Electronic Supporting Information

Insertion behavior of imidazolium and pyrrolidinium based ionic liquids into α and β-cyclodextrins: Mechanism and factors leading to host-guest inclusion complexes

Aditi Roy, Subhadeep Saha, Biswajit Datta and Mahendra Nath Roy*

*Department of Chemistry, University of North Bengal, Darjeeling-734013, India.

Email: mahendraroy2002@yahoo.co.in

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 [BMIm]Cl and *α*-cyclodextrin system

$$\gamma = 5.360\, c + 41.21 \quad \text{(S1)}$$

$$\gamma = 0.710\, c + 65.24 \quad \text{(S2)}$$

Solving equation (1) and (2),

$\gamma = 68.91$ mN·m^{-1} and $c = 5.18$ mM

Concentration of ionic liquid at the break point has been estimated from the mutual concentration chart of table S4-S7.

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 [BMP]Cl and *β*-cyclodextrin system

$$\kappa = -0.449c + 5.224 \quad \text{(S3)}$$

$$\kappa = -0.16\, c + 3.775 \quad \text{(S4)}$$

Solving equation (3) and (4),

κ = 2.974 mS·m^{-1} and c = 5.013 mM

Concentration of ionic liquid at the break point has been estimated from the mutual concentration chart of table S4-S7.

- 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 two ionic liquids [BMIm]Cl and [BMP]Cl 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 S8.

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

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 S9.

$$\phi_V = \phi^0_V + S_V^* \cdot \sqrt{m} \quad \text{(S6)}$$

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

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

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]

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

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 S8.

Refractive index

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

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

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 S9,[4]

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

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 [BMIm]Cl, [BMP]Cl, α-CD, β-CD and inclusion complexes

[BMIm]Cl (300MHz, Solv: D_2O) δ /ppm	[BMP]Cl (300MHz, Solv: D_2O) δ /ppm
0.87-0.92 (3H, t, J = 7.26 Hz), 1.26-1.33(2H, m), 1.78-1.85 (2H, m), 3.87 (3H, s), 4.15-4.20 (2H, t, J = 7.11 Hz), 7.40 (1H, s), 7.45 (1H, s), 8.69 (1H, s)	0.91-0.96 (3H, t, J = 7.29 Hz), 1.34-1.41 (2H, m), 1.74-1.81(2H,m), 2.19 (4H, m), 3.02 (3H, s), 3.28-3.34 (2H, m), 3.48 (4H, m)
α-Cyclodextrin (500 MHz, Solv: D_2O) δ /ppm	β-Cyclodextrin (400 MHz, Solv: D_2O) δ /ppm
3.48-3.51 (6H, t, J= 9.00 Hz), 3.53-3.56 (6H, dd, J=	3.49-3.54 (6H, t, J = 9.2 Hz), 3.57-3.60 (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)	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)
[BMIm]Cl-α-CD (1:1 molar ratio, 300 MHz, Solv: D_2O) δ /ppm	[BMP]Cl- α-CD (1:1 molar ratio, 300 MHz, Solv: D_2O) δ /ppm
0.84-0.89 (3H, t, *J* = 7.26 Hz), 1.22-1.29 (2H, m), 1.74-1.81 (2H, m), 3.48-3.51 (6H, t, *J*= 9.00 Hz), 3.53-3.56 (6H, dd, *J*= 10.00, 3.00 Hz), 3.71-3.79 (18H, m), 3.80-3.83 (6H, t, *J* = 9 Hz), 3.84 (3H, s), 4.11-4.16 (2H, t, *J* = 7.11 Hz), 4.96-4.97 (6H, d, *J* = 3 Hz), 7.40 (1H, s), 7.45 (1H, s), 8.69 (1H, s)	0.88-0.93 (3H, t, *J* = 7.29 Hz), 1.31-1.38 (2H, m), 1.71-1.78 (2H,m), 2.19 (4H, m), 3.00 (3H, s), 3.25-3.31 (2H, m), 3.48 (4H, m), 3.49-3.51 (6H, t, *J*= 9.00 Hz), 3.53-3.56 (6H, dd, *J*= 10.00, 3.00 Hz), 3.80-3.85 (18H, m), 3.88-3.93 (6H, t, *J* = 9 Hz), 4.96-4.97 (6H, d, *J* = 3 Hz)
[BMIm]Cl-β-CD (1:1 molar ratio, 300 MHz, Solv: D_2O) δ /ppm	[BMP]Cl- β-CD (1:1 molar ratio, 300 MHz, Solv: D_2O) δ /ppm
0.85-0.90 (3H, t, *J* = 7.26 Hz), 1.23-1.30 (2H, m), 1.75-1.82 (2H, m), 3.49-3.54 (6H, t, *J* = 9.2 Hz), 3.57-3.60 (6H, dd, *J* = 9.6, 3.2 Hz), 3.72-3.80 (18H, m), 3.81-3.84 (6H,t, *J* = 9.2 Hz), 3.85 (3H, s), 4.12-4.17 (2H, t, *J* = 7.11 Hz), 5.00-5.01 (6H, d, *J* = 3.6 Hz), 7.40 (1H, s), 7.45 (1H, s), 8.69 (1H, s)	0.89-0.94 (3H, t, *J* = 7.29 Hz), 1.32-1.40 (2H, m), 1.72-1.79 (2H,m), 2.19 (4H, m), 3.03 (3H, s), 3.27-3.34 (2H, m), 3.48 (4H, m), 3.49-3.51 (6H, t, *J*= 9.00 Hz), 3.53-3.56 (6H, dd, *J*= 10.00, 3.00 Hz), 3.82-3.87 (18H, m), 3.89-3.95 (6H, t, *J* = 9 Hz), 4.96-4.97 (6H, d, *J* = 3 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	$\rho\times10^{-3}$ /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 liquids in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K[a]

molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s	n_D	molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s	n_D
[BMIm]Cl							
w_1 = 0.001[b]				w_2 = 0.001[b]			
0.010034	0.99836	1.36	1.3330	0.010032	0.99858	1.38	1.3330
0.025113	0.99988	1.41	1.3331	0.025106	1.00014	1.43	1.3331
0.040225	1.00140	1.44	1.3332	0.040212	1.00171	1.47	1.3333
0.055370	1.00293	1.47	1.3333	0.055350	1.00329	1.49	1.3334
0.070548	1.00446	1.50	1.3334	0.070518	1.00488	1.53	1.3336
0.085760	1.00599	1.52	1.3335	0.085717	1.00648	1.56	1.3338
w_1 = 0.003[b]				w_2 = 0.003[b]			
0.010027	0.99901	1.39	1.3334	0.010025	0.99924	1.40	1.3334
0.025096	1.00053	1.45	1.3335	0.025088	1.00087	1.46	1.3335
0.040198	1.00207	1.49	1.3336	0.040178	1.00255	1.50	1.3337
0.055332	1.00361	1.54	1.3337	0.055295	1.00428	1.54	1.3339
0.070497	1.00517	1.56	1.3338	0.070432	1.00610	1.57	1.3341
0.085695	1.00674	1.59	1.3339	0.085595	1.00789	1.60	1.3343
w_1 = 0.005[b]				w_2 = 0.005[b]			
0.010021	0.99962	1.41	1.3339	0.010018	0.99999	1.42	1.3336
0.025083	1.00105	1.48	1.3340	0.025066	1.00173	1.49	1.3337
0.040181	1.00249	1.53	1.3341	0.040138	1.00355	1.54	1.3338
0.055311	1.00398	1.57	1.3342	0.055227	1.00549	1.57	1.3340
0.070475	1.00548	1.60	1.3343	0.070333	1.00749	1.61	1.3342
0.085671	1.00702	1.64	1.3344	0.085459	1.00948	1.65	1.3343
[BMP]Cl							
w_1 = 0.001[b]				w_2 = 0.001[b]			
0.010035	0.99832	1.37	1.3347	0.010032	0.99855	1.39	1.3345
0.025116	0.99983	1.42	1.3348	0.025110	1.00008	1.45	1.3346
0.040233	1.00130	1.46	1.3349	0.040220	1.00163	1.49	1.3347
0.055383	1.00282	1.50	1.3350	0.055364	1.00320	1.53	1.3348
0.070570	1.00433	1.52	1.3351	0.070540	1.00479	1.56	1.3349
0.085792	1.00583	1.55	1.3352	0.085746	1.00641	1.59	1.3350
w_1 = 0.003[b]				w_2 = 0.003[b]			

0.010028	0.99894	1.39	1.3352	0.010025	0.99924	1.41	1.3346
0.025103	1.00034	1.45	1.3353	0.025088	1.00092	1.47	1.3347
0.040215	1.00175	1.50	1.3354	0.040178	1.00269	1.52	1.3348
0.055363	1.00318	1.53	1.3355	0.055285	1.00461	1.55	1.3349
0.070550	1.00461	1.56	1.3356	0.070408	1.00665	1.60	1.3350
0.085770	1.00608	1.60	1.3357	0.085544	1.00875	1.63	1.3352
	w_1 = 0.005[b]				w_2 = 0.005[b]		
0.010022	0.99955	1.41	1.3357	0.010018	0.99993	1.43	1.3350
0.025089	1.00087	1.47	1.3358	0.025072	1.00157	1.50	1.3351
0.040196	1.00221	1.52	1.3359	0.040151	1.00332	1.55	1.3352
0.055342	1.00357	1.55	1.3360	0.055252	1.00518	1.60	1.3353
0.070526	1.00494	1.60	1.3361	0.070372	1.00711	1.64	1.3354
0.085747	1.00635	1.64	1.3362	0.085500	1.00921	1.67	1.3355

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

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

Table S4. Data for surface tension and conductivity study of aqueous [BMIm]Cl-α-CD system at 298.15K[a]

Volm of α-CD (mL)	Total volm (mL)	Conc of [BMIm]Cl (mM)	Conc of α-CD (mM)	Surface tension (mN m^{-1})	Conductuvity (mS m^{-1})
0	10	10.000	0.000	42.0	4.52
1	11	9.091	0.909	45.9	4.14
2	12	8.333	1.667	49.8	3.85
3	13	7.692	2.308	53.3	3.57
4	14	7.143	2.857	56.3	3.36
5	15	6.667	3.333	58.8	3.18
6	16	6.250	3.750	61.1	2.98
7	17	5.882	4.118	63.3	2.84
8	18	5.556	4.444	64.9	2.70
9	19	5.263	4.737	66.8	2.57
10	20	5.000	5.000	68.7	2.42

11	21	4.762	5.238	69.0	2.39
12	22	4.545	5.455	69.2	2.36
13	23	4.348	5.652	69.3	2.34
14	24	4.167	5.833	69.4	2.32
15	25	4.000	6.000	69.5	2.30
16	26	3.846	6.154	69.6	2.28
17	27	3.704	6.296	69.7	2.26
18	28	3.571	6.429	69.8	2.24
19	29	3.448	6.552	69.9	2.22
20	30	3.333	6.667	70.0	2.20

[a] Standard uncertainties in temperature *u* are: *u*(T) = ±0.01 K.

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

Volm of *β*-CD (mL)	Total volm (mL)	Conc of [BMIm]Cl (mM)	Conc of *β*-CD (mM)	Surface tension (mN m^{-1})	Conductuvity (mS m^{-1})
0	10	10.000	0.000	42.0	4.58
1	11	9.091	0.909	46.3	4.21
2	12	8.333	1.667	50.3	3.93
3	13	7.692	2.308	53.5	3.70
4	14	7.143	2.857	56.6	3.48
5	15	6.667	3.333	58.9	3.29
6	16	6.250	3.750	61.2	3.13
7	17	5.882	4.118	63.0	2.99
8	18	5.556	4.444	64.7	2.86
9	19	5.263	4.737	66.5	2.75
10	20	5.000	5.000	68.1	2.62
11	21	4.762	5.238	68.4	2.59

12	22	4.545	5.455	68.8	2.56
13	23	4.348	5.652	69.2	2.54
14	24	4.167	5.833	69.5	2.52
15	25	4.000	6.000	69.7	2.50
16	26	3.846	6.154	69.9	2.48
17	27	3.704	6.296	70.1	2.46
18	28	3.571	6.429	70.3	2.44
19	29	3.448	6.552	70.5	2.42
20	30	3.333	6.667	70.7	2.40

[a] Standard uncertainties in temperature *u* are: *u*(T) = ±0.01 K.

Table S6. Data for surface tension and conductivity study of aqueous [BMP]Cl-*α*-CD system at 298.15K[a]

Volm of *α*-CD (mL)	Total volm (mL)	Conc of [BMP]Cl (mM)	Conc of *α*-CD (mM)	Surface tension (mN m^{-1})	Conductuvity (mS m^{-1})
0	10	10.000	0.000	39.0	5.00
1	11	9.091	0.909	42.9	4.59
2	12	8.333	1.667	47.2	4.25
3	13	7.692	2.308	50.9	3.99
4	14	7.143	2.857	54.0	3.76
5	15	6.667	3.333	56.8	3.55
6	16	6.250	3.750	59.4	3.38
7	17	5.882	4.118	61.6	3.21
8	18	5.556	4.444	63.7	3.08
9	19	5.263	4.737	65.7	2.95
10	20	5.000	5.000	67.6	2.80
11	21	4.762	5.238	67.8	2.77
12	22	4.545	5.455	68.0	2.74

13	23	4.348	5.652	68.2	2.71
14	24	4.167	5.833	68.4	2.68
15	25	4.000	6.000	68.5	2.65
16	26	3.846	6.154	68.6	2.62
17	27	3.704	6.296	68.7	2.59
18	28	3.571	6.429	68.8	2.56
19	29	3.448	6.552	68.9	2.53
20	30	3.333	6.667	69.0	2.50

[a] Standard uncertainties in temperature *u* are: *u*(T) = ±0.01 K.

