Supporting Information

Infinite Dilution Diffusion Coefficients of Chlorinated Methane in PET by Inverse Gas Chromatography

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Table S1 Characteristics of the Packed Column

Column Items	Parameters or conditions
Polymer	Polyethylene terephthalate
Solvent	Hexafluoro-isopropanol
Support	Chromsorb-G (60-80 mesh)
Column length (m)	2
Column inner diameter (mm)	3
Weight of support (g)	4.7562
Weight of polymer (g)	0.2352
Time of ageing (h)	12

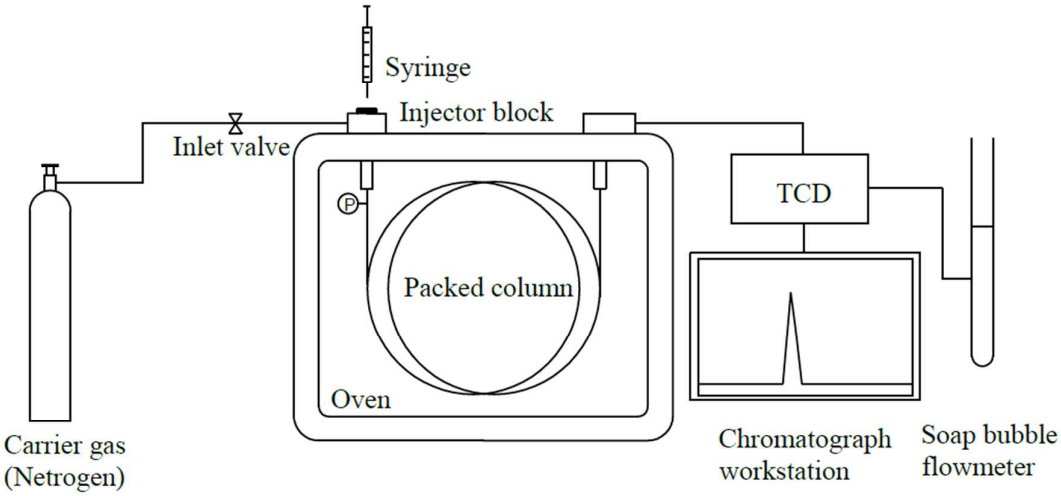

Figure S1 Schematic diagram of the IGC apparatus used for the determination of diffusion coefficient

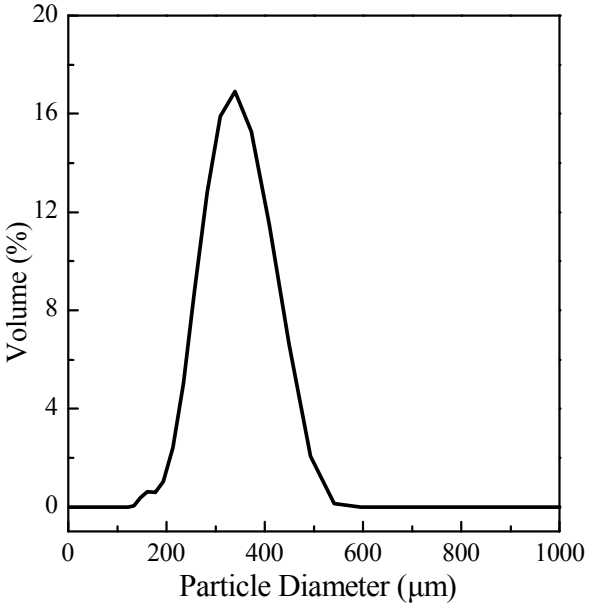

Figure S2 The particle size distribution of support in column

The average thickness of the polymer coating was calculated from the known volume of polymer on the support and the geometric surface area of the support, which were assumed to be spherical. Thus a sample of N beads of radius r have a surface area of $S=N\times4\pi r^2 = 3V/r$, where r is an average radius, and $r=d_{\mathrm{d}}/2$. If this sample of beads is coated with a weight ω_{p} of polymer having a density ρ_{p}, then the average thickness of the polymer layer was taken to be:

$$d_{\mathrm{p}} = \frac{V_p}{S} = \frac{\omega_{\mathrm{p}}/\rho_{\mathrm{p}}}{3V/r} = \frac{\omega_{\mathrm{p}}\rho_{\mathrm{d}}d_{\mathrm{d}}}{6\rho_{\mathrm{p}}\omega_{\mathrm{d}}} \tag{S1}$$

