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w T -100 β- : A 3H-

, , k

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29 2007; 2007; 15 2007
A 21 2007

Abstract

W T -100 w β- (β-CD) 2-(*p*-)-3,3- -5- -3*H*- (**1**) fl . T 1:1 1:2 (:) w fi w . T -100 , w w **1**. , T -100 w β-CD w . w T -100 w β1

1. Introduction

C (CD) - , 6, 7, 8 D-(+)- α-, β-, γ-CD , . T , w . T w w 17 , . k . T w - w , , , , , 1 . w CD 2 22 , , , , CD , . .

β-CD T -100 23 . T , w T -100 β-CD fi . T w CD fl - 2,3,8,11,13,15 , 16 , 5,18 , 7 , 19 , 20 , (CD) 21 22 . , w w . A (D) - w β-CD 4 . D /β-CD , , , 4 . , w fl w 4 . T -

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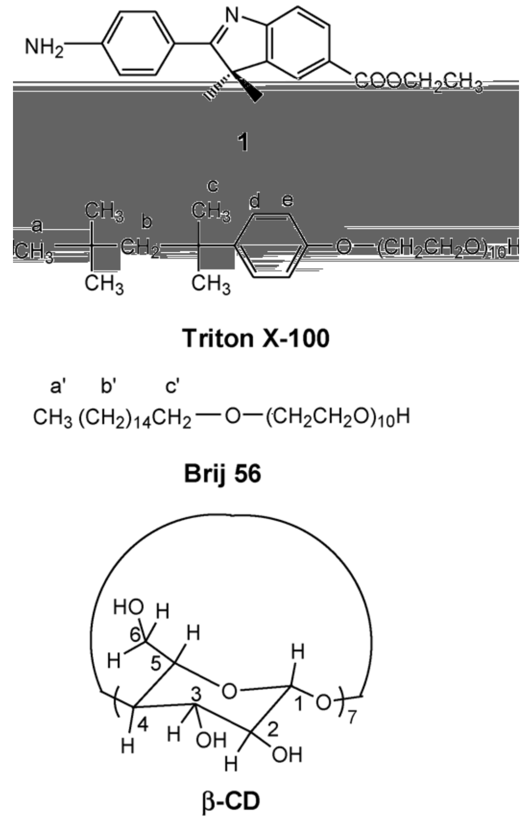
, ,
fl , w w fi k
. [2], w -
w CD . T
T -100/β-CD .
,
[5–14]. -
, w T -100 1:1
(:) w β-CD [5–11]. T
1:2 w T -100 β-CD w
[12,14]. w , B .
1:1 1:2 [13]. B
, -
w , ,
1:1 w
145 $(1.82 \pm 0.15) \times 10^{5}$ $^{-1}$. ,
.
F 3*H*- -
[24],
[25], [26,37], [27]
[3,28–30,35,36]. W
- 3*H*- -
w
,
w β-CD [29]. T
- 3*H*- A T (
-(2-))- w/
T -100
w [31–33]. , w
3*H*- -β-CD, w w
w
[34].
w 3*H*- , **1** (1) [3,28,35–37]. **1**
β-CD w
, . ., 1:1 1:2 , w
D β-CD w -
1 [3].
w k, w **1** T -100
fl w T -100
w β-CD. F , w B j 56
β-CD w .

2. Experimental

2.1. Materials

T fi **1** w
[38]. β-CD (A , F C
k) w w
w [24]. T -100
B j 56 w A w -
fi w w
[24]. T w w
. D_2 (99.9% ,
B j C C) w
.



1, T -100, B j 56 β-CD.

2.2. Instruments

A w 0-3010 (,
) 1- . T
w w 1 . F w F -
4500 (,) . E w
w 1
(356 **1** 275 T -100, -
). B w 5
. T w 240 / . F -
w -
- fl F 920 (E). T
w fl
w
w -
. T w 10%. T -
w w 356 470 **1**. T
w
fl
w w [39]. T 2D E
w B k A0 400 .
2D E w ,
(D_1) (D_8) w 2000 400 , .