Table S7. Data for surface tension and conductivity study of aqueous [BMP]Cl-*β*-CD system at 298.15K[a]

Volm of *β*-CD (mL)	Total volm (mL)	Conc of [BMP]Cl (mM)	Conc of *β*-CD (mM)	Surface tension (mN m^{-1})	Conductuvity (mS m^{-1})
0	10	10.000	0.000	39.0	5.21
1	11	9.091	0.909	43.2	4.82
2	12	8.333	1.667	47.5	4.47
3	13	7.692	2.308	51.0	4.21
4	14	7.143	2.857	53.9	3.95
5	15	6.667	3.333	56.7	3.73
6	16	6.250	3.750	59.1	3.53
7	17	5.882	4.118	61.3	3.37
8	18	5.556	4.444	63.3	3.22
9	19	5.263	4.737	65.0	3.09
10	20	5.000	5.000	66.9	2.98
11	21	4.762	5.238	67.4	2.94
12	22	4.545	5.455	67.8	2.90
13	23	4.348	5.652	68.1	2.87

14	24	4.167	5.833	68.4	2.84
15	25	4.000	6.000	68.7	2.81
16	26	3.846	6.154	69.0	2.79
17	27	3.704	6.296	69.3	2.77
18	28	3.571	6.429	69.6	2.75
19	29	3.448	6.552	69.8	2.73
20	30	3.333	6.667	70.0	2.71

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

Table S8. Apparent molar volume (ϕ_V), $(\eta_r\text{-}1)/\sqrt{m}$ and molar refraction (R_M) of selected ionic liquids 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}	$(\eta_r\text{-}1)/\sqrt{m}$ /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}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	$R_M \times 10^6$ /m^3 mol^{-1}
[BMIm]Cl							
w_1 = 0.001[b]				w_2 = 0.001[b]			
0.010034	73.87	0.542	35.9878	0.010032	71.85	0.614	35.9799
0.025113	73.67	0.587	35.9429	0.025106	71.24	0.631	35.9336
0.040225	73.62	0.580	35.8982	0.040212	70.84	0.652	35.8968
0.055370	73.41	0.593	35.8532	0.055350	70.48	0.621	35.8501
0.070548	73.29	0.613	35.8083	0.070518	70.13	0.666	35.8128
0.085760	73.22	0.609	35.7636	0.085717	69.78	0.683	35.7753
w_1 = 0.003[b]				w_2 = 0.003[b]			
0.010027	75.82	0.691	36.0036	0.010025	69.80	0.686	35.9954
0.025096	74.42	0.728	35.9587	0.025088	67.59	0.723	35.9465
0.040198	73.57	0.729	35.9132	0.040178	65.79	0.724	35.9058
0.055332	73.18	0.785	35.8679	0.055295	64.06	0.747	35.8634
0.070497	72.67	0.753	35.8220	0.070432	61.78	0.748	35.8180
0.085695	72.22	0.762	35.7758	0.085595	60.66	0.757	35.7738
w_1 = 0.005[b]				w_2 = 0.005[b]			
0.010021	80.78	0.763	36.0306	0.010018	70.74	0.757	35.9879
0.025083	79.98	0.819	35.9889	0.025066	63.54	0.813	35.9352
0.040181	79.52	0.838	35.9470	0.040138	59.73	0.832	35.8798
0.055311	78.41	0.844	35.9034	0.055227	55.82	0.806	35.8300
0.070475	77.63	0.834	35.8596	0.070333	52.73	0.828	35.7783
0.085671	76.65	0.861	35.8145	0.085459	50.84	0.855	35.7175
[BMP]Cl							
w_1 = 0.001[b]				w_2 = 0.001[b]			
0.010035	80.38	0.619	36.6735	0.010032	77.90	0.691	36.6451

0.025116	78.18	0.636	36.6280	0.025110	76.70	0.728	36.5990
0.040233	78.63	0.657	36.5841	0.040220	75.90	0.729	36.5523
0.055383	77.92	0.692	36.5386	0.055364	75.17	0.752	36.5049
0.070570	77.66	0.671	36.4935	0.070540	74.46	0.753	36.4571
0.085792	77.61	0.688	36.4489	0.085746	73.66	0.762	36.4082
	w_1 = 0.003[b]				w_2 = 0.003[b]		
0.010028	85.34	0.691	36.7003	0.010025	72.84	0.762	36.6298
0.025103	84.54	0.728	36.6589	0.025088	68.63	0.771	36.5782
0.040215	84.09	0.767	36.6172	0.040178	65.33	0.800	36.5235
0.055363	83.52	0.752	36.5749	0.055285	61.09	0.779	36.4636
0.070550	83.19	0.753	36.5327	0.070408	56.96	0.834	36.3996
0.085770	82.51	0.788	36.4892	0.085544	53.57	0.835	36.3434
	w_1 = 0.005[b]				w_2 = 0.005[b]		
0.010022	90.29	0.763	36.7276	0.010018	79.25	0.833	36.6442
0.025089	89.69	0.771	36.6890	0.025072	72.45	0.861	36.5941
0.040196	89.04	0.800	36.6499	0.040151	67.99	0.870	36.5401
0.055342	88.38	0.779	36.6101	0.055252	63.96	0.902	36.4824
0.070526	87.86	0.834	36.5700	0.070372	60.66	0.914	36.4223
0.085747	87.05	0.860	36.5286	0.085500	56.52	0.907	36.3564

[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 S9. 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 liquids 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}
		[BMIm]Cl			
w_1 = 0.001[b]	74.22	-3.423	0.332	0.517	36.12
w_1 = 0.003[b]	77.44	-18.18	0.384	0.661	36.14
w_1 = 0.005[b]	83.24	-21.15	0.431	0.736	36.16
		[BMP]Cl			
w_1 = 0.001[b]	81.08	-12.87	0.374	0.582	36.80
w_1 = 0.003[b]	86.8	-14.06	0.422	0.658	36.82
w_1 = 0.005[b]	92.17	-16.54	0.470	0.702	36.84
		[BMIm]Cl			
w_2 = 0.001[b]	72.93	-10.58	0.305	0.581	36.10
w_2 = 0.003[b]	75.06	-48.50	0.349	0.657	36.12
w_2 = 0.005[b]	80.6	-104	0.4	0.731	36.14
		[BMP]Cl			

w_2 = 0.001[b]	80.12	-21.54	0.349	0.662	36.78
w_2 = 0.003[b]	84.12	-100.8	0.390	0.715	36.80
w_2 = 0.005[b]	90.95	-115.7	0.432	0.79	36.82

[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 S10. Frequencies at FTIR spectra of [BMIm]Cl, [BMP]Cl, α-CD, β-CD and solid inclusion complexes

[BMIm]Cl		[BMP]Cl	
wave number / cm^{-1}	group	wave number / cm^{-1}	group
3436.81	=C-H	3409.96	–C-H from ring
2963.45	–C-H from $–CH_3$	2970.44	–C-H from $–CH_3$
1634.59	–C=N	1465.54	bending of –C-H from $–CH_2$
1574.80	C=C	1400.30	bending of –C-H from $–CH_3$
1464.89	bending $–CH_2$	1166.82	-C-N
1400.30	bending $–CH_2$		
1168.58	-C-N		