Table S2 Measured IGC Data of Chlorinated Methane in PET at 398.15 K

Solvents	F (mL/min)	t_a (min)	t_r (min)	$\omega_{1/2}$ (min)	u (m/s)	H (m)
Dichloromethane	8.82	1.367	1.415	0.219	0.02907	0.00862
	15.54	0.809	0.832	0.136	0.04686	0.00968
	21.90	0.593	0.611	0.105	0.06105	0.01061
	30.61	0.440	0.459	0.082	0.07872	0.01159
	38.96	0.357	0.373	0.068	0.09292	0.01200
Chloroform	8.82	1.367	1.465	0.228	0.02907	0.00877
	15.54	0.809	0.863	0.146	0.04686	0.01033
	21.90	0.593	0.634	0.116	0.06105	0.01209
	30.61	0.440	0.473	0.093	0.07872	0.01381
	38.96	0.357	0.382	0.079	0.09292	0.01554
Carbon tetrachloride	8.82	1.367	1.417	0.235	0.02907	0.00991
	15.54	0.809	0.838	0.157	0.04686	0.01269
	21.90	0.593	0.615	0.127	0.06105	0.01533
	30.61	0.440	0.461	0.104	0.07872	0.01828
	38.96	0.357	0.375	0.092	0.09292	0.02158

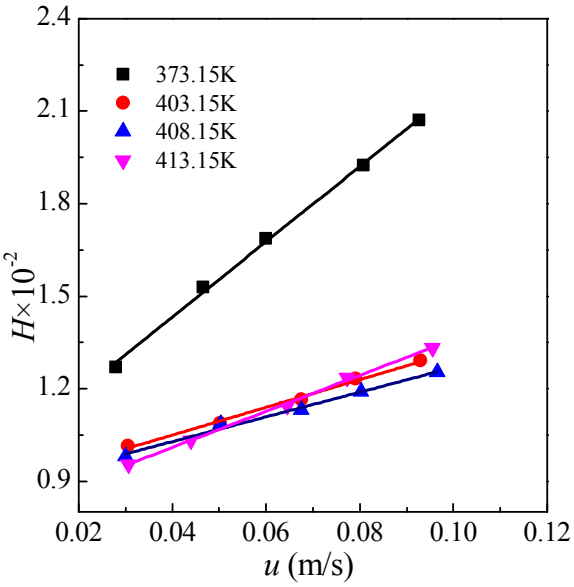

Figure S3 Relationships between the plate height and the flow rate of dichloromethane in column under different temperatures (Lines in Figure S3 to S5 represent the corresponding fitting lines.)

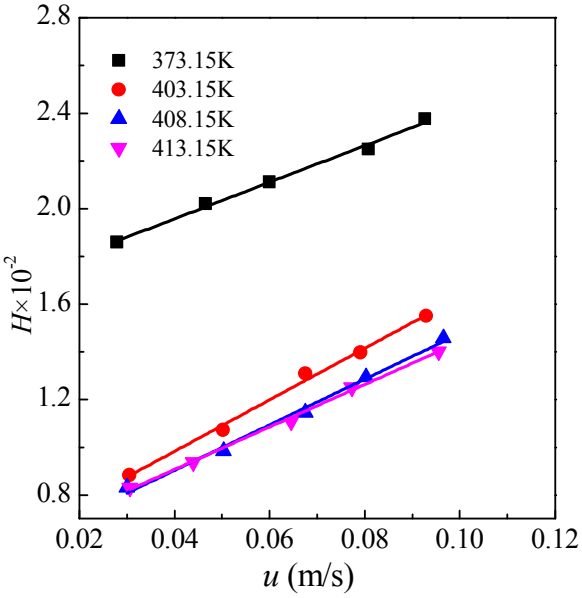

Figure S4 Relationships between the plate height and the flow rate of chloroform in column under different temperatures