2.3. Methods

F w fl -
. k **1** w

. T w 1
w j 9.5
w 35,36 . T 1 -
fl w 10^{-5} 10^{-6},
. T -100 w ,
W w fi 6.0 × 10^{-6}
w j .
1 w , w
δ W ( ) k D_2 -
(δ = 4.77 , 298) 40 . T w
298.0 ± 0.1 . A w
.

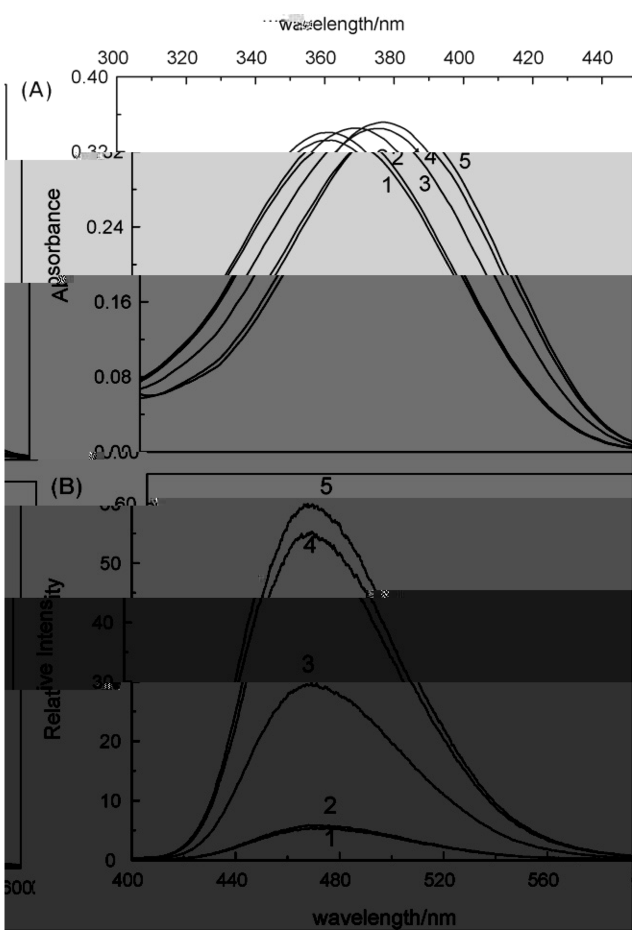
3. Results

3.1. Interaction of Triton X-100 with β-CD

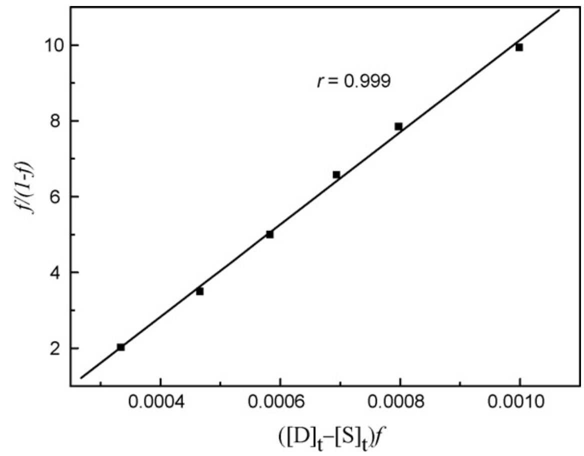
3.1.1. Interaction of *1* with the Triton X-100 micelle

T fl 1 w
T -100 w F . 1.

k



F . 1. A (A) fl (B) 1
T -100 ( ): 0 (1); 0.10 (2); 0.40 (3); 1.00 (4); 3.00 (5).



