Cage to cage study of ionic liquid and cyclic oligosaccharides to form inclusion complexes

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Theory:

Surface tension

Concentration of cyclodextrin and corresponding surface tension at which maximum inclusion took place (break point at the curve) have been calculated by solving the equations of two intercepting straight lines and represented in table 1. For instance, in case of the ionic liquid TTP and α-cyclodextrin system

$$\gamma = 1.663\ c + 36.75 \tag{S1}$$

$$\gamma = 3.885\ c + 24.96 \tag{S2}$$

Solving equation (1) and (2),

$\gamma = 45.57$ mN·m^{-1} and $c = 5.30$ mM

Concentration of ionic liquid at the break point has been estimated from the mutual concentration chart of table S4-S5.

Conductivity

The concentration and corresponding conductivity at which maximum inclusion took place (break point at the curve) have been calculated by solving the equations of two intercepting straight lines and represented in table 2. For instance, in case of the ionic liquid TTP and β-cyclodextrin system

$$\kappa = -0.149c + 3.297 \tag{S3}$$

$$\kappa = -0.661\ c + 5.832 \tag{S4}$$

Solving equation (3) and (4),

$\kappa = 2.56$ mS·m^{-1} and $c = 4.95$ mM

Concentration of ionic liquid at the break point has been estimated from the mutual concentration chart of table S4-S5.

- The physical properties of binary aqueous mixtures in different mass fractions (w_n=0.001, 0.003, 0.005, where n =1, 2 for α and β-CD respectively) of α and β-CD at 298.15K have been reported in table S2. The experimental measured values of density, viscosity and refractive index of selected ionic liquid TTP in different mass fractions of aqueous α and β-CD mixture have been listed in table S3 as a function of concentration (molality).

- **Apparent molar volume**

The apparent molar volumes ϕ_V were determined from the solutions densities using the equation and given in table S6.

$$\phi_V = M / \rho - 1000(\rho - \rho_o)/ m\rho\rho_o \tag{S5}$$

where M is the molar mass of the ionic liquids, m is the molality of the solution, ρ and ρ_o are the density of the solution and aqueous α and β-CD mixture respectively.

The limiting apparent molar volumes ϕ^0_V were obtained by a least-square treatment to the plots of ϕ_V versus $\sqrt{m}$ using the Masson equation[1] and shown in table S7.

$$\phi_V = \phi^0_V + S_V^* \cdot \sqrt{m} \tag{S6}$$

The standard deviations (σ) were determined using the following equation:

$$\sigma = \sqrt{[\sum (Y_{exp} - Y_{obs})^2 / (N - 1)]} \tag{S7}$$

where N is the number of data points.

Viscosity

The experimental viscosity data for the studied systems are listed in table S3. The relative viscosity (η_r) has been analyzed using the Jones-Dole equation [2]

$$(\eta/\eta_o - 1)/ \sqrt{m} = (\eta_r - 1)/ \sqrt{m} = A + B \sqrt{m} \tag{S8}$$

where $\eta_r = \eta/\eta_o$, η and η_o are the relative viscosities, the viscosities of the ternary solutions (ionic liquid + aq. CD) and binary aqueous mixture (aq. CD) and m is the molality of the ionic liquids in ternary solutions. A and B are empirical constants known as viscosity A and B-coefficients, which are specific to solute-solute and solute-solvent interactions respectively and have been estimated by least-square method by plotting $(\eta_r - 1)/ \sqrt{m}$ against $\sqrt{m}$ and reported in table S7.

Refractive index

The molar refraction, R_M can be evaluated from the Lorentz-Lorenz relation [3]

$$R_M = \{(n_D{}^2 - 1)/(n_D{}^2 + 2)\}(M/\rho) \qquad (S9)$$

where R_M, n_D, M and ρ are the molar refraction, the refractive index, the molar mass and the density of solution respectively. The Limiting molar refraction $(R_M{}^o)$ have been estimated from the following relation and reported in table S8,[4]

$$R_M = R_M{}^o + R_S \sqrt{m} \qquad (S10)$$

References:

(1) D.O. Masson, *Phil Mag.* **1929**, *8,* 218-223.

(2) G. Jones, D. Dole*, J. Am. Chem. Soc.* **1929**, *51,* 2950-2964.

(3) V.Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry.* New York, Plenum Press, **1970**.

(4) M.N. Roy, D. Ekka, S. Saha, M. C. Roy, *RSC Adv.* **2014**, *4,* 42383-42390.

