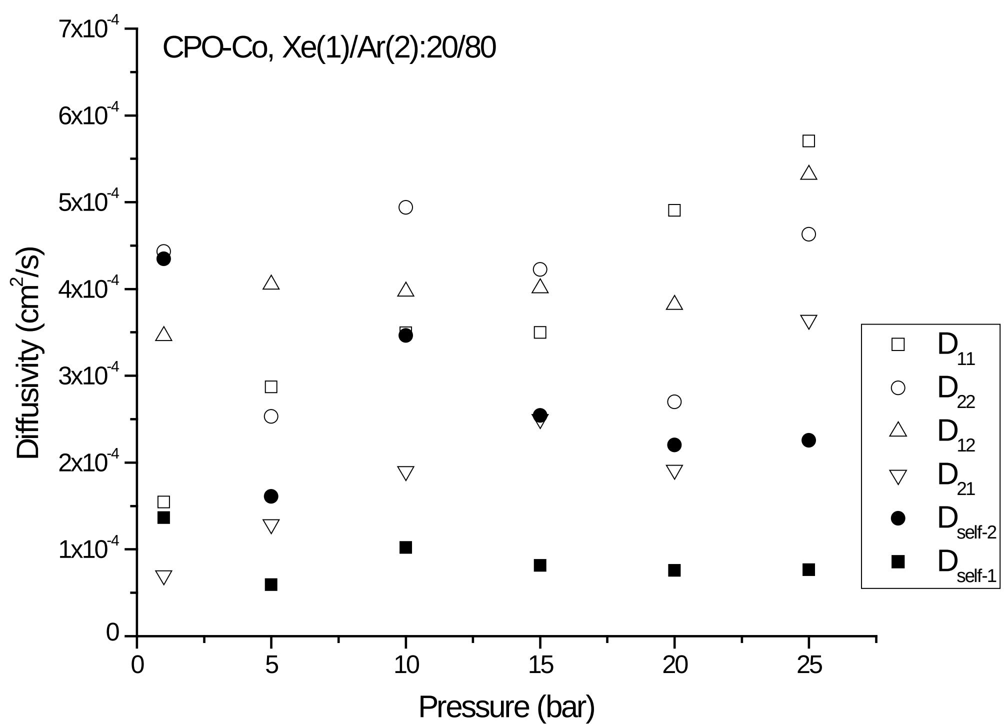
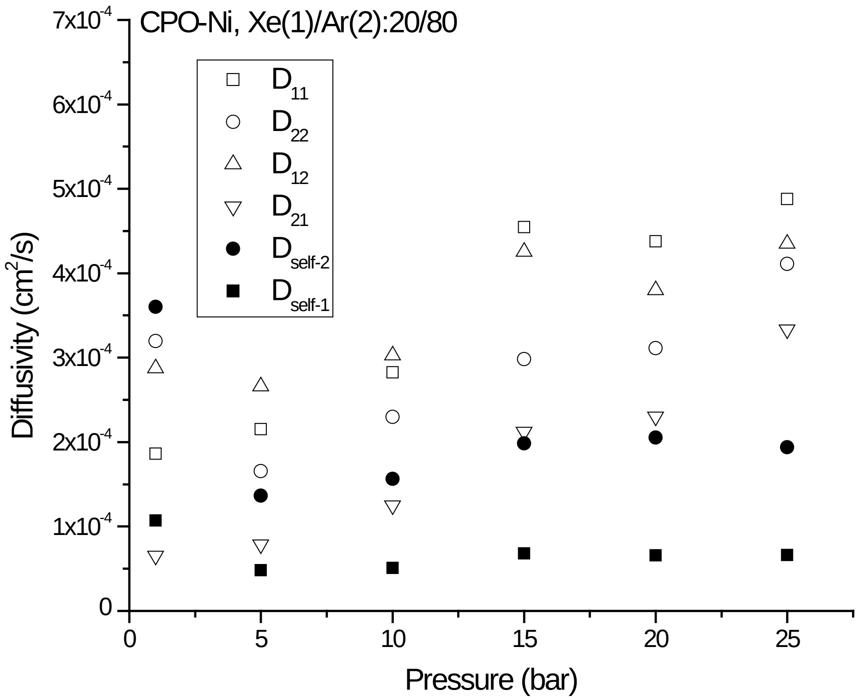
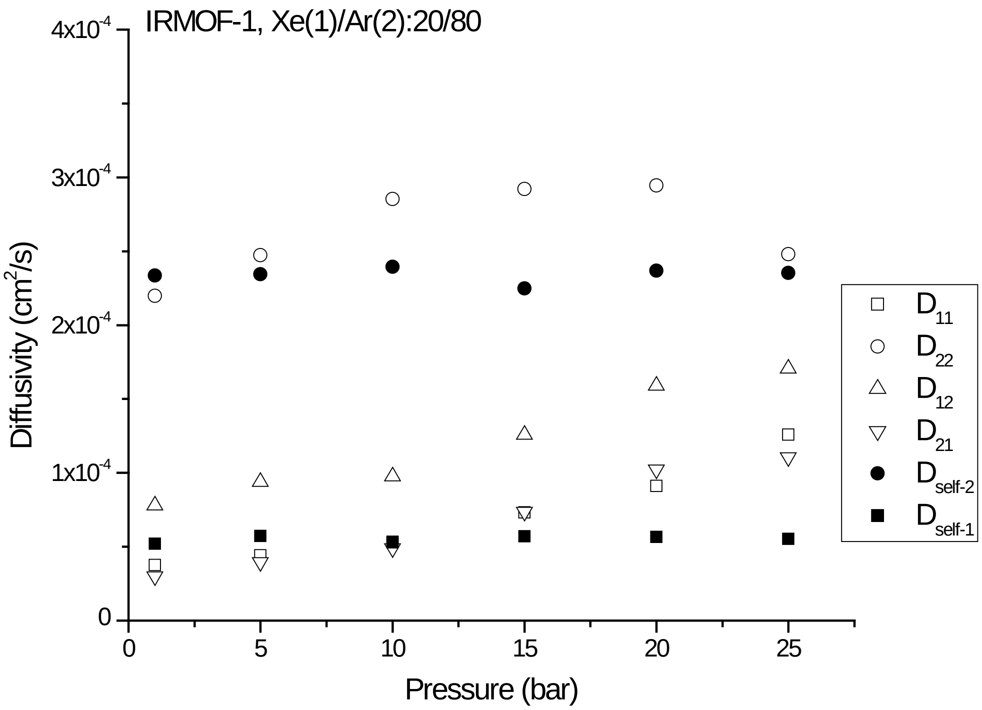


