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Multiple Equilibria Interaction Pattern between the Ionic Liquids $C_n$mimPF$_6$ and β-Cyclodextrin in Aqueous Solutions

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■ INTRODUCTION

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t tt t i l ti , t t ti

$$f_{\pm}{}^2 = \left[-\frac{\kappa\beta}{1 + \kappa R}\right] \quad (5)$$

$$\alpha = \frac{-1 + \sqrt{1 + 4K\ cf_{\pm}{}^2}}{2K\ cf_{\pm}{}^2} \quad (6)$$

$$\kappa = \left(\frac{\pi N\ e^2|z|^2\alpha c}{1000\varepsilon kT}\right)^{1/2} \quad (\ )$$

$$\vartheta = \frac{|z|Fe}{(2\ \ .\ \ )(3\pi\eta)} \quad (\ )$$

$$\beta = \frac{z^2e^2}{\varepsilon kT} \quad (\ )$$

C_i $(i = 1-5)$ i l ti t t κR, i i t lit t .[4] $f_{\pm}$ R t ti it i i t t i t i i t t , ti l , Λ^0 K t li iti l ti it i i i ti t t t , ti l . t t t l i .

l α, Λ^0, K , $f_{\pm}{}^2$ t i li l t- it ti . ti , t l l ti fi i t l t t t i t j ti ti 10 t i i [52,53]

$$S = \sum_{i=1}^{n}(\Lambda_{i}^{1} - \Lambda_{i})^2 w_i \quad (10)$$

w_i i t i ti t .

RESULTS AND DISCUSSION

Competitive Fluorescence Method. titi l - t li t t t i t ti t t t ll .[36,3 ,54] tit t 3H- i l l l l iti t i t t t l t i - l l t ,[55,56] i i ll it l t t i t ti t t t , . ., β- 1- t l-3- t li i li l i (4 l).[32] fl t 1 i t n 6/β- t , t i t 2 6/β- t i i 1 . it i t t ti t i i t i , t n 6 i it i fl i . fl i t it 1 i t l ti n 6 i li tl l t t t i t , i t t t fl 1. tl , ll t fl t i i t l 1. i il t t i t,[46] t K'_1, K'_2, I_1/I_0, I_2/I_0 l (K'_1 K'_2 t i ti t t 1 1 1 2 l t 1 β- , ti l I_0, I_1, I_2 t t fl i t it 1 i t , i t 1 1 l , i t 1 2 l , ti l) ti t 56 ± 1 $^{-1}$, 22 ± 1 $^{-1}$, 5.1 ± 1.45, 13. ± 0.2, ti l , it l ti ffi i t r^2 ≈ 0. li i l i . l l t t t i t lit t .[55,56] ili i t ti β- , i. ., , t iff t n 6 0 (t i iti l t ti n 6) l l t i t K'_1, K'_2, I_1/I_0, I_2/I_0

l .[55] t ti β- i i it n 6 t i $_0$ − . i 1 t i ti n 6 0 ti . t 1 1 i l i l , n 6 0 i l t t t ll i ti

$$[n\ \ 6]_0 = \frac{([\ \ ]_0 - [\ \ ])(1 + K_1[\ \ ])}{K_1[\ \ ]} \quad (11)$$

t i t 1 1 1 2 i l i l , K_1 K_2 t i t ll i ti

$$[n\ \ 6]_0 = \frac{([\ \ ]_0 - [\ \ ])(1 + K_1[\ \ ] + K_1K_2[\ \ ]^2)}{K_1[\ \ ] + 2K_1K_2[\ \ ]^2} \quad (12)$$

lt t i t ti t β- n 6 i l 1. t 2 6 4 6 1 1 i l i l it β- , i ti t t li tl l t t t 6 it β- . 6 6 l t 1 1 l it β

Table 1. Stoichiometry and Association Constants of KPF_6 and $C_n$mimPF_6 (n = 2, 4, 6, 8) with β-CD in Water and of C_8mimPF_6 with β-CD in the Aqueous Solution of Urea by Competitive Fluorescence Method

					mimPF 6		
	6	2mimPF 6	4mimPF 6	6mimPF 6	= 0	= 3	= 5
t i i t	1 1	1 1	1 1	1 1	1 1 1 2	1 1 1 2	1 1
K_1/ −1	100 ± 1	121 ± 2	15 ± 3	3 1 ± 15	11 ± 5	[illegible] 6 ± 5	[illegible] ± 4
K_2/ −1	–	–	–	–	25 ± 3	46 ± 15	–