Tables:

Table S1. ^{1}H NMR data of TTP, α-CD, β-CD and inclusion complexes

α-Cyclodextrin: (500 MHz, Solv: D_2O) δ=3.48-3.51 (6H, t, *J*= 9.00 Hz), 3.53-3.56 (6H, dd, *J*=10.00, 3.00 Hz), 3.74-3.83 (18H, m), 3.87-3.91 (6H, t, *J* = 9 Hz), 4.96-4.97 (6H, d, *J* = 3 Hz)
β-Cyclodextrin: (500 MHz, Solv: D_2O) δ=3.49-3.54 (6H, t, *J* = 9.2 Hz), 3.57-3.60 (6H, dd, *J* = 9.6, 3.2 Hz), 3.79-3.84 (18H, m), 3.87-3.92 (6H,t, *J* = 9.2 Hz), 5.00-5.01 (6H, d, *J* = 3.6 Hz)
TTP: (400 MHz, Solv: D_2O) δ=0.71-0.77(9H,d,*J*=), 1.0-1.61(48H,m), 2.0-2.07(2H,d,*J*=), 2.29(6H,s)
TTP-α-CD: (1:1 molar ratio, 300 MHz, Solv: D_2O) : δ= 0.90-1.22(54H,m), 3.22-3.26(6H, t, *J*= Hz),3.30-3.32(6H, dd,J=)3.47-3.57(18H, m),3.59-3.62(6H, t, *J* = Hz)
TTP-β-CD: (1:1 molar ratio, 300 MHz, Solv: D_2O) : 0.88-1.20(54H,m),1.35-1.37(2H,d,*J*=),3.18-3.22(6H, t, *J*=),3.28-3.30(6H, dd,J=), 3.42-3.52(18H, m), 3.52-3.67(6H, t, *J* = Hz)

Table S2: Experimental values of density (ρ), viscosity (η) and refractive index (n_D) of different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K^a

Aqueous solvent mixture	$\rho \times 10^{-3}$ /kg·m^{-3}	η /mP·s	n_D
aq. α-CD			
w_1 = 0.001	0.99735	1.29	1.3329
w_1 = 0.003	0.99802	1.30	1.3332
w_1 = 0.005	0.99868	1.31	1.3335
aq. β-CD			
w_2 = 0.001	0.99755	1.30	1.3328
w_2 = 0.003	0.99819	1.31	1.3331
w_2 = 0.005	0.99895	1.32	1.3334

^{a} Standard uncertainties u are: $u(\rho)$ = 5×10^{-5} g·cm^{-3}, $u(\eta)$ = 0.003 mP·s, $u(n_D)$ =0.0002, and u(T) = ±0.01K.

Table S3. Experimental values of density (ρ), viscosity (η) and refractive index (nD) of selected ionic liquid in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K^a

molality /mol·kg^{-1}	$\rho \times 10^{-3}$ /kg·m^{-3}	η /mP·s	n_D	molality /mol·kg^{-1}	$\rho \times 10^{-3}$ /kg·m^{-3}	η /mP·s	n_D
TTP							
w_1 = 0.001^b				w_2 = 0.001^b			
0.010073	0.99791	1.31	1.3335	0.010073	0.99795	1.33	1.3341
0.025352	0.99911	1.33	1.3336	0.025361	0.99876	1.35	1.3342
0.040821	1.00066	1.34	1.3338	0.040859	0.99974	1.37	1.3343
0.056485	1.00228	1.36	1.3339	0.056567	1.00086	1.39	1.3344
0.072328	1.00416	1.37	1.3340	0.072482	1.00211	1.41	1.3345
0.088371	1.00599	1.38	1.3342	0.088605	1.00345	1.43	1.3347
w_1 = 0.003^b				w_2 = 0.003^b			
0.010068	0.99841	1.33	1.3346	0.010066	0.99859	1.34	1.3349
0.025349	0.99921	1.35	1.3347	0.025340	0.99955	1.37	1.3350
0.040841	1.00017	1.37	1.3348	0.040816	1.00077	1.39	1.3352

0.056546	1.00122	1.39	1.3349	0.056491	1.00216	1.41	1.3354
0.072462	1.00237	1.40	1.3350	0.072362	1.00371	1.43	1.3356
0.088593	1.00358	1.42	1.3351	0.088440	1.00524	1.45	1.3359
	$w_1 = 0.005^b$				$w_2 = 0.005^b$		
0.010062	0.99902	1.341	1.3353	0.010060	0.99925	1.35	1.3357
0.025335	0.99975	1.365	1.3354	0.025328	1.00003	1.38	1.3358
0.040821	1.00065	1.384	1.3355	0.040807	1.00099	1.40	1.3359
0.056526	1.00156	1.403	1.3356	0.056492	1.00215	1.43	1.3362
0.072434	1.00275	1.421	1.3358	0.072387	1.00337	1.44	1.3364
0.088559	1.00395	1.440	1.3360	0.088500	1.00459	1.46	1.3367