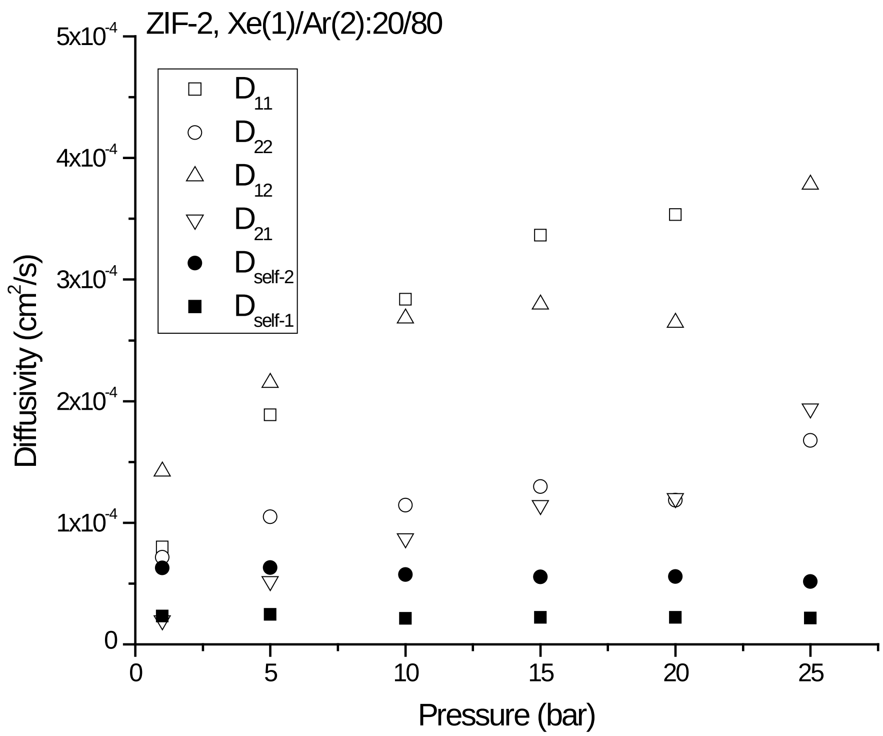
Figure S1. Comparison of the Fickian diffusivity matrix elements and mixture self-diffusivities for Xe/Kr:20/80 mixture at 298 K and varying feed pressures at 1, 5, 10, 15, 20, and 25 bar.