F . 2. $f/(1-f)$. (D)f 1 T -100 .

fl w
T -100 w ,
fl
T -100 w 0.1 l .
w 3H-
D 37 .
T w (K)
w -
(C) w
28,41 :

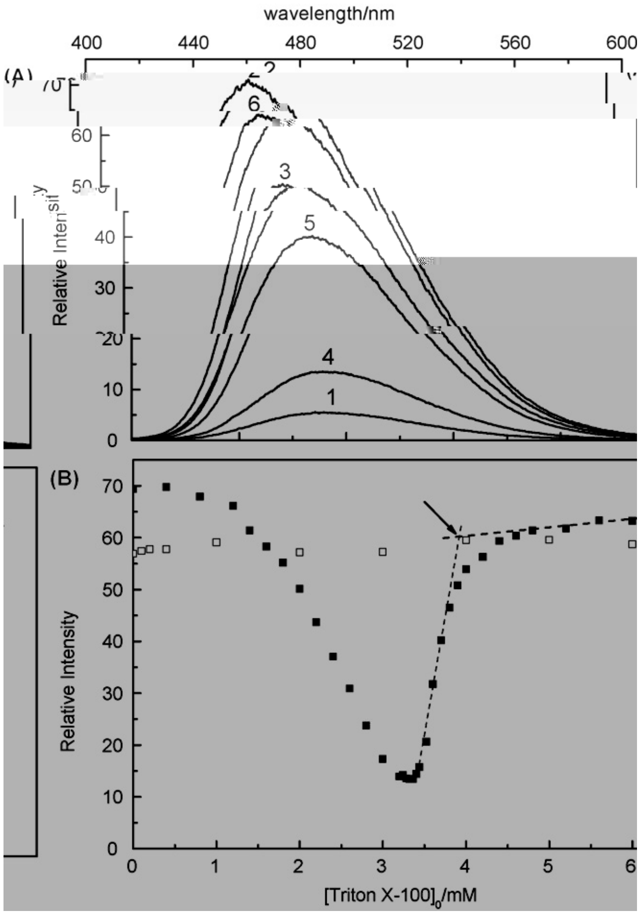
$$\frac{f}{1-f} = K(D -)f - K C \quad (1)$$

$$f = \frac{I - I_w}{I - I_w} \quad (2)$$

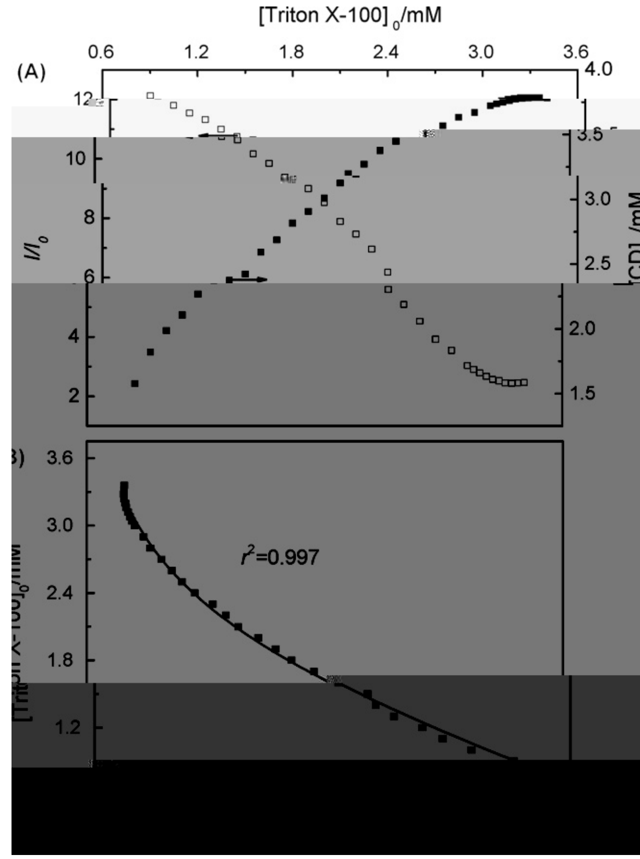
w f -
fl
(I), w (I_w),
(I). D -
, . A
$f/(1-f)$ (D)f ,
w K C
. F . 2 k
1 w T -100 . w -
K C w 12 200 ± 300 $^{-1}$
(1.7 ± 0.2) × 10^{-4} , . T C T -
100 0.14 0.31
6 8,10,12,44,45 . -
, C . 44 D . 10
C T -100 0.14 0.3 ,
fl ,
C W T -100 w 0.24 0.26 45 .
C w
.

