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吡啶基离子液体[C_6py][DCA]热力学性质及利用新 Eötvös 方程预测其表面张力

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Thermodynamic Properties and Predicting the Surface Tension of Pyridinium-Based Ionic Liquids of [C_6py][DCA] Using a New Eötvös Equation

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一、表征

A　[C_6py][DCA]的 ^{1}H NMR 表征

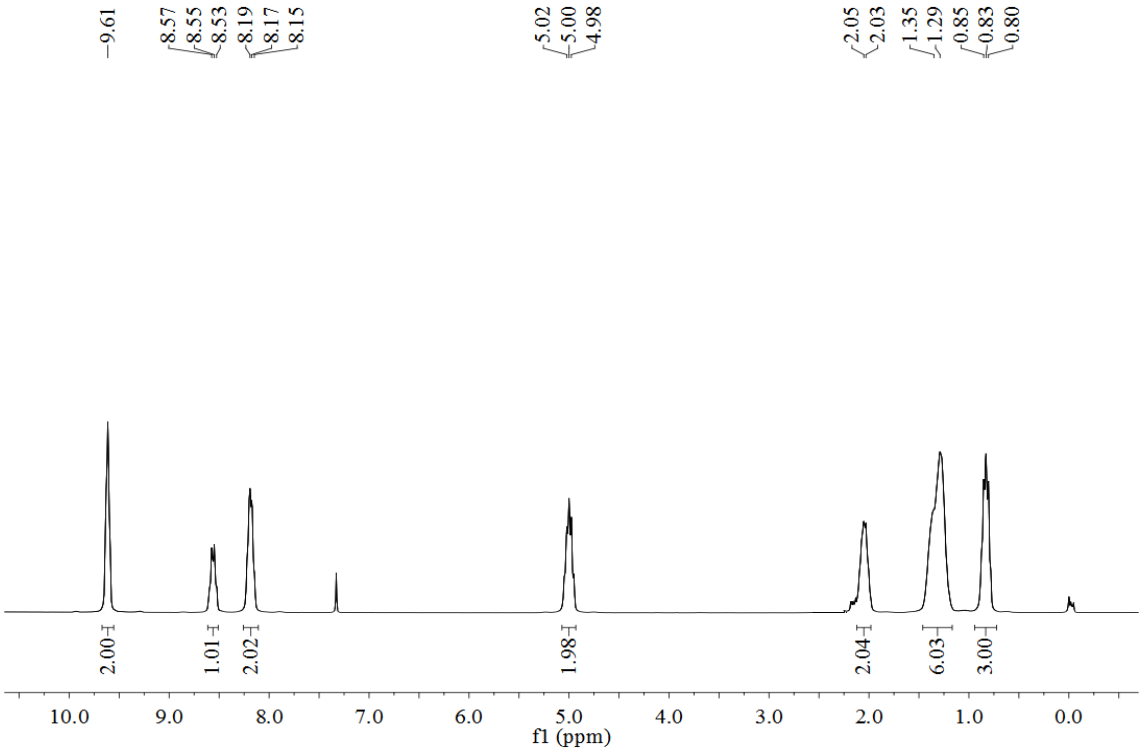


图 S1　离子液体[C_6py][DCA]的 ^{1}H NMR 谱图

Fig.S1　^{1}H NMR of IL [C_6py][DCA]

表 S1　[C_6py][DCA]的 ^{1}H NMR 的化学位移（300 MHz, $CDCl_3$）

Table S1　The ^{1}H NMR spectrum δ_H (300 MHz, $CDCl_3$) of [C_6py][DCA]

Chemical shift (ppm)	Hydrogen number	Radical
0.78 (t)	3	$CH_2CH_2\boldsymbol{CH_3}$
1.28-1.22 (m)	6	$CH_2\boldsymbol{CH_2CH_2CH_2}CH_3$
1.98-1.96 (m)	2	$NCH_2\boldsymbol{CH_2}CH_2$
4.95 (t)	2	$N\boldsymbol{CH_2}$
8.12 (t)	2	C(2)***H***、C(4)***H***
8.51 (t)	1	C(3)***H***
9.55 (d)	2	C(1)***H***、C(5)***H***