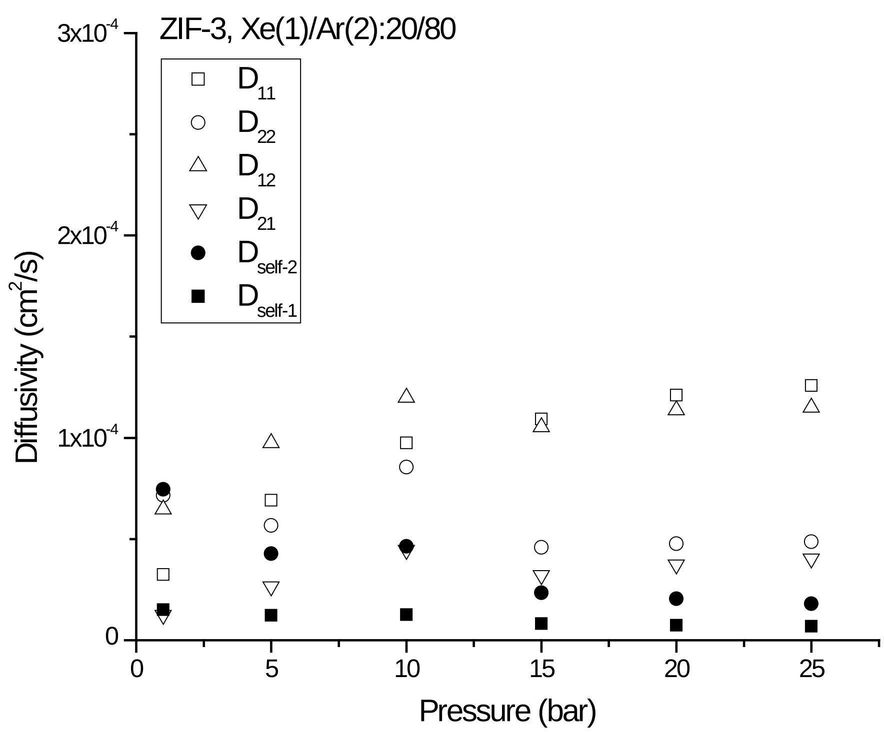

CuBTC, Xe(1)/Ar(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
0
1x10-4
2x10-4
3x10-4
0
5
10
15
20
25


CPO-Co, Xe(1)/Ar(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
0
1x10-4
2x10-4
3x10-4
4x10-4
5x10-4
6x10-4
7x10-4
0
5
10
15
20
25


CPO-Ni, Xe(1)/Ar(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
0
1x10-4
2x10-4
3x10-4
4x10-4
5x10-4
6x10-4
7x10-4
0
5
10
15
20
25


IRMOF-1, Xe(1)/Ar(2):20/80
D11
D22
D12
D21
Dself-2
Dself-1
Diffusivity (cm2/s)
Pressure (bar)
0
1x10-4
2x10-4
3x10-4
4x10-4
0
5
10
15
20
25


ZIF-2, Xe(1)/Ar(2):20/80
5x10-4
4x10-4
3x10-4
2x10-4
1x10-4
0
Diffusivity (cm2/s)
D11
D22
D12
D21
Dself-2
Dself-1
0
5
10
15
20
25
Pressure (bar)


ZIF-3, Xe(1)/Ar(2):20/80
3x10-4
2x10-4
1x10-4
0
Diffusivity (cm2/s)
D11
D22
D12
D21
Dself-2
Dself-1
0
5
10
15
20
25
Pressure (bar)