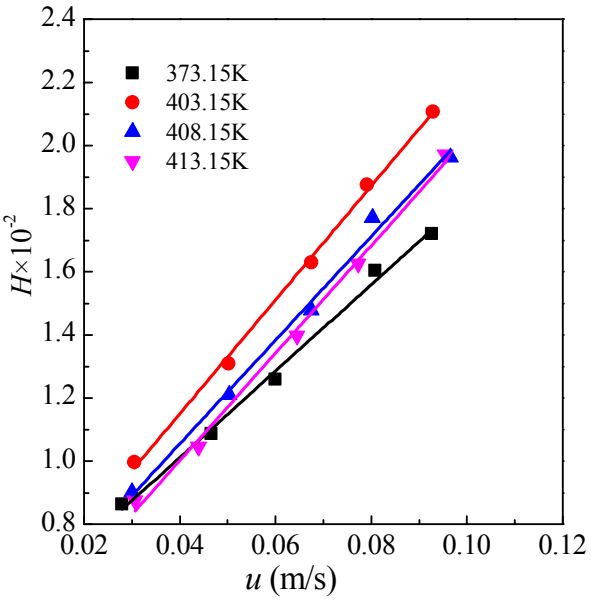

Figure S5 Relationships between the plate height and the flow rate of carbon tetrachloride in column under different temperatures

Table S3 Correlation Coefficients in all Linear Fittings

Temperature(K)	Dichloromethane	Chloroform	Carbon tetrachloride
373.15	0.9976	0.99236	0.99345
378.15	0.9957	0.9971	0.9918
383.15	0.9994	0.9958	0.9927
388.15	0.9965	0.9984	0.9996
393.15	0.9938	0.9958	0.9960
398.15	0.9972	0.9939	0.9972
403.15	0.9924	0.9943	0.9972
408.15	0.9880	0.9915	0.9917
413.15	0.9982	0.9970	0.9953

Table S4 Model Parameters of Chlorinated Methane in PET at Various Temperatures

Temperature (K)	Dichloromethane		Chloroform		Carbon tetrachloride	
	k	*C*	*k*	*C*	*k*	*C*
373.15	0.0481	0.1222	0.0194	0.0768	0.0100	0.1369
378.15	0.0482	0.1055	0.0482	0.1518	0.0093	0.0841
383.15	0.0451	0.0859	0.0699	0.1778	0.0136	0.0902
388.15	0.0460	0.0773	0.0747	0.1664	0.0265	0.1348
393.15	0.0370	0.0568	0.0791	0.1526	0.0351	0.1586
398.15	0.0448	0.0606	0.0667	0.1063	0.0511	0.1810
403.15	0.0348	0.0450	0.0740	0.1081	0.0602	0.1806
408.15	0.0334	0.0401	0.0700	0.0956	0.0635	0.1643
413.15	0.0549	0.0585	0.0723	0.0892	0.0724	0.1703

It is known that the volume of a molecule is determined by the bond length of it, and it doesn't vary much with the temperature. So, here we adopted the volume data of three solvents molecule at absolute zero, which can be estimated by group contribution methods,[21] and they are listed in Table S5.

Table S5 Molecule Volume Data of Three Solvents

Solvents	Dichloromethane	Chloroform	Carbon tetrachloride
Volume (cm^3/mol)	53.1	65.7	78.3

Table S6 Fitting Diffusion Constant and Diffusion Activation Energy of Solvent in PET

Systems	Dichloromethane	Chloroform	Carbon tetrachloride
$D_{0A}\times10^{8}$ (m^2/s)	0.016	0.122	6.555
Q (kJ/mol)	27.193	34.677	50.336

Table S7 Group Contribution Methods to Estimate Molar Volume at 0 K[21]