注：d: 二重峰；t: 三重峰；m: 多重峰。

B　[C_6py][DCA]的 ^{13}C NMR 表征

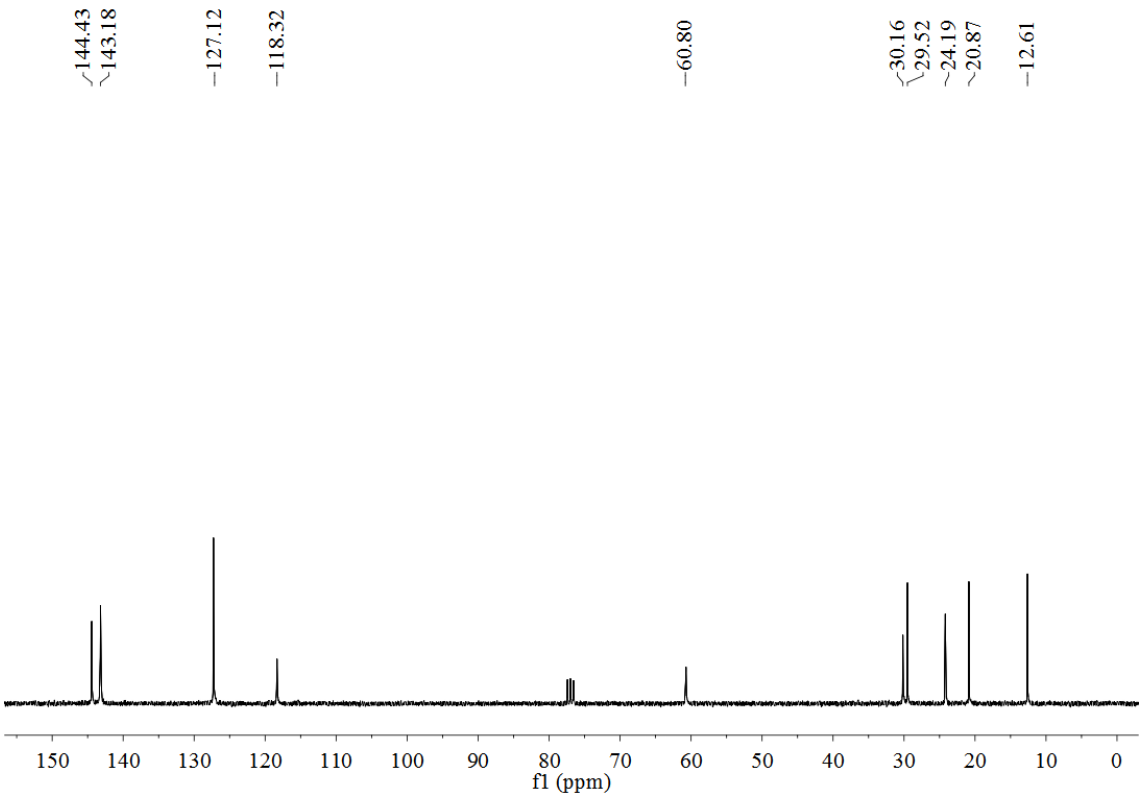


图 S2　离子液体[C_6py][DCA]的 ^{13}C NMR 谱图

Fig.S2　^{13}C NMR of IL [C_6py][DCA]

表 S2　[C_6py][DCA]的 ^{13}C NMR 的化学位移（70 MHz, $CDCl_3$）

Table S2　The ^{13}C NMR spectrum δ_C (70 MHz, $CDCl_3$) of [C_6py][DCA]

Chemical shift (ppm)	Radical
12.61	–CH_3
20.87~30.16	–CH_2–
60.80	–CH_2–N–
118.32	=CH–
127.12	=CH–
143.18	=CH–N–
144.43	–C≡N

C　傅里叶变换红外光谱（FT-IR）表征

红外光谱谱图数据的大致归属: C=C的骨架振动$\nu_{C=C}$位于1500-1600 cm^{-1}, C-N的伸缩振动$\nu_{=C-N}$位于1700-1900 cm^{-1}, C-H的伸缩振动$\nu_{=C-H}$位于2900-3200 cm^{-1},–C≡N的伸缩振动$\nu_{C\equiv N}$位于2050-2250 cm^{-1}.