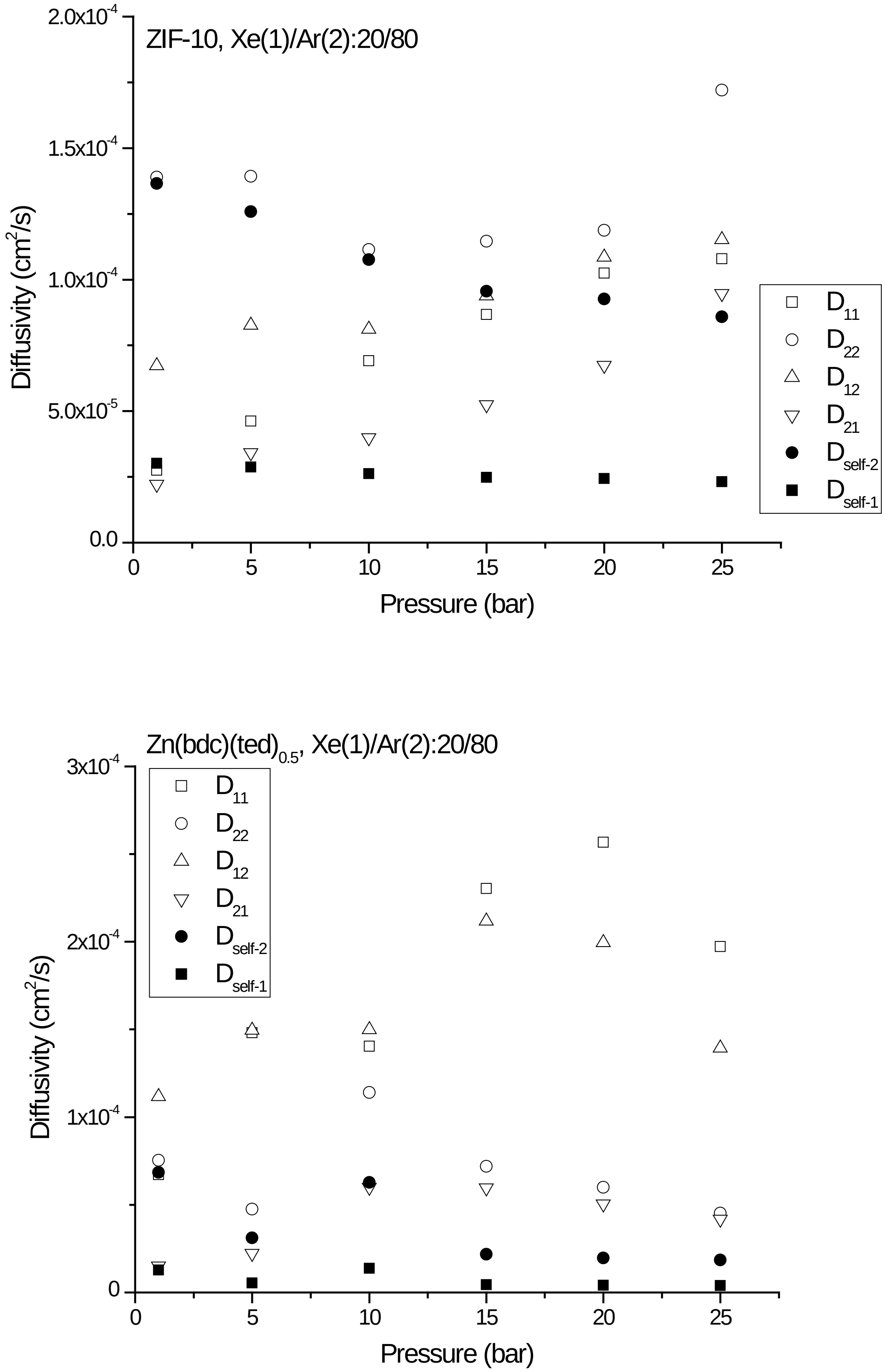


Figure S2. Comparison of the Fickian diffusivity matrix elements and mixture self-diffusivities for Xe/Ar:20/80 mixture at 298 K and varying feed pressures at 1, 5, 10, 15, 20, and 25 bar.