Table S4. Data for surface tension and conductivity study of aqueous TTP-α-CD system at 298.15K^a

Volm of α-CD (mL)	Total volm (mL)	Conc of TTP (mM)	Conc of α-CD (mM)	Surface tension (mN m^{-1})	Conductuvity (mS m^{-1})
0	10	10.000	0.000	25.5	5.81
1	11	9.091	0.909	28.4	5.29
2	12	8.333	1.667	31.3	4.77
3	13	7.692	2.308	33.6	4.34
4	14	7.143	2.857	35.9	3.98
5	15	6.667	3.333	37.7	3.64
6	16	6.250	3.750	39.5	3.35
7	17	5.882	4.118	40.8	3.14
8	18	5.556	4.444	42.1	2.93
9	19	5.263	4.737	43.5	2.75
10	20	5.000	5.000	45.0	2.60
11	21	4.762	5.238	45.4	2.54
12	22	4.545	5.455	45.9	2.51
13	23	4.348	5.652	46.2	2.48

14	24	4.167	5.833	46.5	2.45
15	25	4.000	6.000	46.8	2.43
16	26	3.846	6.154	47.0	2.41
17	27	3.704	6.296	47.2	2.39
18	28	3.571	6.429	47.4	2.37
19	29	3.448	6.552	47.6	2.35
20	30	3.333	6.667	47.8	2.33

[a] Standard uncertainties in temperature u are: $u(T) = \pm0.01$ K.

Table S5. Data for surface tension and conductivity of aqueous TTP-β-CD system at 298.15K[a]

Volm of β-CD (mL)	Total volm (mL)	Conc of TTP (mM)	Conc of β-CD (mM)	Surface tension (mN m^{-1})	Conductuvity (mS m^{-1})
0	10	10.000	0.000	25.5	5.81
1	11	9.091	0.909	28.8	5.27
2	12	8.333	1.667	31.7	4.74
3	13	7.692	2.308	34.1	4.31
4	14	7.143	2.857	36.4	3.95
5	15	6.667	3.333	38.3	3.61
6	16	6.250	3.750	39.9	3.31
7	17	5.882	4.118	41.2	3.10
8	18	5.556	4.444	42.5	2.89
9	19	5.263	4.737	43.9	2.71
10	20	5.000	5.000	45.4	2.56
11	21	4.762	5.238	45.8	2.51
12	22	4.545	5.455	46.2	2.48
13	23	4.348	5.652	46.6	2.45

14	24	4.167	5.833	46.9	2.42
15	25	4.000	6.000	47.2	2.40
16	26	3.846	6.154	47.4	2.38
17	27	3.704	6.296	47.6	2.36
18	28	3.571	6.429	47.8	2.34
19	29	3.448	6.552	48.0	2.32
20	30	3.333	6.667	48.2	2.30

[a] Standard uncertainties in temperature u are: $u(T) = \pm 0.01$ K.

Table S6. Apparent molar volume (ϕ_V), (η_r-1)/$\sqrt{m}$ and molar refraction (R_M) of selected ionic liquid TTP in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K[a]

molality /mol·kg^{-1}	$\phi_V \times 10^6$ / m^3 mol^{-1}	(η_r-1)/$\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	$R_M \times 10^6$ /m^3 mol^{-1}	molality /mol·kg^{-1}	$\phi_V \times 10^6$ / m^3 mol^{-1}	(η_r-1)/$\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	$R_M \times 10^6$ /m^3 mol^{-1}
			TTP				
		$w_1 = 0.001^b$				$w_2 = 0.001^b$	
0.010073	464.54	0.162	106.5855	0.010073	480.49	0.230	107.3600
0.025352	450.10	0.180	107.1893	0.025361	472.07	0.261	107.3020
0.040821	437.72	0.200	107.0897	0.040859	465.70	0.278	107.2260
0.056485	430.82	0.212	106.9820	0.056567	460.26	0.294	107.1350
0.072328	423.15	0.225	106.8381	0.072482	455.28	0.314	107.0304
0.088371	418.77	0.235	106.6671	0.088605	451.00	0.328	106.9455
		$w_1 = 0.003^b$				$w_2 = 0.003^b$	
0.010068	481.26	0.222	107.4476	0.010066	480.18	0.251	107.5027
0.025349	472.65	0.246	107.3874	0.025340	465.75	0.293	107.4167
0.040841	466.48	0.259	107.3167	0.040816	455.63	0.310	107.3450
0.056546	462.04	0.278	107.2364	0.056491	447.94	0.331	107.2659
0.072462	458.07	0.294	107.1488	0.072362	441.25	0.346	107.1774
0.088593	454.80	0.305	107.0592	0.088440	437.16	0.359	107.1095
		$w_1 = 0.005^b$				$w_2 = 0.005^b$	
0.010062	485.95	0.236	107.5943	0.010060	489.82	0.249	107.6730
0.025335	477.14	0.264	107.5448	0.025328	476.61	0.286	107.6149
0.040821	470.68	0.280	107.4772	0.040807	468.80	0.315	107.5428

