New Journal of Chemistry

Electronic Supplementary Information

NMR, Surface Tension and Conductivity Studies to Determine Inclusion Mechanism: Thermodynamics of Host-Guest Inclusion Complexes of Natural Amino Acids in Aqueous Cyclodextrins

Subhadeep Saha, Tanusree Ray, Saptarshi Basak and Mahendra Nath Roy

---

Theory

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 has been reported in Table S1. The experimental measured values of pH, density, viscosity and refractive index of selected two α-amino acids (*i.e.*, L-Arg and L-His) 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 S5.

$$\phi_V = M / \rho - 1000(\rho - \rho_o)/ m\rho\rho_o \quad (1)$$

where M is the molar mass of the amino acids, m is the molality of the solution, ρ and ρ_o are the density of the solution and aq. 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 S6.

$$\phi_V = \phi^0_V + S_V^* \cdot \sqrt{m} \quad (2)$$

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

$$\sigma = \sqrt{[\sum (Y_{exp} - Y_{obs})^2 / (N - 1)]} \quad (3)$$

where *N* is the number of data points.

- Contributions of zwitter ionic group (NH_3^+), (COO^-); (CH), (CH_2) groups and end group to the limiting apparent molar volume (ϕ^0_V) :

The ϕ^0_V value of zwitterionic group, (CH), (CH_2) groups and end group of the amino acids were estimated from the following equations[2].

$$\phi^0_V = \phi^0_V (NH_3^+, COO^-) + \phi^0_V (CH) + n\,\phi^0_V (CH_2) + \phi^0_V (\text{end grp}) \quad (4)$$

$$\phi^0_V (R) = \phi^0_V - \phi^0_V (NH_3^+, COO^-) - \phi^0_V (CH) \quad (5)$$

$$\phi^0_V (CH) = ½\, \phi^0_V (CH_2) \quad (6)$$

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[3]

$$(\eta/\eta_o - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B\sqrt{m} \quad (7)$$

where $\eta_r = \eta/\eta_o$, η and η_o are the relative viscosities, the viscosities of the ternary solutions (amino acid + aq. CD) and binary aqueous mixture (aq. CD) and *m* is the molality of the amino acids 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, are estimated by least-square method by plotting $(\eta_r - 1)/\sqrt{m}$ against $\sqrt{m}$ and reported in Table S5.

- The *B*-coefficients of zwitterionic group, (CH), (CH_2) groups and end group of the amino acids have been resolved as follows:

$$B = B\,(NH_3^+, COO^-) + B\,(CH) + n\,B\,(CH_2) + B\,(\text{end grp}) \quad (8)$$

$$B\,(R) = B - B\,(NH_3^+, COO^-) - B\,(CH) \quad (9)$$

$$B\,(CH) = \tfrac{1}{2}\,B\,(CH_2) \quad (10)$$

Refractive index

The molar refraction, R_M can be evaluated from the Lorentz-Lorenz relation [4]

$$R_M = \{(n_D^2 - 1)/(n_D^2 + 2)\}(M/\rho) \quad (11)$$

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 S6, [5]

$$R_M = R_M^o + R_S\sqrt{m} \quad (12)$$

References:

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

(2) H. Zhao, *Biophys Chem.*, 2006, **122**, 157-183.

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

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

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

Tables:

Table S1. Experimental values of density (ρ), viscosity (η), refractive index (n_D) and pH of different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K[a]

Aq. solvent mixture	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s	n_D	pH
aq. α-CD				
w_1 = 0.001	0.99737	1.29	1.3329	6.65
w_1 = 0.003	0.99800	1.30	1.3332	6.60
w_1 = 0.005	0.99865	1.31	1.3335	6.56
aq. β-CD				
w_2 = 0.001	0.99752	1.30	1.3330	6.58
w_2 = 0.003	0.99817	1.31	1.3333	6.53
w_2 = 0.005	0.99893	1.32	1.3336	6.50

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

Table S2. Experimental values of density (ρ) and viscosity (η) of glycine 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	molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s
Glycine					
	w_1 = 0.001[b]			w_2 = 0.001[b]	
0.0100	0.99767	1.31	0.0100	0.99779	1.31
0.0251	0.99820	1.31	0.0251	0.99835	1.32
0.0402	0.99874	1.32	0.0402	0.99891	1.33