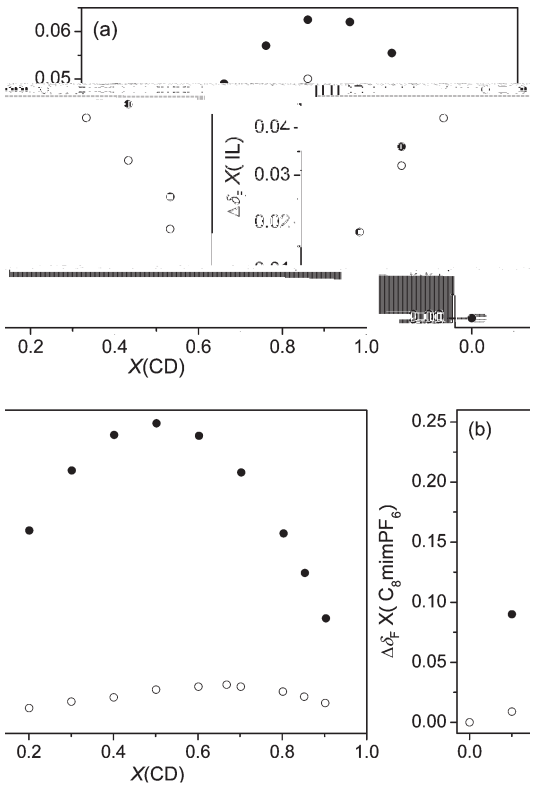

Figure 2. l t i t i l i t fl i t i 6 β- D l ti i it ( ) 6 (○) 6mimPF 6 (●), ( ) mimPF 6 i t (○) (●) 5 .

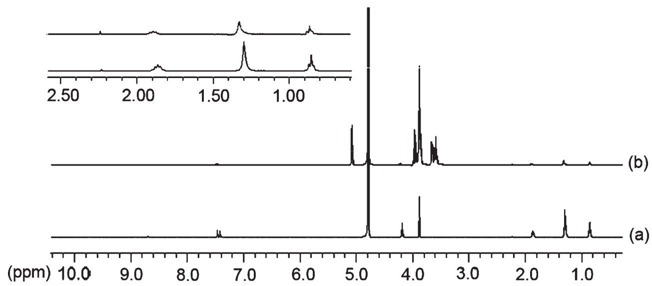

Figure 3. [1]H t ( ) 6mimPF 6, ( ) i t 6mimPF 6 β- D i D_2O. i ti t i i l t 0.6 t 2.6 .

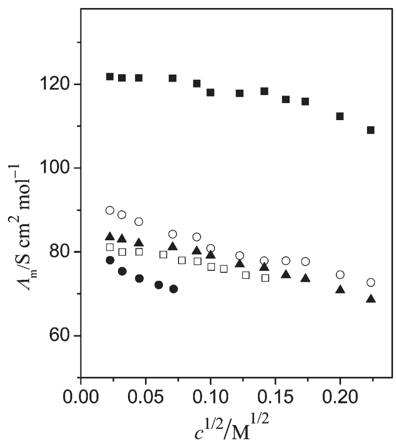

Figure 4. l ti it t t ti nmimPF 6 6 i t . tt t t mimPF 6 (●), 6mimPF 6 (□), 4mimPF 6 (▲), 2mimPF 6 (○), 6 (■).

l . t 5 i , l t 1 1 l i .

NMR Measurements. t li t ti t i ti i t l t i t l t i i t ,[1,5] i i i ll t t t t l i t t l i l i t. t i t ti t D, t t li t l ti t 2 β- D.[1] l t 6 nmimPF 6 it β- D i i 2. i 2 , t l 6 t 0.5. t i l β- D t [1] i l 2mimPF 6 4mimPF 6 t t , t 0.5, i l t t t 6, (t t), ti i t t 6, 2mimPF 6, 4mimPF 6 1 1 i l i l it β- D. i it t [1]H i l 2mimPF 6 4mimPF 6 i t β- D. 6mimPF 6 mimPF 6, i ii ti l β- D t t [1]H [1] i l t . i i i 3, t [1]H i l H_2 i t l l i

i i i t iti β- D i t - i l 1.30 (i 3) t 1.31 (i 3), i i ti t t t l l l i 6mimPF 6 mimPF 6 l t t it β- D.[32] t [1] i l t 0.5 i i 2 t 6mimPF 6/β- D t t ti l t 1 1 i l i l . i 2 , [1] i ti 0.5 t t i t l t mimPF 6 [1] β- D. t iti 5 , t i l t i t 0.5 i i t t ti l t 1 1 i l i l t i iti , i t it t lt t titi l t .