α-Cyclodextrin		β-Cyclodextrin	
wave number / cm^{-1}	group	wave number / cm^{-1}	group
3412.10	stretching of O-H	3349.84	stretching of O-H
2930.79	stretching of –C-H from $–CH_2$	2921.52	stretching of –C-H from $–CH_2$
1406.76	bending of –C-H from $–CH_2$ and bending of O-H	1412.36	bending of –C-H from $–CH_2$ and bending of O-H
1154.39	bending of C-O-C	1157.57	bending of C-O-C
1030.39	stretching of C-C-O	1033.51	stretching of C-C-O
952.36	skeletal vibration involving α-1,4linkage	938.53	skeletal vibration involving α-1,4linkage

[BMIm]Cl-α-CD inclusion complex		[BMP]Cl-α-CD inclusion complex	
wave number / cm^{-1}	group	wave number / cm^{-1}	group
3370.61	stretching of O-H of α-CD	3362.56	stretching of O-H of α-CD
2931.03	stretching of –C-H from –CH_2 of α-CD	2955.06	stretching of –C-H from –CH_2 of α-CD
1630.02	stretching of –C=N	1401.22	bending of –C-H from –CH_2 and bending of O-H of α-CD
1410.13	bending of –C-H from –CH_2 and bending of O-H of α-CD	1149.61	bending of C-O-C α-CD
1150.07	bending of C-O-C of α-CD	946.52	skeletal vibration involving α-1,4linkage
948.07	skeletal vibration involving α-1,4linkage		

[BMIm]Cl-β-CD inclusion complex		[BMP]Cl-β-CD inclusion complex	
wave number / cm^{-1}	group	wave number / cm^{-1}	group
3364.47	stretching of O-H Of β-CD	3369.85	stretching of O-H of β-CD
2932.46	stretching of –C-H from –CH_2 Of β-CD	2931.03	stretching of –C-H from –CH_2 Of β-CD
1407.57	bending of –C-H from –CH_2 and bending of O-H of β-CD	1408.47	bending of –C-H from –CH_2 and bending of O-H Of β-CD
1150.87	bending of C-O-C of β-CD	1150.31	bending of C-O-C Of β-CD
1039.00	stretching of C-C-O of β-CD	1030.00	stretching of C-C-O Of β-CD
944.27	skeletal vibration involving α-1,4linkage of β-CD	943.16	skeletal vibration involving α-1,4linkage of β-CD

Figures:

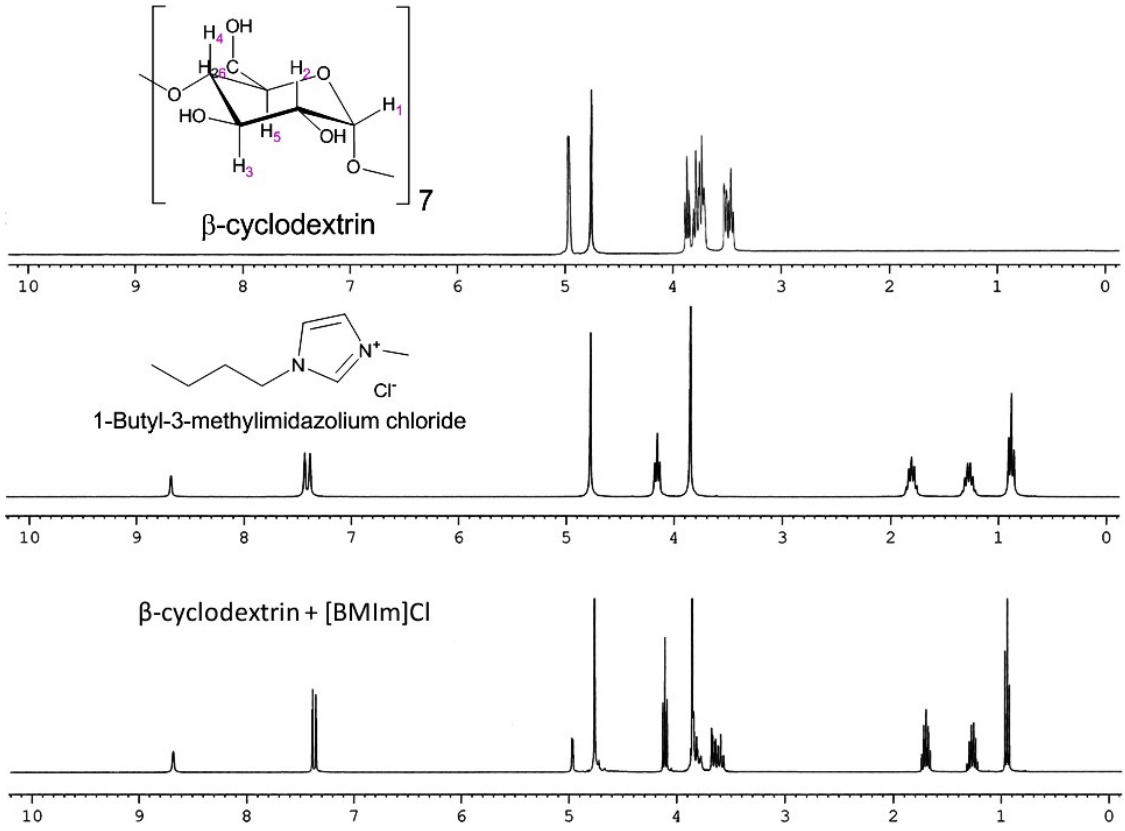


Figure S1(a). ^{1}H NMR Spectra of (a)β-CD (b) [BMIm]Cl (c) 1:1 molar ratio of β-CD and [BMIm]Cl in D_2O in 298.15 K.