0.0553	0.99930	1.32	0.0553	0.99946	1.33
0.0704	0.99983	1.33	0.0704	1.00002	1.34
0.0855	1.00041	1.33	0.0855	1.00060	1.35
	w_1 = 0.003[b]			w_2 = 0.003[b]	
0.0100	0.99825	1.32	0.0100	0.99851	1.33
0.0251	0.99880	1.33	0.0251	0.99904	1.34
0.0401	0.99932	1.34	0.0401	0.99955	1.35
0.0552	0.99988	1.34	0.0552	1.00012	1.35
0.0703	1.00045	1.35	0.0703	1.00070	1.36
0.0855	1.00107	1.35	0.0854	1.00133	1.37
	w_1 = 0.005[b]			w_2 = 0.005[b]	
0.0100	0.99892	1.33	0.0100	0.99924	1.34
0.0251	0.99948	1.34	0.0251	0.99979	1.35
0.0401	1.00005	1.35	0.0401	1.00036	1.36
0.0552	1.00062	1.36	0.0552	1.00090	1.37
0.0703	1.00121	1.37	0.0703	1.00153	1.38
0.0854	1.00181	1.38	0.0854	1.00213	1.39

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

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

Table S3. Experimental values of density (*ρ*), viscosity (*η*), refractive index (*n*D), and pH of selected amino acids 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	pH	molality /mol·kg^{-1}	$\rho\times10^{-3}$ /kg·m^{-3}	η /mP·s	n_D	pH
L-Arginine									
w_1 = 0.001[b]					w_2 = 0.001[b]				
0.010038	0.99792	1.31	1.3330	10.32	0.010038	0.99800	1.33	1.3332	10.25
0.025140	0.99878	1.33	1.3332	10.44	0.025141	0.99875	1.34	1.3334	10.35
0.040295	0.99965	1.34	1.3333	10.54	0.040300	0.99953	1.36	1.3335	10.43
0.055503	1.00052	1.36	1.3335	10.63	0.055514	1.00033	1.39	1.3337	10.54
0.070763	1.00141	1.37	1.3336	10.69	0.070782	1.00114	1.40	1.3339	10.61
0.086075	1.00232	1.39	1.3339	10.73	0.086105	1.00197	1.42	1.3341	10.69
w_1 = 0.003[b]					w_2 = 0.003[b]				
0.010032	0.99851	1.32	1.3334	10.30	0.010031	0.99862	1.34	1.3335	10.12
0.025127	0.99932	1.34	1.3335	10.42	0.025126	0.99934	1.36	1.3336	10.25
0.040275	1.00013	1.36	1.3336	10.55	0.040277	1.00010	1.38	1.3337	10.36
0.055478	1.00097	1.37	1.3338	10.62	0.055485	1.00084	1.40	1.3339	10.44
0.070735	1.00181	1.39	1.3340	10.66	0.070747	1.00164	1.42	1.3341	10.55
0.086043	1.00268	1.40	1.3342	10.70	0.086063	1.00245	1.44	1.3343	10.64
w_1 = 0.005[b]					w_2 = 0.005[b]				
0.010026	0.99911	1.34	1.3337	9.99	0.010024	0.99935	1.35	1.3338	9.80
0.025113	0.99985	1.35	1.3338	10.12	0.025108	1.00004	1.37	1.3340	9.95
0.040256	1.00062	1.37	1.3339	10.27	0.040249	1.00077	1.40	1.3341	10.17
0.055453	1.00141	1.39	1.3341	10.40	0.055448	1.00150	1.42	1.3342	10.32
0.070708	1.00218	1.41	1.3342	10.52	0.070702	1.00226	1.43	1.3344	10.46

0.086017	1.00298	1.42	1.3344	10.61	0.086013	1.00303	1.45	1.3346	10.60
L-Histidine									
w_1 = 0.001[b]					w_2 = 0.001[b]				
0.010037	0.99791	1.30	1.3330	7.45	0.010036	0.99801	1.320	1.3331	7.44
0.025128	0.99878	1.32	1.3331	7.48	0.025126	0.99885	1.330	1.3332	7.46
0.040262	0.99969	1.33	1.3333	7.51	0.040259	0.99977	1.340	1.3334	7.48
0.055437	1.00065	1.34	1.3334	7.53	0.055431	1.00075	1.360	1.3336	7.50
0.070655	1.00159	1.35	1.3335	7.55	0.070644	1.00175	1.370	1.3338	7.51
0.085911	1.00258	1.36	1.3336	7.56	0.085893	1.00279	1.400	1.3339	7.52
w_1 = 0.003[b]					w_2 = 0.003[b]				
0.010031	0.99850	1.32	1.3333	7.44	0.010029	0.99863	1.34	1.3334	7.45
0.025114	0.99932	1.33	1.3334	7.47	0.025112	0.99943	1.35	1.3335	7.46
0.040242	1.00020	1.35	1.3335	7.49	0.040237	1.00032	1.36	1.3337	7.47
0.055412	1.00109	1.37	1.3337	7.51	0.055402	1.00127	1.39	1.3338	7.48
0.070629	1.00196	1.38	1.3338	7.53	0.070609	1.00223	1.40	1.3340	7.50
0.085882	1.00292	1.39	1.3339	7.55	0.085854	1.00324	1.44	1.3341	7.52
w_1 = 0.005[b]					w_2 = 0.005[b]				
0.010024	0.99911	1.33	1.3336	7.40	0.010022	0.99936	1.35	1.3337	7.38
0.025100	0.99989	1.35	1.3338	7.45	0.025094	1.00012	1.37	1.3338	7.40
0.040221	1.00072	1.36	1.3339	7.47	0.040210	1.00098	1.39	1.3339	7.42
0.055386	1.00156	1.39	1.3341	7.49	0.055368	1.00189	1.41	1.3341	7.44
0.070597	1.00240	1.39	1.3342	7.51	0.070566	1.00284	1.43	1.3342	7.47
0.085852	1.00326	1.41	1.3343	7.53	0.085806	1.00379	1.45	1.3343	7.49