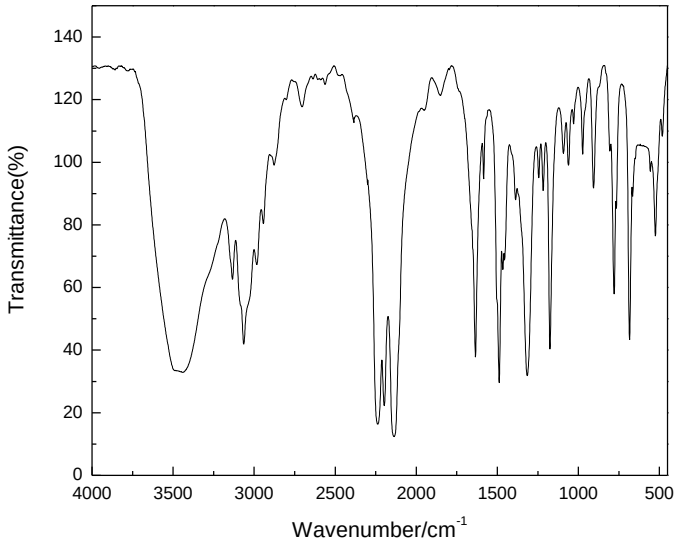


图 S3　离子液体[C_6py][DCA]的 FT-IR 谱图

Fig.S3　FT-IR of ILs [C_6py][DCA]

D　差热扫描量热 DSC 表征

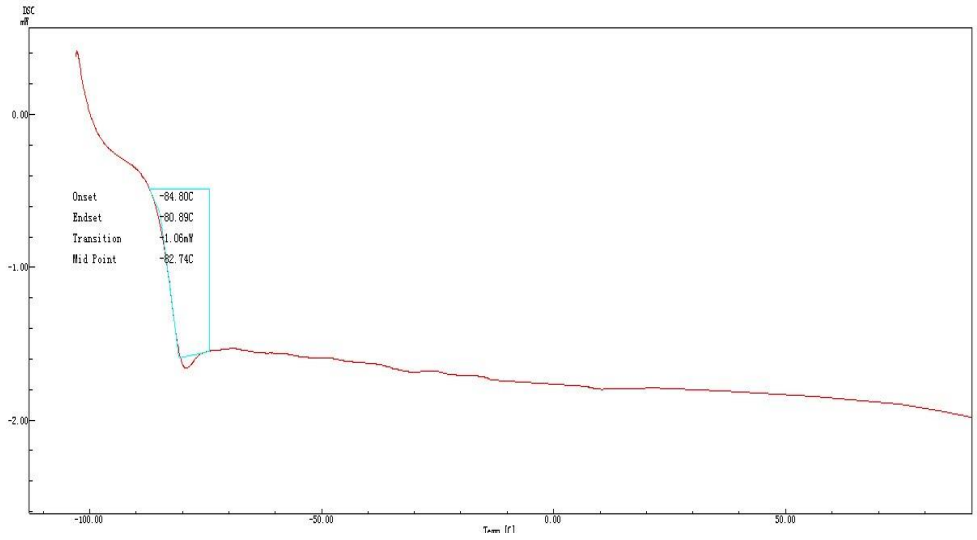
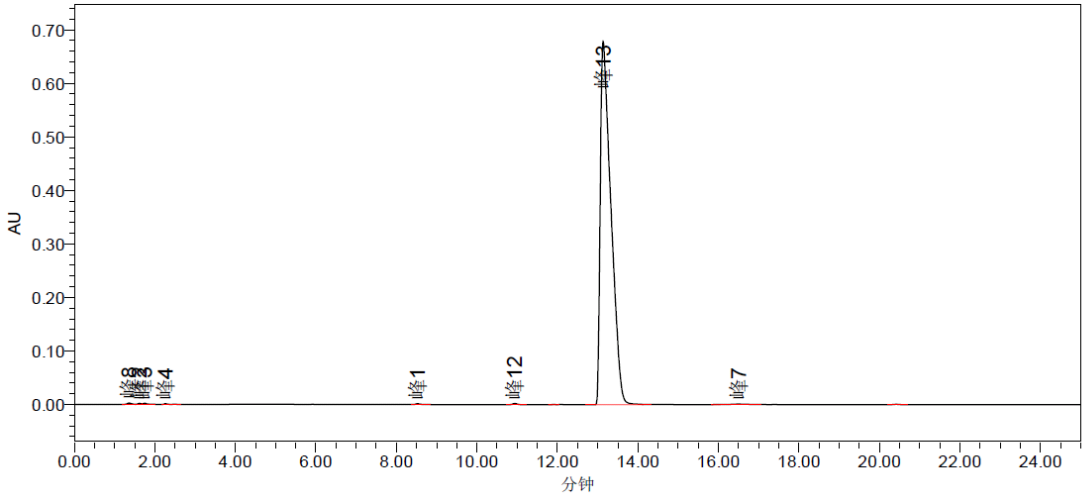


