

Table 1s. DSC data.^a

m_{CD}	T_{onset}	T_C	ΔH_C
HP- α -CD			
0	36.5	42.4	52.4
0.0485	38.1	43.5	56.9
0.1180	38.4	43.6	55.1
0.1770	38.5	44.5	53.8
HP- β -CD			
0.0217	38.2	45.4	48.5
0.0558	42.7	48.2	35.6
0.0929	46.4	52.9	31.5
0.1197	48.8	54.9	25.2
HP- γ -CD			
0.0261	38.4	43.7	55.4
0.0529	39.2	44.6	48.3
0.0726	39.8	45.6	48.9
0.1138	41.2	46.9	43.8

^aUnits are: m_{CD} , mol kg⁻¹; T , °C; ΔH_C , kJ mol⁻¹.

Table 2s. ITC fitting results.^a

T	K	z	ΔH°_{IC}
HP- β -CD			
10.1	44±1	1.26±0.01	16.2±0.2
17.1	48±3	1.39±0.01	17.1±0.5
25.1	26±2	1.06±0.02	20.1±1.0
30.0	16±2	0.80±0.04	21±2
37.0	11±2	1.10±0.04	22±2
HP- γ -CD			
25.0	12±7	2.6±0.5	21±5

^aUnits are: T , °C; ΔH°_{IC} , kJ mol⁻¹.

Cyclodextrin role on the solubility equilibrium of PPG 725 in water: the equation

One may write the following solubility equilibrium of the polymer and the equilibrium of inclusion complex formation



where $P_{(aq)}$ represents the polymer in water and P^* is the polymeric phase.

At the equilibrium, keeping constant the pressure, the variation of the chemical potential of the polymer in water and in the polymeric phase (refer to equilibrium 1s) may be caused by temperature and concentration changes according to

$$RTd\ln X_{(aq)} - S_{(aq)}dT = RTd\ln X_{(P^*)} - S^*dT \quad (3s)$$

where $X_{(aq)}$ is the polymer solubility in water (mole fraction scale) and $X_{(P^*)}$ is the mole fraction of the polymeric phase. $S_{(aq)}$ is the partial molar entropy of the polymer in water and S^* is the molar entropy of the polymer.

Similarly for the equilibrium 2s, one may write

$$RTd\ln X_{(aq)} - S_{(aq)}dT + zRTd\ln X_{CD} - zS_{CD}dT = RTd\ln X_{IC} - S_{IC}dT \quad (4s)$$

where X_{CD} and X_{IC} are the mole fractions of the cyclodextrin and the inclusion complexes in the aqueous phase, respectively, while S_{CD} and S_{IC} are the corresponding partial molar entropies. By combining eqns (3s) and (4s) and assuming that $X_{(P^*)} = 1$ (*i.e.* the polymeric phase is coincident with the pure polymer), one obtains

$$zRTd\ln X_{CD} - zS_{CD}dT - S^*dT = RTd\ln X_{IC} - S_{IC}dT \quad (5s)$$

Stating that $(S^* - S_{(aq)}) = \Delta S_C = \Delta H_C/T$ and $(S_{IC} - zS_{CD} - S_u) = \Delta S^{\circ}_{IC} = \Delta H^{\circ}_{IC}/T$, from the variable separations one obtains

$$\int_{T_C^*}^{T_C} \frac{\Delta H_{IC} - \Delta H_C}{RT^2} dT = \int_0^{x_{IC}} d \ln \frac{X_{IC}}{X_{CD}^z} \quad (6s)$$

where T_C^* and T_C represent the cloud temperature in water and in the presence of CD, respectively. By considering the equilibrium constant for the IC formation ($K = X_{IC}/[X_{CD}^z X_{(aq)}]$) and changing the integration variable on the right hand side of eqn (6s) the following equation is obtained

$$\int_{T_C^*}^{T_C} \frac{\Delta H_{IC} - \Delta H_C}{RT^2} dT = \int_{X_0}^{X_{CD}} d \ln(KX_{(aq)}) \quad (7s)$$

where X_0 and X_{CD} are the mole fractions of the polymer in the aqueous phase in the absence and the presence of CD, respectively.

By assuming that both ΔH_C and ΔH°_{IC} are independent of temperature, integrating eqn 7s one obtains

$$\frac{(\Delta H^{\circ}_{IC} - \Delta H_C)(T_C - T_C^*)}{R T_C T_C^*} = \ln \frac{X_{CD}}{X_0} \quad (8s)$$

Note that

$$X_{CD} = m_0/(m_P + m_{CD} + 55.55) \quad X_0 = m_P/(m_P + 55.55) \quad (9s)$$

m_0 is the polymer solubility in water, m_{CD} and m_P are the stoichiometric molalities of the cyclodextrin and the polymer, respectively. By neglecting m_{CD} and m_P with respect to the moles of

water (55.55), the ratio (X_{CD}/X_0) can be expressed as $(1 - m_{IC}/m_P)$, where m_{IC} is the molality of the inclusion complex.

Assuming that that $T_C \times T_C^* \approx (T_C^*)^2$ and $\ln(1 - m_{IC}/m_P) \approx m_{IC}/m_P$ one finally obtains

$$T_C = T_C^* - \frac{R (T_C^*)^2}{(\Delta H_{IC}^\circ - \Delta H_{C,w})} \frac{X_{I,CD} m_{CD}}{z m_P} \quad (10s)$$