[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. Apparent molar volume (ϕ_V) and $(\eta_r\text{-}1)/\sqrt{m}$ of glycine 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$^{-1/2}$	molality /mol·kg^{-1}	$\phi_V \times 10^{-6}$ / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$
Glycine					
	w_1 = 0.001[b]			w_2 = 0.001[b]	
0.0100	41.20	0.070	0.0100	41.19	0.082
0.0251	40.39	0.079	0.0251	40.35	0.093
0.0402	39.95	0.083	0.0402	39.65	0.100
0.0553	39.55	0.087	0.0553	39.38	0.105
0.0704	39.19	0.094	0.0704	38.90	0.106
0.0855	38.95	0.096	0.0855	38.61	0.108
	w_1 = 0.003[b]			w_2 = 0.003[b]	
0.0100	41.17	0.091	0.0100	41.17	0.115
0.0251	40.36	0.102	0.0251	40.36	0.119
0.0401	39.67	0.106	0.0401	39.63	0.130
0.0552	39.17	0.113	0.0552	38.95	0.132
0.0703	38.73	0.116	0.0703	38.45	0.136
0.0855	38.36	0.119	0.0854	37.94	0.143
	w_1 = 0.005[b]			w_2 = 0.005[b]	
0.0100	41.15	0.123	0.0100	41.14	0.129
0.0251	39.95	0.130	0.0251	39.93	0.137
0.0401	39.10	0.134	0.0401	39.10	0.145
0.0552	38.59	0.137	0.0552	38.36	0.150
0.0703	38.00	0.144	0.0703	37.67	0.153
0.0854	37.52	0.150	0.0854	37.13	0.159

[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 S5. Apparent molar volume (ϕ_V), $(\eta_r\text{-}1)/\sqrt{m}$ and molar refraction (R_M) of selected amino acids in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K[a]

molality /mol·kg^{-1}	ϕ_V ×10^{-6} / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	R_M /m^3 mol^{-1}	molality /mol·kg^{-1}	ϕ_V ×10^{-6} / m^3 mol^{-1}	$(\eta_r\text{-}1)/\sqrt{m}$ /kg$^{1/2}$mol$^{-1/2}$	R_M /m^3 mol^{-1}
L-Arginine							
w_1 = 0.001[b]				w_2 = 0.001[b]			
0.010038	119.51	0.155	35.9068	0.010038	126.51	0.230	35.9235
0.025140	118.11	0.196	35.8955	0.025141	125.31	0.194	35.9161
0.040295	117.51	0.193	35.8740	0.040300	124.26	0.230	35.8979
0.055503	117.24	0.230	35.8623	0.055514	123.42	0.294	35.8887
0.070763	116.79	0.233	35.8402	0.070782	122.79	0.289	35.8791
0.086075	116.27	0.264	35.8369	0.086105	122.15	0.315	35.8689
w_1 = 0.003[b]				w_2 = 0.003[b]			
0.010032	123.45	0.154	35.9247	0.010031	129.44	0.229	35.9306
0.025127	121.64	0.194	35.9054	0.025126	127.63	0.241	35.9144
0.040275	121.19	0.230	35.8861	0.040277	126.18	0.266	35.8969
0.055478	120.44	0.229	35.8755	0.055485	125.88	0.292	35.8899
0.070735	120.01	0.246	35.8649	0.070747	124.86	0.316	35.8807
0.086043	119.38	0.262	35.8532	0.086063	124.07	0.338	35.8712
w_1 = 0.005[b]				w_2 = 0.005[b]			
0.010026	128.37	0.191	35.9325	0.010024	132.34	0.227	35.9336
0.025113	126.37	0.193	35.9157	0.025108	129.94	0.239	35.9284
0.040256	125.12	0.228	35.8978	0.040249	128.34	0.302	35.9119
0.055453	124.19	0.259	35.8889	0.055448	127.61	0.322	35.8955
0.070708	123.94	0.287	35.8711	0.070702	126.76	0.313	35.8877