Conductivity Measurements. t t t t t t nmimPF 6 i l ti , ti it t i t. l ti iti 6 nmimPF 6 l ti i i 4.

l ti it , Λ, l 0.5−50 6, 0.5−50 2 i 6, 0.5−50 4 i 6, 0.5−20 6 i 6, 0.5−5 i 6 l ti 12 −10 .0 . − 2. 3.5− .6 1.1− , .0− 1.1 · 2 · l−1, ti l .

t i t ti tt t n i 6 β- D i l ti i i , l i t t t t . i ifi t tt ti t t t t t - i t t t — i i . t t t t, it t ti i i t t t , t t t t i i t i i l t , i t i i t i t t - i i .[41] l t t t t il t

l ti i l 5. ti ΔG l
t t t i l i t l . t
6 2 i 6 4 i 6 ti ΔH ΔS
l t t t i l i l ti i t i
t l t ll , t t t i . i i t
it ti i t ti i l i l
t D i t l l . t ti
ΔS

Table 3. Comparison between Observed m/z Values (m/z_{obs}) and Calculated m/z Values (m/z_{calc}) for Equal Moles of C_2mimPF_6 and β-CD (Obtained by ESI/HRMS)

[illegible]	[illegible]	m/z [illegible]	m/z [illegible]	[illegible] [a]
-4	($_2$[illegible]–β-CD)$^+$	1245.461 44	1245.45 05	++
-2	($_2$[illegible]·$_6$–β-CD + [illegible])$^+$	1413.415 3	1413.4[illegible] 3	+
-5	($_6$–β-CD)$^-$	12 .333 40	12 .333[illegible]	++
-2	($_2$[illegible]·$_6$–β-CD + [illegible]OO)$^-$	1435.423 2	1435.423 00	+
-2	($_2$[illegible]·$_6$–β-CD + $_6$)$^-$	1535[illegible] 0	1535[illegible] 5	+

[a] [illegible] (45%) ++, [illegible] (45%).

Table 4. Comparison between Observed m/z Values (m/z_{obs}) and Calculated m/z Values (m/z_{calc}) for Different Molar Ratios of C_8mimPF_6/β-CD (Obtained by ESI/HRMS)

[illegible]	[illegible]	m/z [illegible]	m/z [illegible]	[illegible] [a]
	[illegible]$_6$/β-CD = 1			
-4	([illegible]–β-CD)$^+$	132 .555 34	132 .553[illegible]	++
-1	([illegible]·$_6$–β-CD + [illegible])$^+$	166 . 05 64	166 . 02 6	+
-5	($_6$–β-CD)$^-$	12 .333 40	12 .336 2	++
	[illegible]$_6$/β-CD = 0.5			
-6	([illegible]–β-CD$_2$ + 1 − 2[illegible])$^{2-}$	12[illegible] . 40 5	12[illegible] . 40 6	+
-6	([illegible]–β-CD$_2$ + 2 1 − [illegible])$^{2-}$	126 .4[illegible] 21	126 .42 13	+

[a] [illegible] (45%) ++, [illegible] (45%).

β-CD.[1,32] [illegible] β-CD [illegible] -1 -2, [illegible] ($_6^-$–β-CD) (-3) [illegible] (-4) $_6^-$–β-CD (-5). [illegible] β-CD, [illegible] 1 2 [illegible]–β-CD$_2$ (-6) [illegible] β-CD. [illegible] β-CD [illegible] β-CD [illegible] β-CD [illegible] β-CD.[36,3] [illegible] β-CD (2). [illegible] β-CD [illegible] β-CD. [illegible] 2. [illegible] β-CD [illegible] β-CD [illegible] (-1) [illegible] (-2), [illegible] (-3) [illegible] –β-CD (-4) [illegible] –β-CD (-5) [illegible]

[illegible] β-CD [illegible] $_6^-$ [illegible] β-CD 1 1 $_6^-$–β-CD (-5) [illegible] β-CD 1 1 [illegible]–β-CD (-4) [illegible] β-CD 1 2 [illegible]–β-CD$_2$ (-6) [illegible] 2, [illegible] β-CD, [illegible] 1 1 -1 -2, -4, -5 [illegible] -3 [illegible] -4 -5 [illegible] β-CD [illegible] -1 -2, -4, -5. [illegible] β-CD, [illegible] -1, -4, -5 [illegible] -3 [illegible] -4 -5. [illegible] -4 [illegible] β-CD [illegible] -6. [illegible] β-CD [illegible] -1, -4, -5, [illegible] -6. [illegible] β-CD.