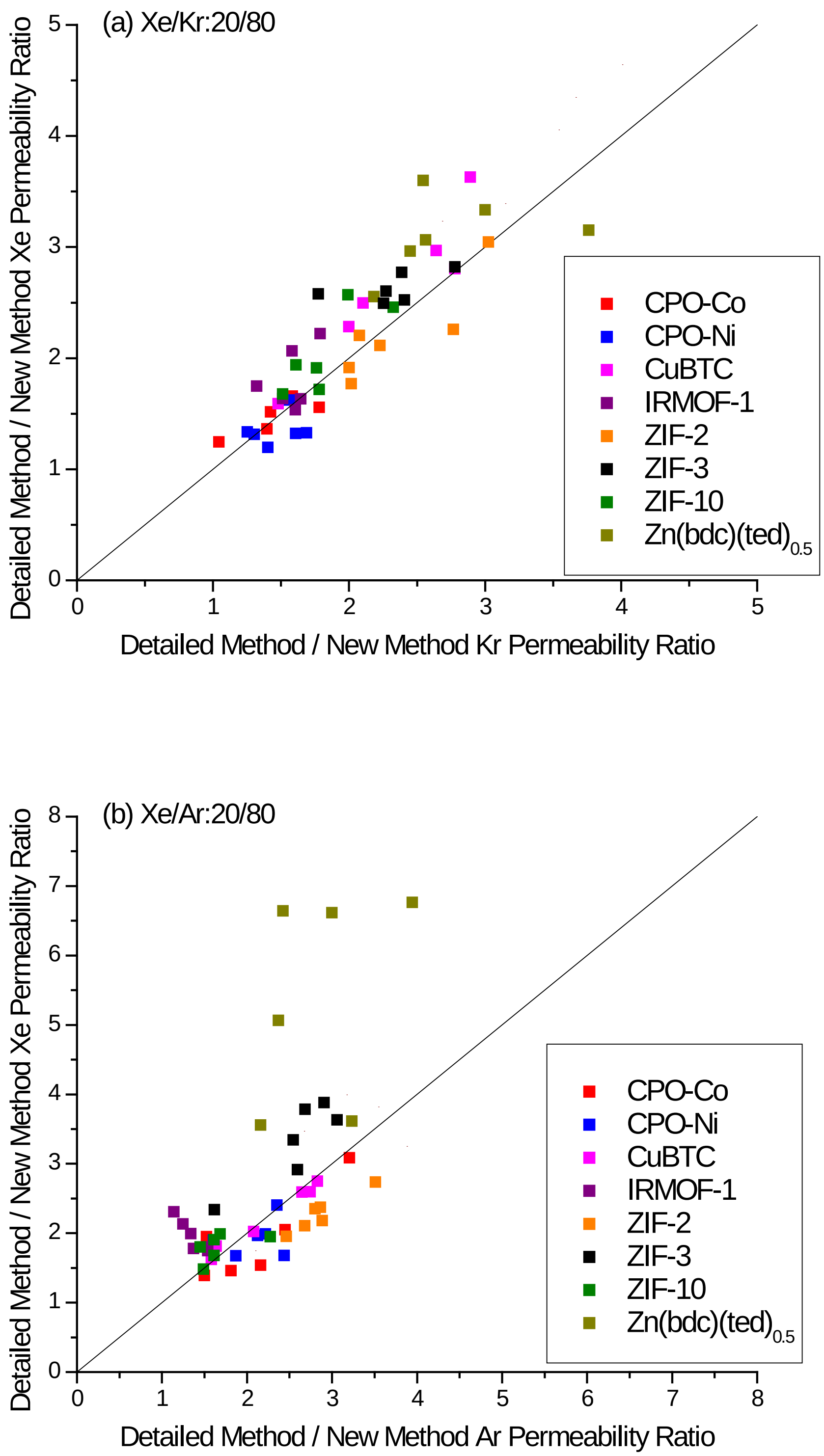


Figure S3. Comparison of Xe permeability predictions with (a)Kr (b)Ar permeability predictions obtained at 298 K and varying feed pressures at 1, 5, 10, 15, 20, and 25 bar.