图 S4　离子液体[C_6py][DCA]的 DSC 谱图

Fig.S4　DSC trace of IL [C_6py][DCA]

E　高效液相色谱（HPLC）表征



处理通道说明: W2489 ChA 258nm

	名称	处理通道说明	保留时间 (分钟)	高度 (微伏)	面积 (微伏*秒)	对称因子	分离度	USP 理论塔板数	% 面积
1	峰8	W2489 ChA 258nm	1.362	2595	19522			7.518218e+002	0.16
2	峰2	W2489 ChA 258nm	1.620	1917	11069		1.395918e+000	1.432314e+003	0.09
3	峰3	W2489 ChA 258nm	1.750	1967	13635		7.358148e-001	1.444837e+003	0.11
4	峰4	W2489 ChA 258nm	2.267	1112	6113		3.258071e+000	3.920328e+003	0.05
5		W2489 ChA 258nm	2.491	143	1090			1.424404e+003	0.01
6	峰5	W2489 ChA 258nm	4.933						
7	峰9	W2489 ChA 258nm	5.881						
8	峰6	W2489 ChA 258nm	6.450						
9	峰10	W2489 ChA 258nm	6.889						
10	峰1	W2489 ChA 258nm	8.527	1546	14106	1.637852e+000		2.234604e+004	0.11
11	峰11	W2489 ChA 258nm	9.468						

处理通道说明: W2489 ChA 258nm

	名称	处理通道说明	保留时间 (分钟)	高度 (微伏)	面积 (微伏*秒)	对称因子	分离度	USP 理论塔板数	% 面积
12	峰12	W2489 ChA 258nm	10.940	2256	18802	1.169756e+000	1.100745e+001	4.074485e+004	0.15
13		W2489 ChA 258nm	11.908	192	1185	7.158440e-001	5.248215e+000	7.936148e+004	0.01
14		W2489 ChA 258nm	12.839	171	1147		5.433111e+000	7.612358e+004	0.01
15	峰13	W2489 ChA 258nm	13.139	680896	12429343	2.088395e+000	8.819239e-001	9.611417e+003	99.02
16	峰14	W2489 ChA 258nm	14.097						
17		W2489 ChA 258nm	16.083	192	1592				0.01
18	峰7	W2489 ChA 258nm	16.498	816	27338			4.313509e+003	0.22
19		W2489 ChA 258nm	20.412	834	7852	1.174663e+000	6.525722e+000	1.083133e+005	0.06

图 S5　离子液体[C_6py][DCA]的 HPLC 谱图

Fig.S5　HPLC of IL [C_6py][DCA]

二、SAM 作图

表 S3　288.15 K - 293.15 K 和 303.15 K - 338.15 K[a]，[C_6py][DCA]不同水含量的密度值 ρ(g·cm^{-3})