0.086017	123.43	0.286	35.8620	0.086013	126.10	0.336	35.8796
L-Histidine							
w_1 = 0.001[b]				w_2 = 0.001[b]			
0.010037	101.42	0.077	31.9805	0.010036	106.41	0.154	31.9860
0.025128	99.01	0.147	31.9613	0.025126	102.20	0.146	31.9678
0.040262	97.41	0.155	31.9497	0.040259	99.15	0.153	31.9558
0.055437	95.77	0.165	31.9277	0.055431	96.66	0.196	31.9419
0.070655	95.11	0.175	31.9064	0.070644	94.96	0.203	31.9274
0.085911	94.10	0.185	31.8836	0.085893	93.38	0.262	31.9029
w_1 = 0.003[b]				w_2 = 0.003[b]			
0.010031	105.36	0.154	31.9877	0.010029	109.35	0.229	31.9923
0.025114	102.56	0.146	31.9702	0.025112	104.94	0.193	31.9754
0.040242	100.35	0.192	31.9508	0.040237	101.59	0.190	31.9643
0.055412	99.17	0.229	31.9397	0.055402	98.97	0.259	31.9427
0.070629	98.78	0.232	31.9207	0.070609	97.33	0.259	31.9294
0.085882	97.46	0.236	31.8988	0.085854	95.68	0.339	31.9059
w_1 = 0.005[b]				w_2 = 0.005[b]			
0.010024	109.30	0.152	31.9943	0.010022	112.27	0.227	31.9950
0.025100	105.69	0.193	31.9867	0.025094	107.67	0.239	31.9794
0.040221	103.54	0.190	31.9689	0.040210	104.01	0.264	31.9606
0.055386	102.38	0.259	31.9595	0.055368	101.44	0.290	31.9489
0.070597	101.72	0.230	31.9413	0.070566	99.40	0.314	31.9273
0.085852	101.05	0.261	31.9226	0.085806	98.08	0.336	31.9058

[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 S6. Limiting apparent molar volume (ϕ_V^o), experimental slope (S_V^*), viscosity *A* and *B*-coefficient and limiting molar refraction (R_M^o) of amino acids in different mass fractions of aqueous α and β-cyclodextrin mixtures at 298.15 K[a]

Aq. solvent mixture	ϕ^0_V / m^3 mol^{-1}	S^*_V /$m^3 mol^{-3/2} kg^{1/2}$	B /$kg^{1/2}$ $mol^{-1/2}$	A /kg mol^{-1}	R_M^O /m^3 mol^{-1}
		Glycine			
w_1 = 0.001[b]	41.22	-9.33	0.152	0.0028	
w_1 = 0.003[b]	41.64	-10.85	0.156	0.0030	
w_1 = 0.005[b]	42.08	-12.06	0.160	0.0032	
		L-Arginine			
w_1 = 0.001[b]	120.86	-15.71	0.522	0.102	35.95
w_1 = 0.003[b]	125.18	-19.90	0.538	0.106	35.96
w_1 = 0.005[b]	130.58	-25.55	0.586	0.118	35.97
		L-Histidine			
w_1 = 0.001[b]	105.08	-38.05	0.502	0.045	32.01
w_1 = 0.003[b]	108.98	-40.06	0.528	0.087	32.02
w_1 = 0.005[b]	112.80	-42.37	0.548	0.099	32.03
		Glycine			
w_2 = 0.001[b]	41.88	-10.25	0.152	0.0030	
w_2 = 0.003[b]	42.12	-12.08	0.158	0.0033	
w_2 = 0.005[b]	42.36	-14.50	0.164	0.0035	
		L-Arginine			
w_2 = 0.001[b]	128.84	-22.80	0.546	0.144	35.97
w_2 = 0.003[b]	131.98	-26.97	0.584	0.157	35.98
w_2 = 0.005[b]	135.18	-31.90	0.602	0.164	35.99
		L-Histidine			
w_2 = 0.001[b]	113.02	-68.10	0.528	0.075	32.03
w_2 = 0.003[b]	116.28	-71.60	0.546	0.130	32.04
w_2 = 0.005[b]	119.50	-75.14	0.584	0.156	32.05

[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.