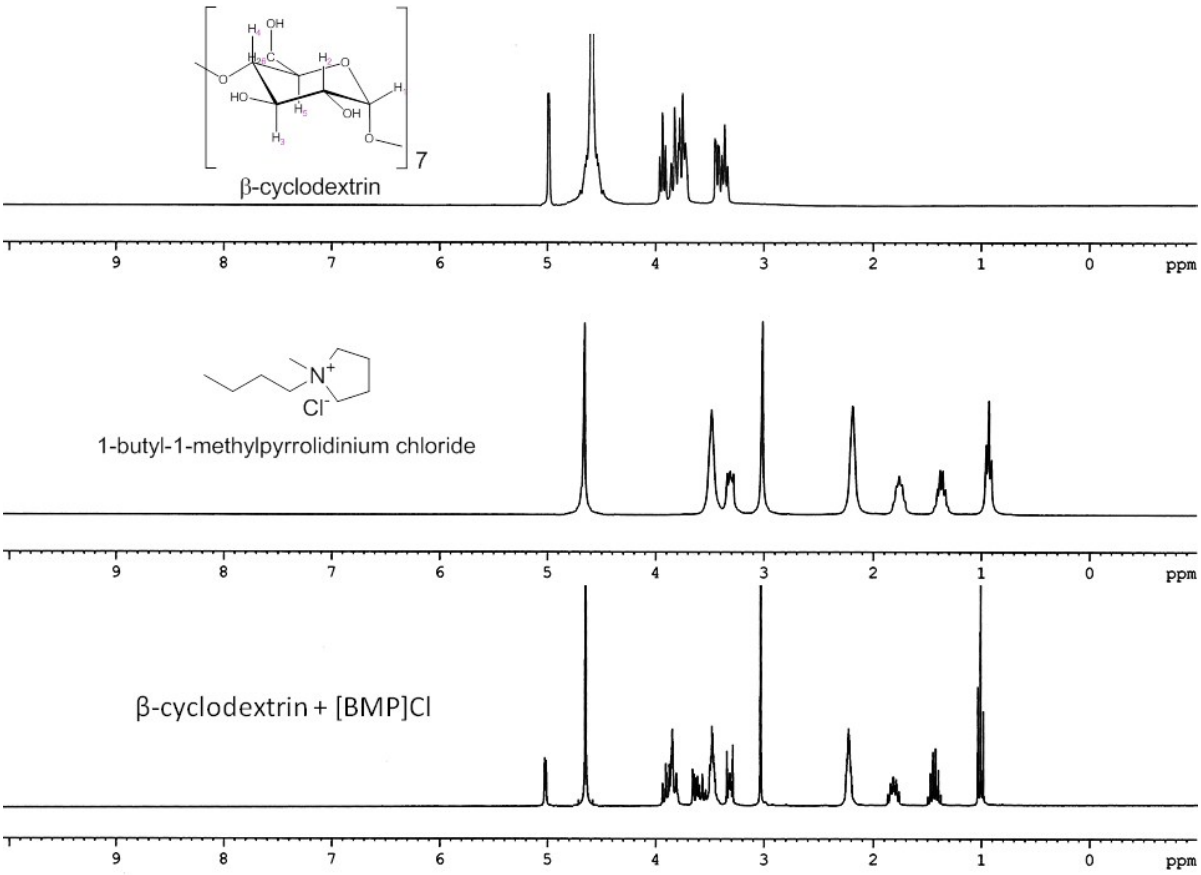


Figure S1(b). ^{1}H NMR Spectra of (a) β-CD (b) [BMP]Cl (c) 1:1 molar ratio of β-CD and [BMP]Cl in D_2O in 298.15 K.

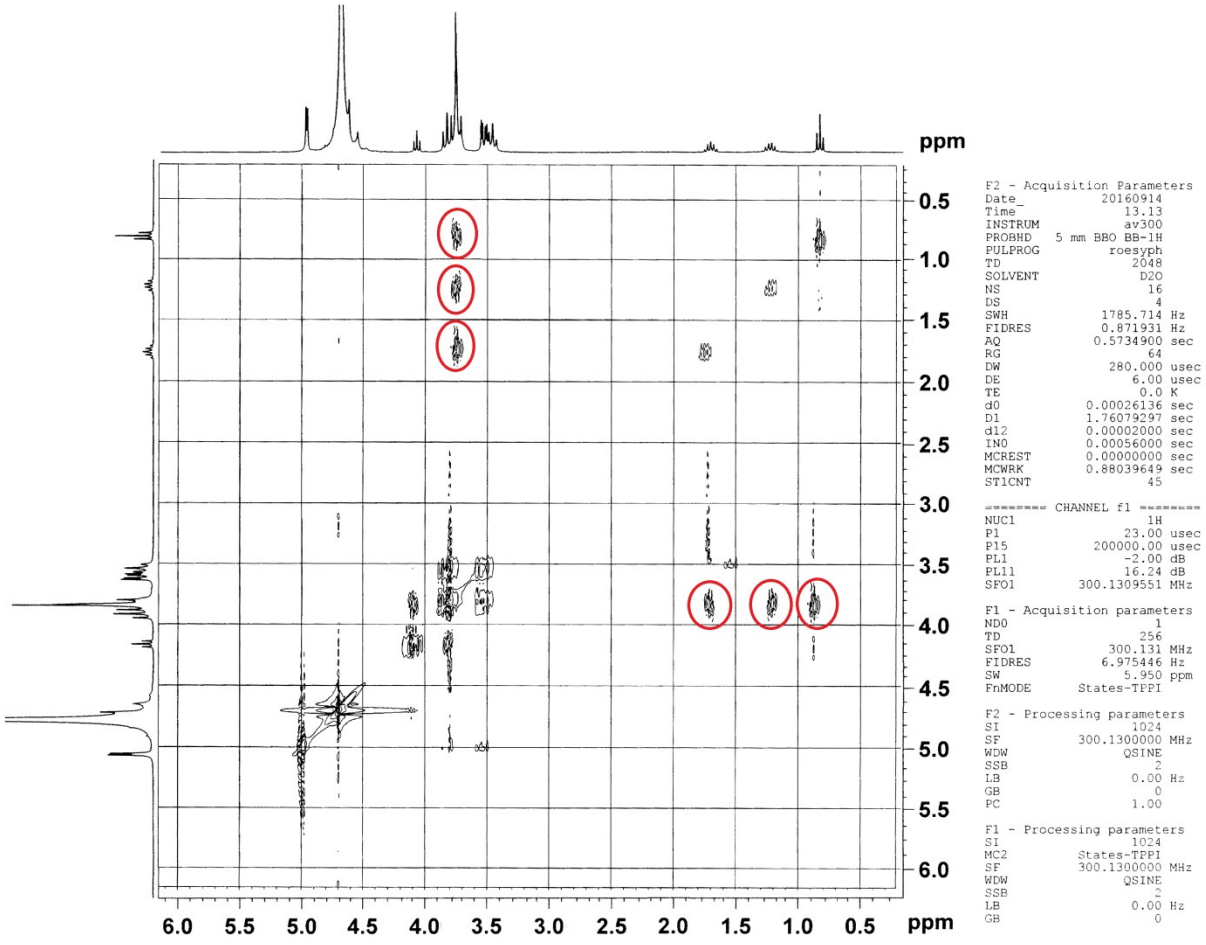


Figure S2(a). 2D ROESY spectra of solid inclusion complex of [BMIm]Cl and β-CD in D_2O (correlation signals are marked by red circles).