Table S5　At 288.15 K - 293.15 K and 303.15 K - 338.15 K, values of density, ρ(g·cm^{-3}), for [C_6py][DCA] contained various amount of water

	[C_6py][DCA]							
T/K	10^3w_2=1.78[b]	3.28	4.79	6.28	7.77	0	r	$s \times 10^5$
288.15	1.04226	1.04216	1.04206	1.04195	1.04189	1.04237	0.996	1.47
293.15	1.03927	1.03918	1.03908	1.03897	1.03890	1.03938	0.998	1.06
303.15	1.03329	1.03321	1.03311	1.03299	1.03291	1.03341	0.998	1.22
308.15	1.03030	1.03022	1.03013	1.02999	1.02992	1.03043	0.995	1.90
313.15	1.02733	1.02725	1.02715	1.02702	1.02694	1.02746	0.997	1.51
318.15	1.02438	1.02430	1.02419	1.02405	1.02397	1.02452	0.996	1.83
323.15	1.02144	1.02136	1.02124	1.02111	1.02102	1.02158	0.997	1.54
328.15	1.01851	1.01842	1.01831	1.01817	1.01808	1.01865	0.997	1.51
333.15	1.01560	1.01551	1.01539	1.01524	1.01515	1.01575	0.997	1.82
338.15	1.01270	1.01261	1.01249	1.01233	1.01224	1.01286	0.995	2.11

标准不确定度（0.68 置信水平）：[a]$u(T)$ = ±0.01 K, [b]$u(10^3w_2)$ = ±0.02.

表 S4　288.15 K - 293.15 K 和 303.15 K - 338.15 K[a]，[C_6py][DCA]不同水含量的表面张力值 γ(mJ·m^{-2})

Table S4　At 288.15 K - 293.15 K and 303.15 K - 338.15 K, values of surface tension, γ(mJ·m^{-2}), for [C_6py][DCA] contained various amount of water

	[C_6py][DCA]							
T/K	10^3w_2=1.90[b]	3.40	4.89	6.39	7.91	0	r	$s \times 10^5$
288.15	50.3	50.5	50.7	51.0	51.3	49.9	0.995	4.71
293.15	50.0	50.2	50.4	50.7	51.0	49.6	0.995	4.71
303.15	49.2	49.5	49.7	50.0	50.3	48.9	0.998	3.03
308.15	48.8	49.1	49.4	49.6	49.9	48.5	0.998	3.19
313.15	48.5	48.8	49.0	49.3	49.6	48.2	0.998	3.03
318.15	48.2	48.5	48.7	49.0	49.2	47.9	0.998	3.22
323.15	48.0	48.2	48.4	48.7	48.9	47.7	0.997	3.15
328.15	47.7	47.9	48.1	48.4	48.6	47.4	0.997	3.15
333.15	47.4	47.6	47.8	48.0	48.3	47.1	0.996	3.52
338.15	47.1	47.3	47.5	47.7	48.0	46.8	0.996	3.52

标准不确定度（0.68 置信水平）：[a]$u(T)$ = ±0.01 K，[b]$u(10^3w_2)$ = ±0.02。

表 S5　288.15 K - 293.15 K 和 303.15 K - 338.15 K[a]，[C_6py][DCA]不同水含量的折光率值 n_D

Table S5　At 288.15 K - 293.15 K and 303.15 K - 338.15 K, values of refractive index, n_D, for [C_6py][DCA] contained various amount of water

[C_6py][DCA]								
T/K	10^3w_2=1.90	3.43	4.91	6.57	8.07	0	r	$s \times 10^5$
288.15	1.5295	1.5292	1.5290	1.5288	1.5285	1.5298	0.996	4.02
293.15	1.5279	1.5277	1.5275	1.5273	1.5270	1.5282	0.996	3.74
303.15	1.5249	1.5247	1.5243	1.5241	1.5238	1.5253	0.994	5.74
308.15	1.5235	1.5233	1.5231	1.5228	1.5226	1.5238	0.998	2.48
313.15	1.5219	1.5216	1.5214	1.5212	1.5210	1.5221	0.995	3.96
318.15	1.5202	1.5199	1.5197	1.5194	1.5191	1.5205	0.998	2.85
323.15	1.5188	1.5186	1.5183	1.5181	1.5179	1.5191	0.996	3.56
328.15	1.5174	1.5172	1.5170	1.5168	1.5166	1.5176	0.999	0.62
333.15	1.5157	1.5155	1.5152	1.5150	1.5148	1.5160	0.996	3.56
338.15	1.5141	1.5139	1.5137	1.5134	1.5132	1.5144	0.998	2.48