0.056526	467.56	0.299	107.4085	0.056492	461.61	0.338	107.5129
0.072434	461.78	0.315	107.3390	0.072387	456.65	0.349	107.4454
0.088559	457.91	0.333	107.2686	0.088500	453.43	0.367	107.4049

[a] Standard uncertainties u are: u(T) =0.01K.

[b] w_1 and w_2 are mass fractions of α and β-cyclodextrin in aqueous mixture respectively.

Table S7. Limiting apparent molar volume (ϕ_V^o), experimental slope (S_V*), viscosity A and B-coefficient and limiting molar refraction (R_M^o) of ionic liquid TTP in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K[a]

Aq. solvent mixture	$\phi^0_V \times 10^6$ / m^3 mol^{-1}	$S^*_V \times 10^6$ /m^{3}mol$^{-3/2}$kg$^{1/2}$	B /kg mol^{-1}	A /kg$^{1/2}$ mol$^{-1/2}$	$R_M^O \times 10^6$ /m^3 mol^{-1}
TTP					
$w_1 = 0.001^b$	487.4	-236.5	0.376	0.122	107.59
$w_1 = 0.003^b$	494.2	-134.3	0.423	0.178	107.68
$w_1 = 0.005^b$	499.7	-140.2	0.483	0.185	107.79
TTP					
$w_2 = 0.001^b$	495.7	-149.9	0.492	0.180	107.61
$w_2 = 0.003^b$	501.3	-221.3	0.540	0.201	107.72
$w_2 = 0.005^b$	507.1	-186.3	0.596	0.191	107.82

Table S8. Frequencies at FTIR spectra of TTP, α-CD, β-CD and solid inclusion complexes

	Wave Number / cm^{-1}	Group
TTP	3372.75	Symmetrical Stretching of –C-H from CH$_3$
	2941.63	Symmetrical Stretching of -C-H from –CH$_2$
	1624.43	Bending of -C-H from –CH$_2$

	1454.58	Stretching of P-CH$_2$-
	1215.23	Bending of P-CH$_2$-
	1111.34	Weak Stretching of -C-C-
	989.76	Weak bending of -C-C-
α-Cyclodextrin	3412.10	stretching of O-H
	2930.79	stretching of –C-H from –CH$_2$
	1406.76	bending of –C-H from –CH$_2$ and bending of O-H
	1154.39	bending of C-O-C
	1030.39	stretching of C-C-O
	952.36	skeletal vibration involving α-1,4 linkage
β-Cyclodextrin	3349.84	stretching of O-H
	2921.52	stretching of –C-H from –CH$_2$
	1412.36	bending of –C-H from –CH$_2$ and bending of O-H
	1157.57	bending of C-O-C
	1033.51	stretching of C-C-O
	938.53	skeletal vibration involving α-1,4 linkage
TTP+α-CD	3378.08	Stretching of –O-H of α-CD
	2927.03	Stretching of –C-H from –CH$_2$ of TTP
	2364.96	Stretching of –C-H from –CH$_2$ of TTP
	1626.46	Bending of –C-H from –CH$_2$ of TTP
	1148.51	Bending of –C-O-C of α-CD
	1017.64	Stretching of –C-C-O of α-CD

TTP+β-CD	3335.76	Stretching of –O-H of β-CD
	2916.86	Stretching of –C-H from –CH_2 of TTP
	1646.96	Bending of –C-H from –CH_2 of TTP
	1385.73	Stretching of P-CH_2 from TTP
	1156.87	Bending of –C-O-C- from β-CD
	1080.34	Weak stretching of C-C of TTP
	1021.32	Stretching of –C-C-O of β-CD