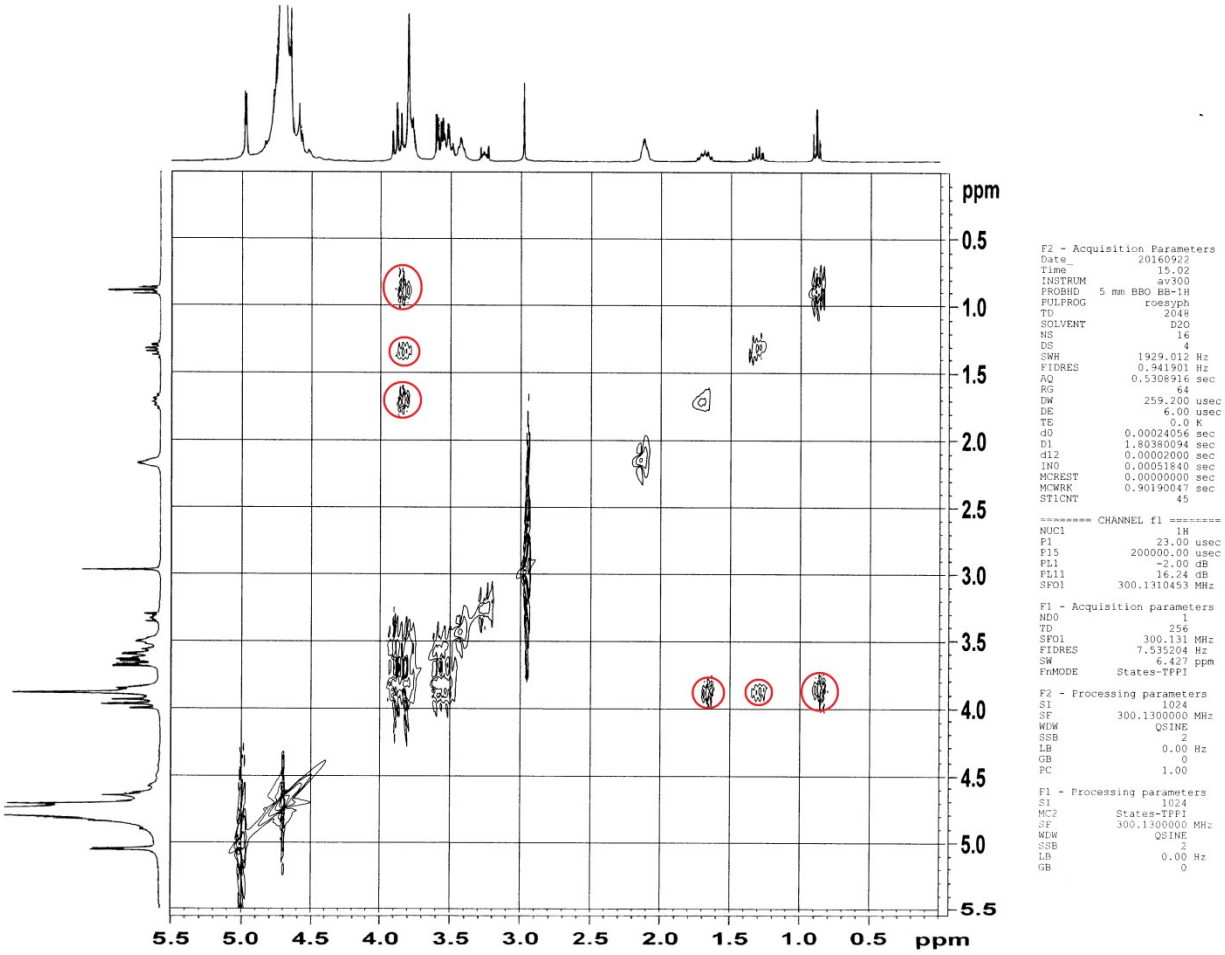


Figure S2(b). 2D ROESY spectra of solid inclusion complex of [BMP]Cl and β-CD in D_2O (correlation signals are marked by red circles).

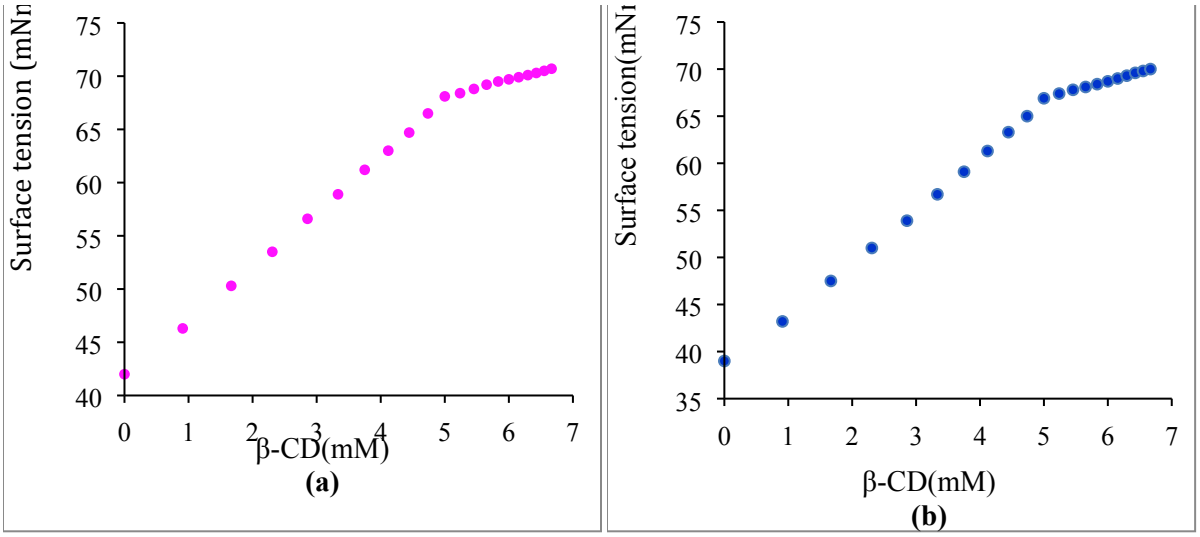


Figure S3. Variation of surface tension of aqueous (a) [BMIm]Cl-β-CD and (b) [BMP]Cl-β-CD systems respectively at 298.15 K.

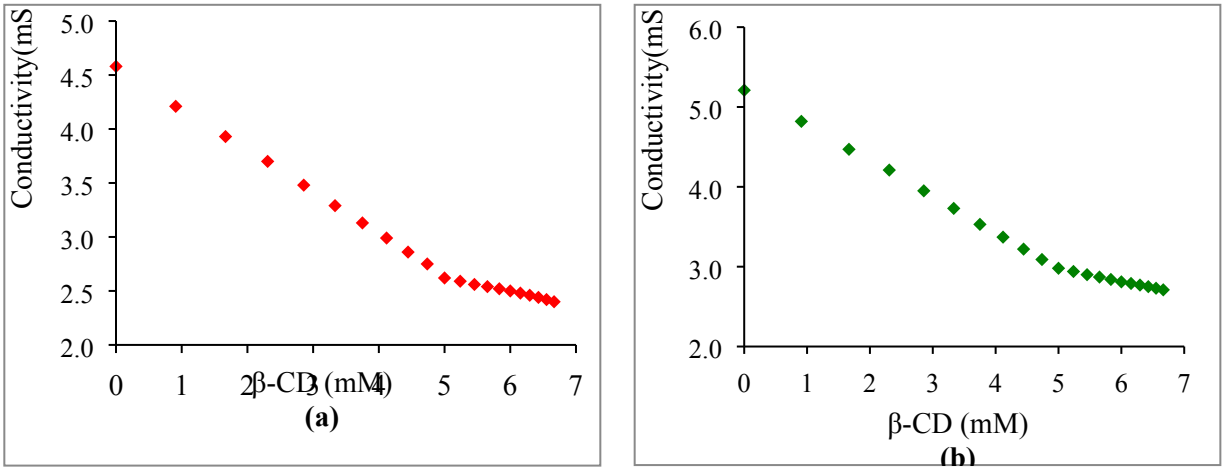


Figure S4. Variation of conductivity of aqueous (a) [BMIm]Cl-β-CD and (b) [BMP]Cl-β-CD systems respectively at 298.15 K.