标准不确定度（0.68 置信水平）：$^a u(T) = \pm 0.01$ K，$^b u(10^3 w_2) = \pm 0.02$。

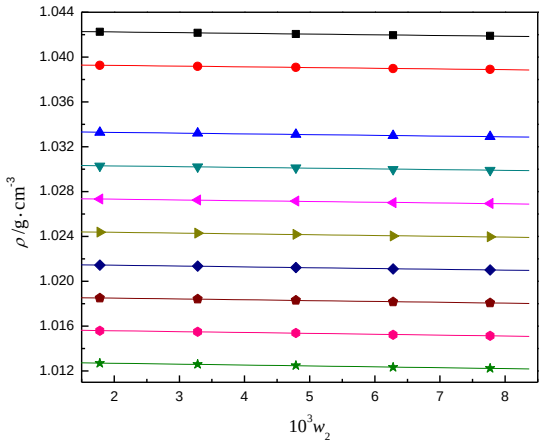


图 S6　[C_6py][DCA]的密度值对其含水量作图

Fig.S6　The plot of density vs. the various amount of water in [C_6py][DCA]

■288.15 K: ρ = 1.04237 – 0.63424 ×10^{-4} w_2, s = 1.47 ×10^{-5}, r = 0.996;

●293.15 K: ρ = 1.03938 – 0.63422 ×10^{-4} w_2, s = 1.06 ×10^{-5}, r = 0.998;

▲303.15 K: ρ = 1.03341 – 0.65418 ×10^{-4} w_2, s = 1.22 ×10^{-5}, r = 0.998;

▼308.15 K: ρ = 1.03043 – 0.66082 ×10^{-4} w_2, s = 1.90 ×10^{-5}, r = 0.995;

◀313.15 K: ρ = 1.02746 – 0.67419 ×10^{-4} w_2, s = 1.51 ×10^{-5}, r = 0.997;

▶318.15 K: ρ = 1.02452 – 0.71425 ×10^{-4} w_2, s = 1.83 ×10^{-5}, r = 0.996;

◆323.15 K: ρ = 1.02158 – 0.72762 ×10^{-4} w_2, s = 1.54 ×10^{-5}, r = 0.997;

⬟328.15 K: ρ = 1.01865 – 0.74095 ×10^{-4} w_2, s = 1.51 ×10^{-5}, r = 0.997;

⬢333.15 K: ρ = 1.01575 – 0.78101 ×10^{-4} w_2, s = 1.83 ×10^{-5}, r = 0.997;

★338.15 K: ρ = 1.01286 – 0.80102 ×10^{-4} w_2, s = 2.11 ×10^{-5}, r = 0.995.

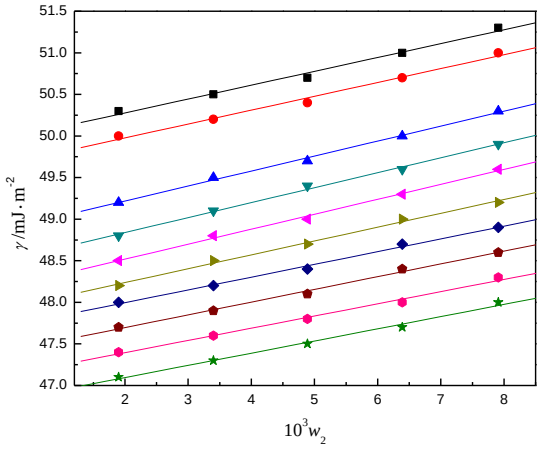


图 S7　[C_6py][DCA]的表面张力对其含水量作图

Fig.S7　The plot of surface tension *vs.* the various amount of water in [C_6py][DCA]