3.1.2. Investigation on the Triton X-100/β-CD inclusion complex using *1* as a probe

T fl fl 1
T -100/β-CD w F . 3. T -



F . 3. (A) F 1 w (1), 4.00 β-CD (2), 4.00 β-CD w T -100): 2.00 (3); 3.32 (4); 3.70 (5); 6.00 (6). (B) F 1 . T -100 (■) B j 56 (□), , 4.00 β-CD.



F . 4. (A) fl 1 T -100- β-CD T -100. (B) T -100 . β-CD. T fi w (5).

T -100 0 6 , w β-CD fi 4 . A - , fl 1 4 β-CD w 1 1:2 , w 1, T -100 β-CD 3 . T β-CD, . ., CD , T -100 0 - , K_1 (990 ± 160 $^{-1}$), K_2 (2500 ± 120 $^{-1}$), I_1/I_0 (3.68 ± 0.40), I_2/I_0 (14.2 ± 0.1) w w 28 . T - β-CD w T -100 CD = CD 0 CD . F . 4A w CD T -100 0. A T -100 0 < 3.32 , CD w T -100 0 1:2 w T -100 β-CD w 1:1 3 . T , w w :

$$\text{T -100} + \text{CD} \overset{K_1'}{\rightleftharpoons} \text{T -100 CD} \tag{3}$$

$$\text{T -100 CD} + \text{CD} \overset{K_2'}{\rightleftharpoons} \text{T -100 (CD)}_2 \tag{4}$$

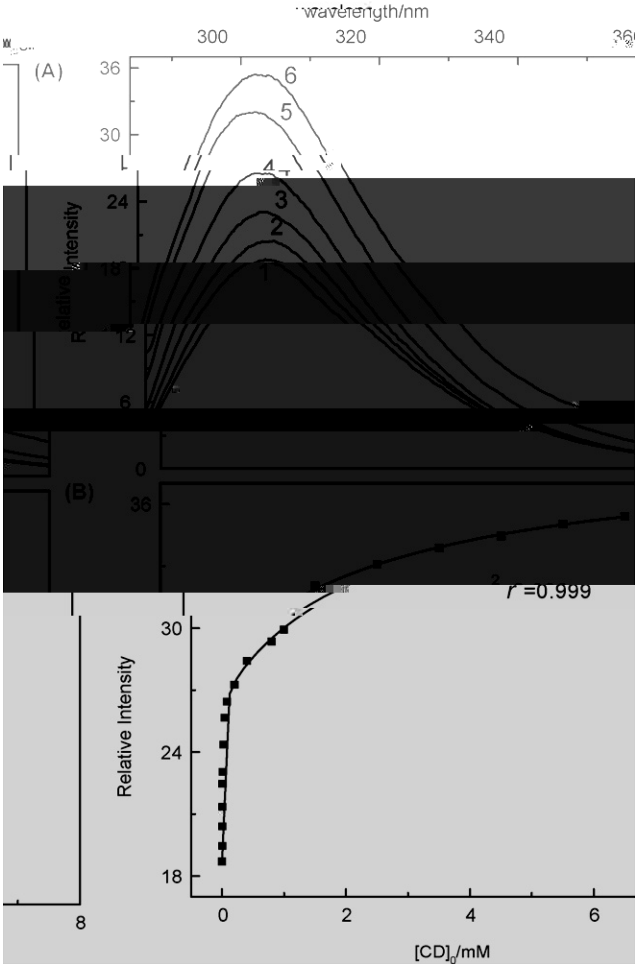
w T -100 CD T -100 (CD)$_2$ 1:1 1:2 , , w K_1' K_2'. C E . (3) (4), T -100 β-CD, w 2,3 :

$$\text{T -100}_0 = \frac{(\text{CD}_0 - \text{CD})(1 + K_1' \text{CD} + K_1' K_2' \text{CD}^2)}{K_1' \text{CD} + 2K_1' K_2' \text{CD}^2} \tag{5}$$

F . 3B, fl w C C T -100 4 β-CD . 3.95 . T , fi F . 4 E . (5) w T -100 w 3.32 . A E . (5), w K_1' K_2' w (1.14 ± 0.32) × 10^5 (1.18 ± 0.05) × 10^3 $^{-1}$, - . F . 4B w w fi w fi r^2 = 0.997. W T -100 w β-CD, w .