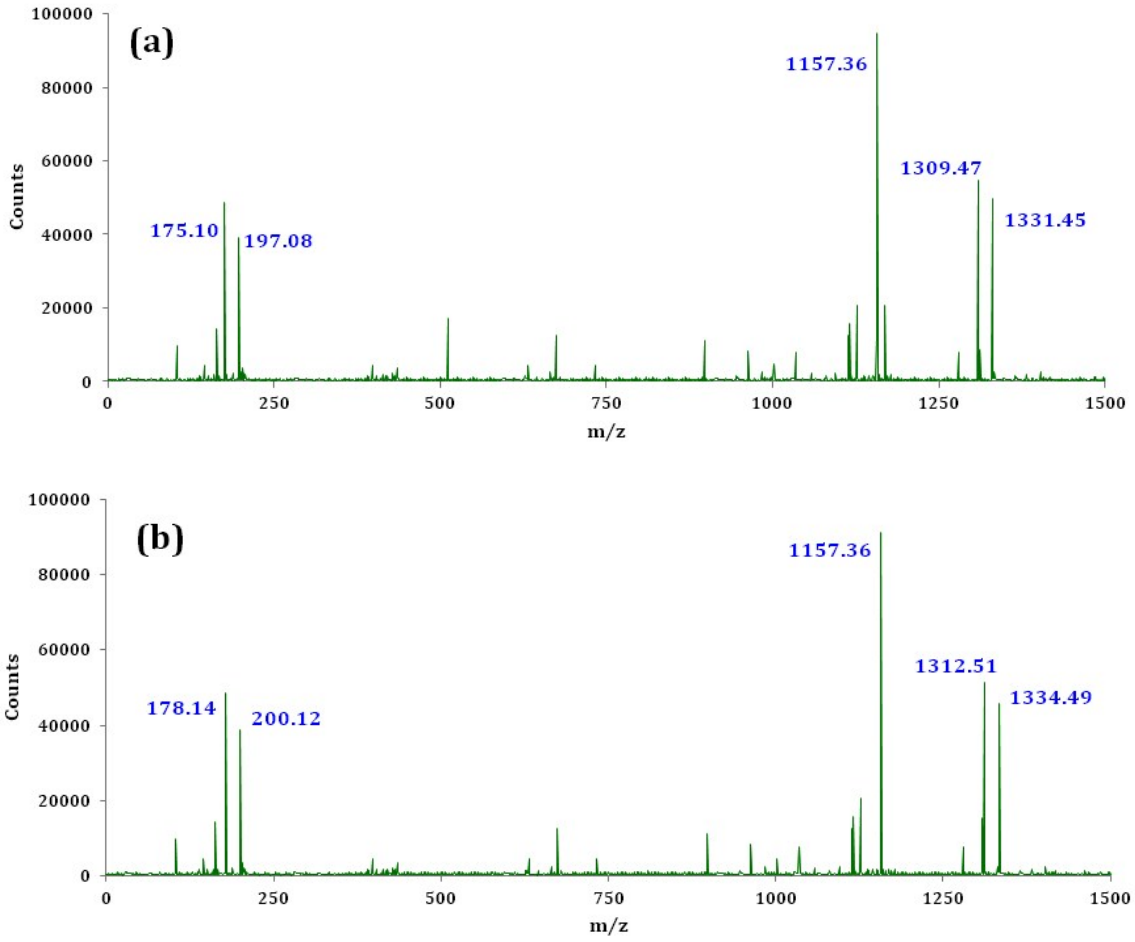


Figure S5. ESI mass spectra of (a) [BMIm]Cl-β-CD inclusion complex and (b) [BMP]Cl-β-CD inclusion complex.

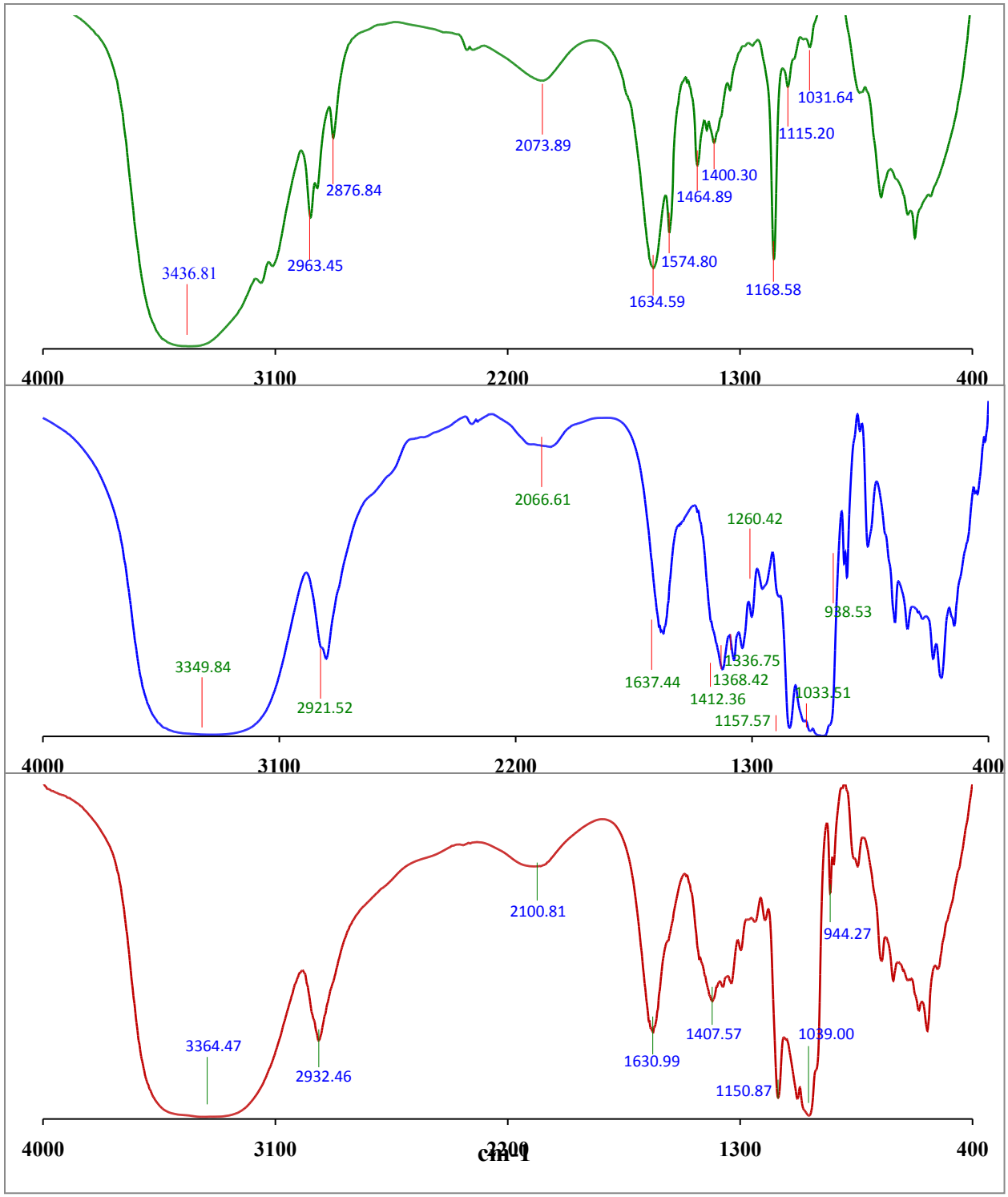


Figure S6(a). FTIR spectra of [BMIm]Cl (top), β-CD (middle) and [BMIm]Cl-β-CD inclusion complex (bottom).