Component	Sugden (cm^3/mol)	Biltz (cm^3/mol)	Component	Sugden (cm^3/mol)	Biltz (cm^3/mol)
H	6.7	6.5	P	12.7	
C(aliphatic)	1.1	0.8	S	14.3	
C(aromatic)	1.1	5.1	triple bond	13.9	16.0
N	3.6		double bond	8.0	8.6
N(in ammonia)	0.9		3-membered ring	4.5	
O	5.9		4-membered ring	3.2	
O(in alcohol)	3.0		5-membered ring	1.8	
F	10.3		6-membered ring	0.6	
Cl	19.3	16.3	OH(alcoholic)		10.5
Br	22.1	19.2	OOH(carboxyl)		23.2
I	28.3	24.5			

Table S8 Free Volume Theory Parameters of Each Polymer-Solvent System

Polymer/Solvent	Parameters		Data resource
Dichloromethane	$D_{01}\times10^{-8}$ (m^2/s)	3.88	Ref. 12
	$V_1^o(0)$ (cm^3/mol)	53.1	Cal. by Ref. 21
	δ_1 $(Cal/cm^3)^{1/2}$	9.7	Ref. 28
Chloroform	$D_{01}\times10^{-8}$ (m^2/s)	5.49	Ref. 12
	$V_1^o(0)$ (cm^3/mol)	65.7	Cal. by Ref. 21
	δ_1 $(Cal/cm^3)^{1/2}$	9.3	Ref. 28
Carbon tetrachloride	$D_{01}\times10^{-8}$ (m^2/s)	9.77	Ref. 12
	$V_1^o(0)$ (cm^3/mol)	78.3	Cal. by Ref. 21
	δ_1 $(Cal/cm^3)^{1/2}$	8.6	Ref. 28
PET	V_{2j}^* (cm^3/mol)	132.23	Cal. by Eq. (13)
	V_{2j}^* (cm^3/mol)	137.92	Experiment
	V_2^* (cm^3/g)	0.652	Cal. by Ref.21
	C_{12}	2.71	Ref. 24
	C_{22} (K)	310.79	Ref. 24
	δ_2 $(Cal/cm^3)^{1/2}$	5.017	Ref. 28

Table S9 Comparison of Experimental Data with the Theoretical Prediction Considering Molecular Interactions between Polymer and Solvent or Not

Systems	Temperature (K)	$D_E^{\infty}\times10^{12}$ $(m^2/s)^a$	$D_{T3}^{\infty}\times10^{9}$ $(m^2/s)^d$	$D_{T2}^{\infty}\times10^{12}$ $(m^2/s)^c$
PET/ Dichloromethane	373.15	2.422	4.197	2.489
	378.15	2.807	4.337	2.837
	383.15	3.250	4.476	3.223
	388.15	3.677	4.616	3.648
	393.15	4.093	4.756	4.116
	398.15	4.579	4.897	4.630
	403.15	4.883	5.037	5.193
	408.15	5.270	5.178	5.807
	413.15	5.690	5.319	6.476
PET/ chloroform	373.15	1.641	3.451	1.737
	378.15	1.951	3.594	2.000
	383.15	2.320	3.738	2.295
	388.15	2.624	3.884	2.623
	393.15	3.006	4.031	2.987
	398.15	3.726	4.180	3.390
	403.15	4.011	4.330	3.836
	408.15	4.321	4.481	4.326
	413.15	4.761	4.633	4.865
PET/carbon	373.15	0.484	3.715	0.655

tetrachloride	378.15	0.735	3.898	0.770
	383.15	0.994	4.084	0.902
	388.15	1.258	4.273	1.051
	393.15	1.396	4.465	1.221
	398.15	1.726	4.660	1.413
	403.15	2.002	4.858	1.628
	408.15	2.309	5.058	1.870
	413.15	2.496	5.262	2.141

[a] D_E^{∞} is experimental infinite dilution diffusion coefficients of chlorinated methane in PET;

[d] D_{T3}^{∞} is theoretical predictions ignoring the molecular interaction between polymer and solvent;

[c] D_{T2}^{∞} is theoretical predictions considering the molecular interaction between polymer and solvent.