3.1.3. Investigation on the Triton X-100/β-CD inclusion complex using Triton X-100 itself as a probe

F . 5 fl T -100 β-CD 1. T fl -

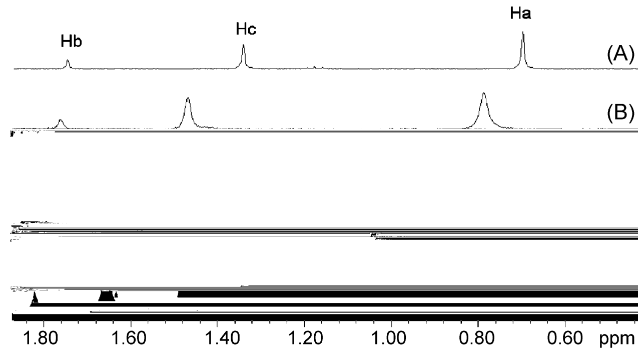


F . 5. (A) F T -100 β-CD): 0 (1); 2.00×10^{-3} (2); 1.00×10^{-2} (3); 8.00×10^{-2} (4); 2.00 (5); 7.00 (6). (B) T fl T -100 (6.0 × 10) . CD 0. T fi .

β-CD w . T -100 β-CD w , . ., 1:1 1:2 w :

$$I = \frac{I_0 + I_1 K_1 [CD] + I_2 K_1 K_2 [CD]^2}{1 + K_1 [CD] + K_1 K_2 [CD]^2} \quad (6)$$

w I_0, I_1 I_2 fl w , 1:1 1:2 - , , w K_1 K_2 1:1 1:2 , 35 . T K_1 K_2 w (1.13 ± 0.05) × 10^5 (3.71 ± 0.27) × 10^2 $^{-1}$, , w fi $r^2 = 0.999$ (F . 5B). T T -100 w β-CD , w .



F . 6. F [1] 0.10 T -100 w (A) 0.10 β-CD (B), .

3.2. Investigation on the Brij 56/β-CD inclusion complex using 1 as a probe

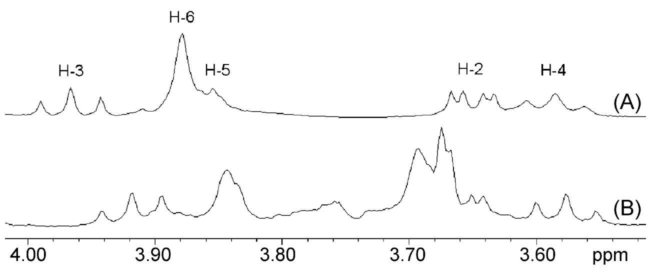
F . 3B w fl 1 - B j 56 4 β-CD. k fl 1 T -100/β-CD w w T -100, fl 1 B j 56/β-CD w . T w B j 56 β-CD w k.

3.3. NMR measurement

T fl β-CD T -100 D_2 - w - (F . 6). T T -100 - β-CD, T -100 w C. T [1] T -100 - k k : (a, δ 0.70), (c, δ 1.34), (b, δ 1.74), k (E) (δ 3.67 3.75), (d δ 6.98 6.96; e δ 7.46 7.44). W 0.10 β-CD w , w a, b, c d 0.10 T -100 (1) w w fi 0.09, 0.02, 0.13 0.05, , e fi 0.05. A , -3 (, δ 3.97), -5 (, δ 3.86) -6 (, δ 3.88) β-CD fi 0.05, 0.03 0.04, , - -1, -2 -4 T -100 (F . 7).

T w T -100 w β-CD , 2D E w 6.6 T -100 10 β-CD (F . 8). A - , C T -100 10 β-CD 7.25 8 . T , w .