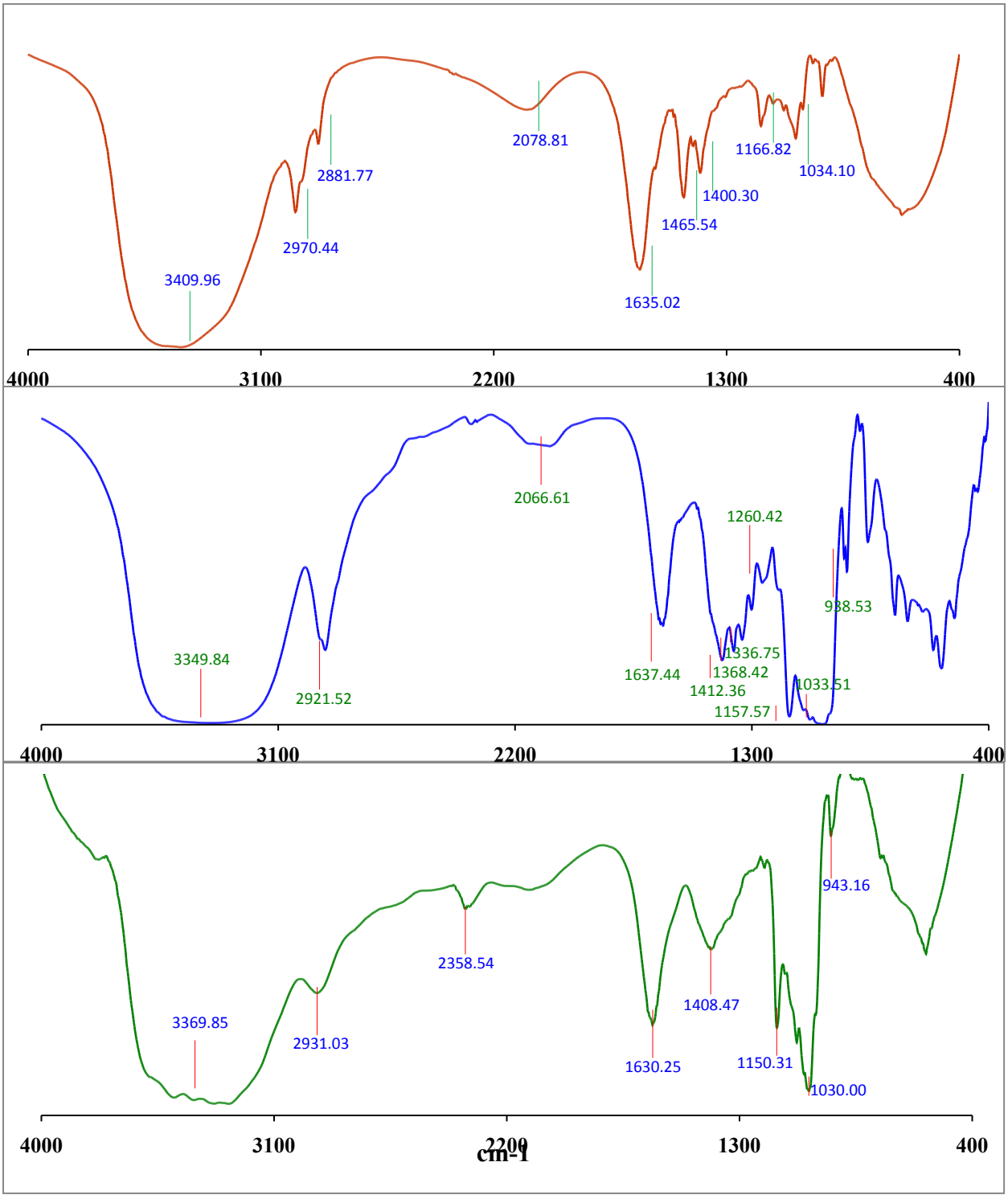
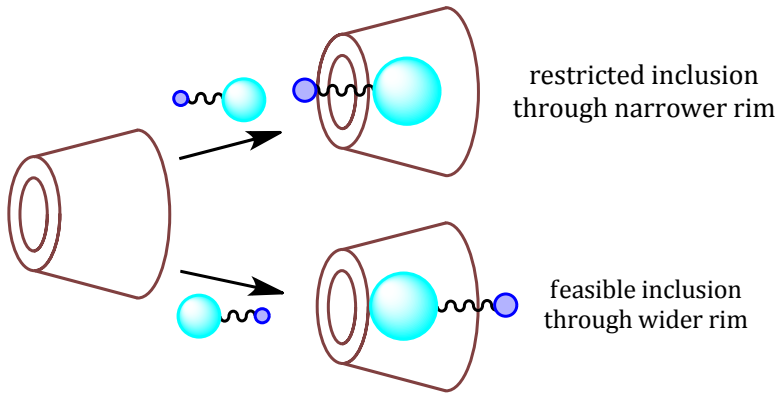
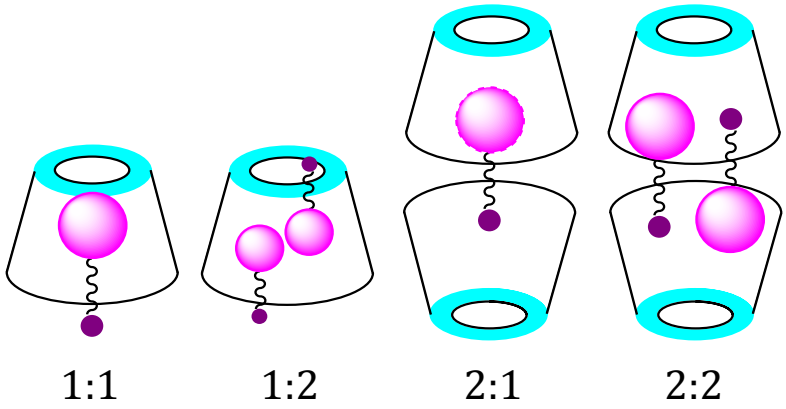


Figure S6(b). FTIR spectra of [BMP]Cl (top), β-CD (middle) and [BMP]Cl-β-CD inclusion complex (bottom).

Schemes:



Scheme S1. Feasible and restricted inclusions of the guest into the host molecule.



Scheme S2. Different stoichiometries of host-guest inclusion complexes.