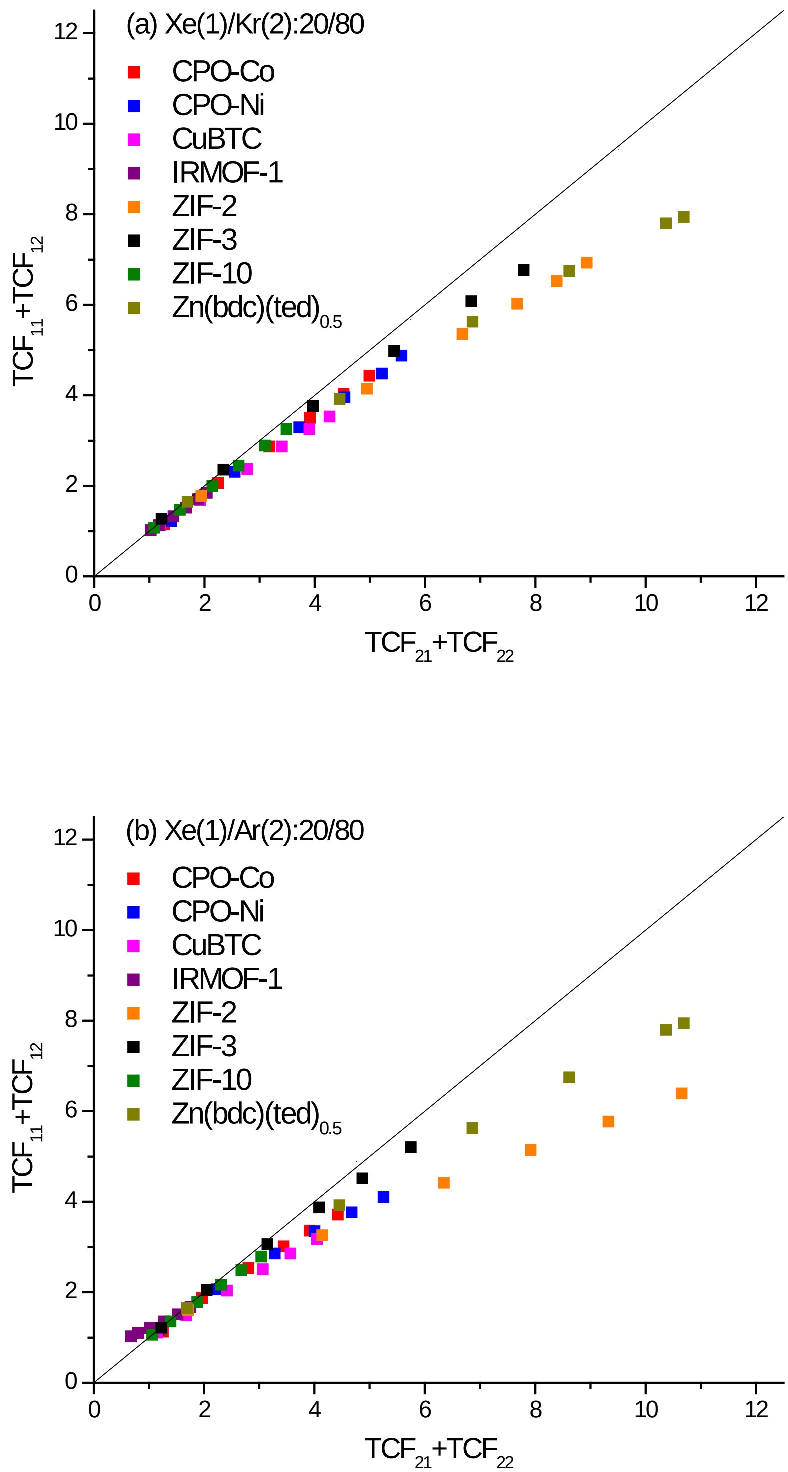


Figure S4. Thermodynamic correction factors for (a) Xe(1)/Kr(2):20/80 (b) Xe(1)/Ar(2):20/80 mixtures at 298 K and varying feed pressures at 1, 5, 10, 15, 20, and 25 bar.