Thermodynamic Parameters of the Inclusion Complexes. [illegible] β-CD [illegible] β-CD [illegible] β-CD. [illegible] $_6$–β-CD (1 1 5). [illegible] β-CD [illegible] ΔS [illegible] (1 5). [illegible] ΔS [illegible]

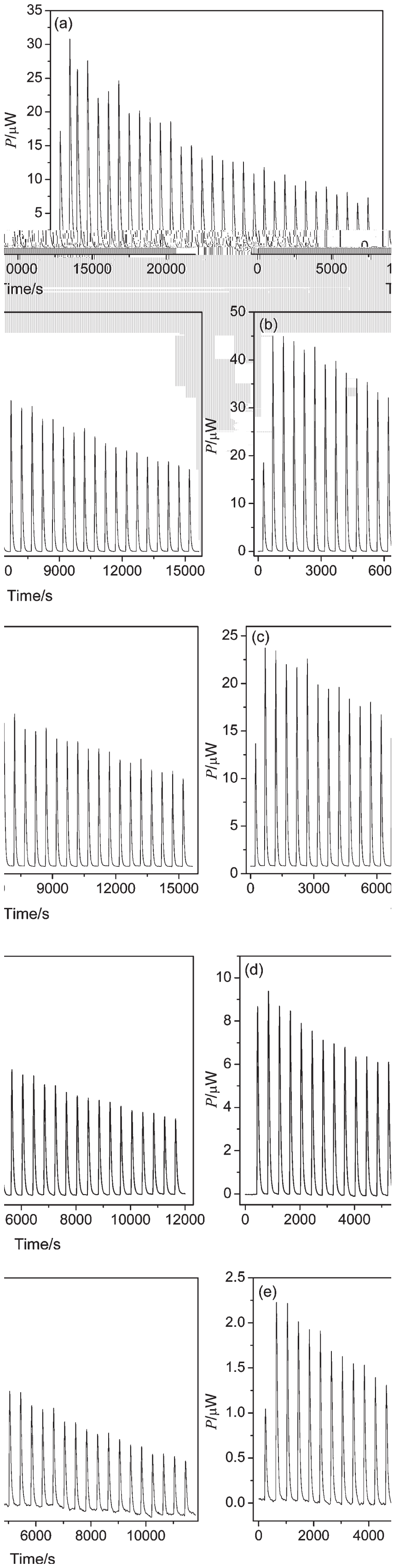

Figure 6. [illegible]

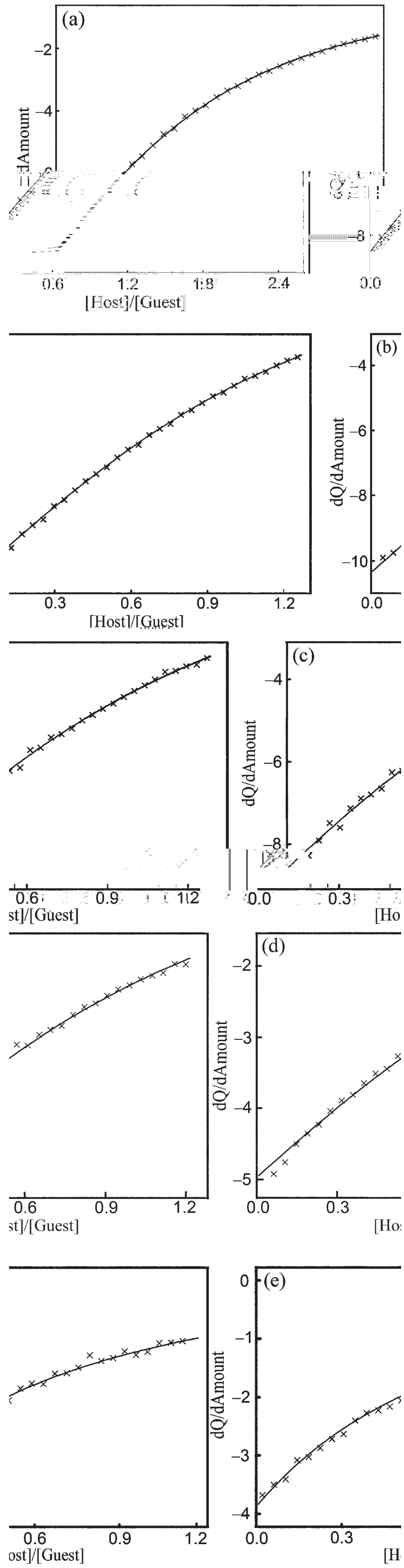

Figure 7. [illegible] β- [illegible]

■ CONCLUSIONS

t i 1 1 i l i l (t), i t ti it l i l l t β- .

AUTHOR INFORMATION

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. . .

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t t lt . i i l i t t ti t i i ti , . i . i (l ti l t t t i i- it) t i l i / t , . i i (iji t) i l i t . i fi i ll t t - ti l t l i ti i (t 100).

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