T fl β-CD B j 56 D_2 - w - . A C B j 56 w



F . 7. F 0.10 β-CD w (A) 0.10 T -100 (B), .

, 1.5 B j 56 w . F k k B j 56: (a, δ 0.90), (b, δ 1.31), w w E (c, δ 1.59), k (E) (δ 3.47 3.71). k T -100, 1.5 β-CD - a, b, c 1.5 B j 56. A , β-CD w B j 56.

3.4. Lifetime measurement

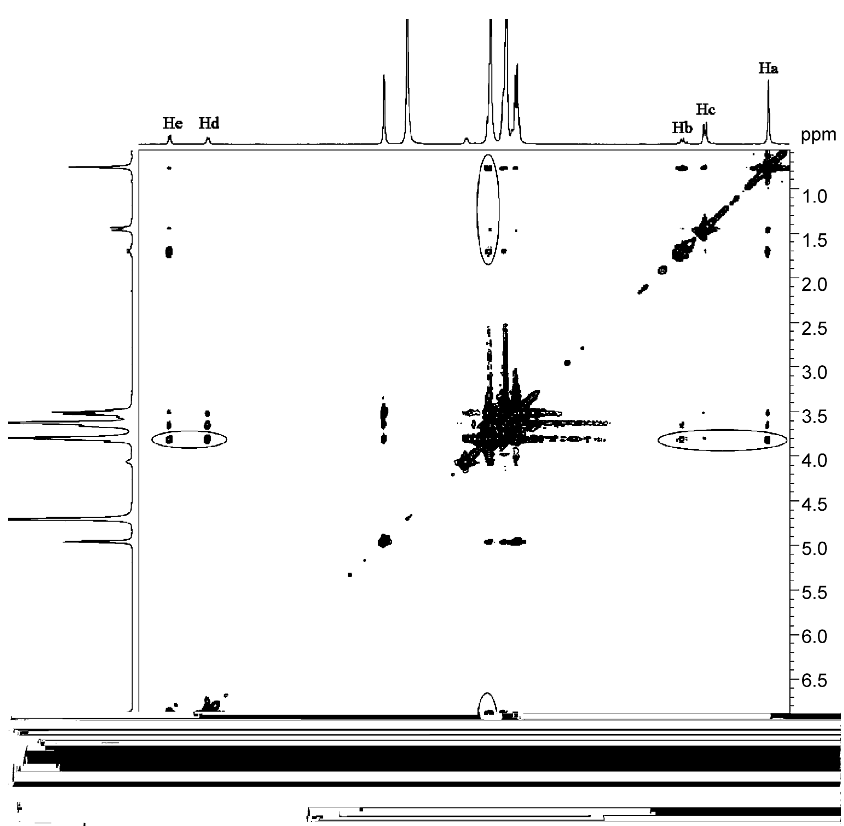
W 1 4 β-CD T -100. F , fl 1 T -100 β-CD w (T 1).

A w T 1, 1 T -100/β-CD w T -100. w- , fl 1 k 2.50 ± 0.05 w B j 56 0 6 4 β-CD.

4. Discussion

4.1. The competitive process of Triton X-100 and **1** interacting with β-CD

A F . 3, fl 1 fi , . T T -100/β-CD/**1** . F , **1** β-CD T -100 fl **1**. T fl 1 . 3.32 T -100, w 1:1 1:2 T -100 w β-CD 1 β-CD . A , w T -100, T -100 1 . , fl 1 . F . 3B, fl w C T -100 4 β-CD . 3.95 . T C T -100 2 10 β-CD . 2.25 7.25 ,



F . 8. 400 2D E w 6.6 T -100 10 β-CD.