■288.15 K: γ = 49.96 + 0.1666 w_2, s = 3.11 ×10^{-2}, r = 0.998;

●293.15 K: γ = 49.72 + 0.1599 w_2, s = 3.57 ×10^{-2}, r = 0.997;

▲303.15 K: γ = 48.86 + 0.1799 w_2, s = 3.03 ×10^{-2}, r = 0.998;

▼308.15 K: γ = 48.48 + 0.1799 w_2, s = 3.19 ×10^{-2}, r = 0.998;

◀313.15 K: γ = 48.16 + 0.1799 w_2, s = 3.03 ×10^{-2}, r = 0.998;

▶318.15 K: γ = 47.90 + 0.1665 w_2, s = 3.22 ×10^{-2}, r = 0.998;

◆323.15 K: γ = 47.69 + 0.1532 w_2, s = 3.15 ×10^{-2}, r = 0.997;

⬟328.15 K: γ = 47.39 + 0.1532 w_2, s = 3.15 ×10^{-2}, r = 0.997;

⬢333.15 K: γ = 47.10 + 0.1466 w_2, s = 3.52 ×10^{-2}, r = 0.996;

★338.15 K: γ = 46.80 + 0.1466 w_2, s = 3.52 ×10^{-2}, r = 0.996.

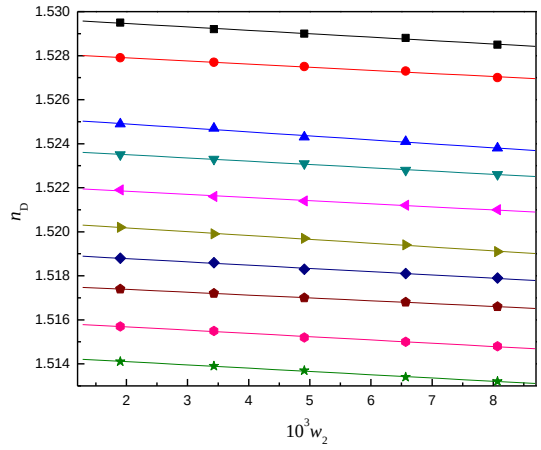


图 S8　[C_6py][DCA]的折光率对其含水量作图

Fig.S8　The plot of refractive index *vs.* the various amount of water in [C_6py][DCA]

■288.15 K: n_D = 1.5298 – 1.5490 ×10^{-4} w_2, s = 4.02 ×10^{-5}, r = 0.996;

●293.15 K: n_D = 1.5282 – 1.4207 ×10^{-4} w_2, s = 3.74 ×10^{-5}, r = 0.996;

▲303.15 K: n_D = 1.5253 – 1.8064 ×10^{-4} w_2, s = 5.74 ×10^{-5}, r = 0.994;

▼308.15 K: $n_D = 1.5238 - 1.4872 \times 10^{-4}\ w_2$, $s = 2.48 \times 10^{-5}$, $r = 0.998$;
◀313.15 K: $n_D = 1.5221 - 1.4200 \times 10^{-4}\ w_2$, $s = 3.96 \times 10^{-5}$, $r = 0.995$;
▶318.15 K: $n_D = 1.5205 - 1.7446 \times 10^{-4}\ w_2$, $s = 2.85 \times 10^{-5}$, $r = 0.998$;
◆323.15 K: $n_D = 1.5191 - 1.4844 \times 10^{-4}\ w_2$, $s = 3.56 \times 10^{-5}$, $r = 0.996$;
⬟328.15 K: $n_D = 1.5176 - 1.2916 \times 10^{-4}\ w_2$, $s = 6.19 \times 10^{-5}$, $r = 0.999$;
⬢333.15 K: $n_D = 1.5160 - 1.4844 \times 10^{-4}\ w_2$, $s = 3.56 \times 10^{-5}$, $r = 0.996$;
★338.15 K: $n_D = 1.5144 - 1.4872 \times 10^{-4}\ w_2$, $s = 2.48 \times 10^{-5}$, $r = 0.998$.