T 1

1 (10 μM) w T -100 β-CD

T -100 $_0$ (μM)	β-CD $_0$ (μM)	τ_1 ( )	B_1	f_1 (%)	τ_2 ( )	B_2	f_2 (%)	χ^2
0	0	0.29	0.285	69.3	1.30	0.028	30.7	1.05
0.10	0	0.29	0.281	68.5	1.40	0.027	31.5	1.05
3.00	0				2.59	0.090	100	1.01
0	4.00				2.52	0.091	100	1.03
2.00	4.00	1.01	0.032	15.5	2.56	0.069	84.5	1.01
3.32	4.00	0.82	0.101	51.9	2.22	0.034	48.1	0.982
3.70	4.00	1.05	0.017	19.3	2.57	0.029	80.7	1.14
6.00	4.00				2.56	0.089	100	0.975

B_i - - w τ_i, $I(t)=\sum B_i$ $(-t/\tau_i)$, $f_i=(B_i\tau_i)/(\sum B_i\tau_i)$ $\sum f_i=1$.

[8]. C F. 3B, T -100 w . 1.14 (= CD / T -100 $_0$ = 3.78 μM/3.32 μM, F. 4A) β-CD. T 1:1 1:2 . T fi . fl 3*H*- w [34]. A T 1, **1** w w . T [35]. F , . ., 0.29 w - (T CT) k w [35,42]. β-CD, w T -100, **1** . T **1** w .

4 μM β-CD w T -100, w T 1 **1** β-CD. w , w T -100, - . T fl **1** β-CD T -100 k w W T -100, . F , . T **1** , . ., T -100.

4.2. The binding type of Triton X-100 with β-CD

μM - w T -100 β-CD. w , (T 2) [5–14]. T 2 : (1) 1:1 . [5,6], E C [7], B . [8], W D . [9–11], ; (2) 1:2 . [12] [14]; (3) - 1:1 1:2 B . [13]. A , T -100/β-CD w . B 2,6-*p*- (T)

1:1 [8]. D . ( ) 1:1 [11]. B B T -100 W T -100/β-CD fl - . w , [6,13]. , w 1:1 1:2 - **1** T -100 . w w **1** . T , **1** - w -fl .

4.3. The binding site of Triton X-100 in the β-CD cavity

μM T -100 β-CD . W (*c*-C $_3$ *b*-C $_2$) w CD [6], W 1.6(8) T

T -100 w C. C. T , 0.1 (C) T -100 w . (a e) T -100 (F . 6) fi -3, -5 -6 β-CD (F . 7), w

T -100 β-CD. T fi 2D E -100 (F . 8), w a, b, c, d e T -100 w -3 -5 β-CD (k w).

F , fi C $_2$C $_2$ T -100 w β-CD C $_2$C $_2$ w β-CD. . ( ) (1) w β-CD 43 . , -

w , w

\- w 29 . T , k ,

w β-CD. , w w 3H- 1 3 C $_2$C $_2$ β-CD 1:3 1:1 w C $_2$C $_2$ 29 . T - ΔH, ΔS ΔG C $_2$C $_2$ w w β-CD 29 .

T fi , w w B j 56 β-CD w w T -100 β-CD. T B j 56 T -100 , , B j 56 k , w T -100 k .

A F . 3B, fl 1 B j 56/β-CD T -100/β-CD . F T -100 B j 56 (10 C $_2$C $_2$ -), . , B j 56 w k w β-CD. T fi , w a, b, c B j 56 w β-CD.

5. Conclusions

T w T -100 β-CD w , - fl , fl - . 1 fl , 1:1 1:2 w , K_1 K_2 w - (1.14 ± 0.32) × 10^5 (1.18 ± 0.05) × 10^3 $^{-1}$, . T w fi T - 100 , K_1 K_2 w (1.13 ± 0.05) × 10^5 (3.71 ± 0.27) × 10^2 $^{-1}$. T - w w , C C T -100 - w 1 T -100 w (1.7 ± 0.2) × 10^{-4} 12200 ± 300 $^{-1}$, . w k 1 fl -fl w . F ^{1} 2D E , w T -100 w β-CD - . k T -100, w B j 56 β-CD w w k.

Acknowledgements

T w k w F C (. 90206020). . k D . A F . A , . k D (B j C) w .

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14 A. . , . . J . 38 (1989) 2963.
15 ( ) B. T , , C. . , Z.Z. C , T 69 (2006) 113;
( ) B. T , J. , C. . , Z.Z. C , . D , J. . C . B 110 (2006) 8877;
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