Aqueous pigment dispersions: The thermodynamics of hierarchical aggregation

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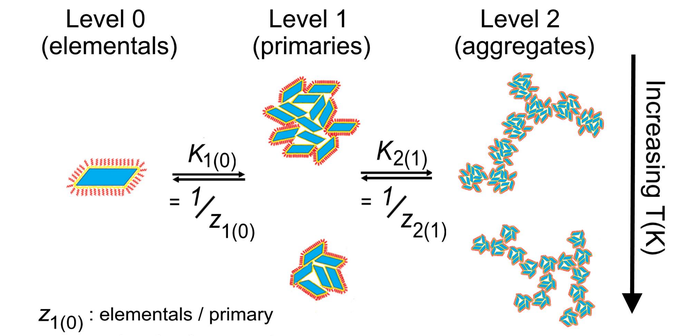
Overview[1]

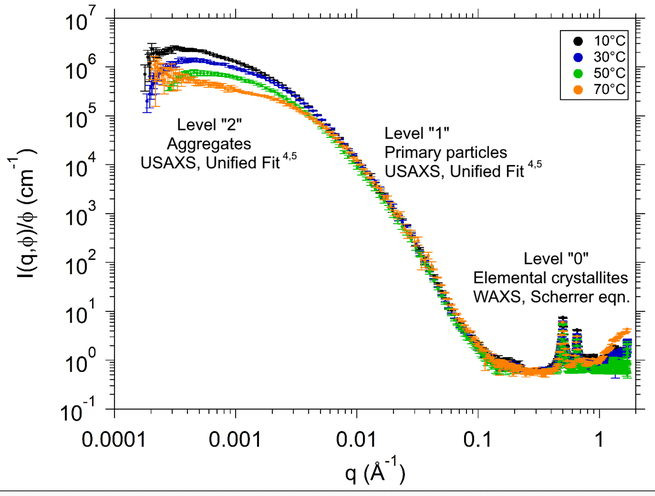


Predictions of the Vogtt Model[3]

	$\Delta S_{1(0)}$	$\Delta S_{2(1)}$	$z_{1(0)}$	$z_{2(1)}$	prediction at elevated temperature
I	+	+	↓	↓	elemental particles increase at the expense of aggregates and primary particles due to a decreased entropic penalty to remove a subunit
II	–	–	↑	↑	aggregates and primary particles grow at the expense of elementals due to an increased entropic penalty for removal of a subunit
III	+	–	↓	↑	aggregates grow at the expense of the primary particle size
IV	–	+	↑	↓	primary particles grow at the cost of aggregate size

Methods

Surfactant (Triton X100) stabilized aqueous pigment dispersions (PY14 & PB15:3). USAXS / SAXS / WAXS at temperatures from 10°C to 80°C.



Smoluchowski aggregation[2,6]

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j\to k} C_{ij} n_i n_j - \sum_{i=1}^{\infty} C_{ik} n_i n_k$$

Rate of change of aggregate concentration

Formation of aggregates by any pair i and j

Loss of aggregates due to aggregation

New Vogtt Model[3]

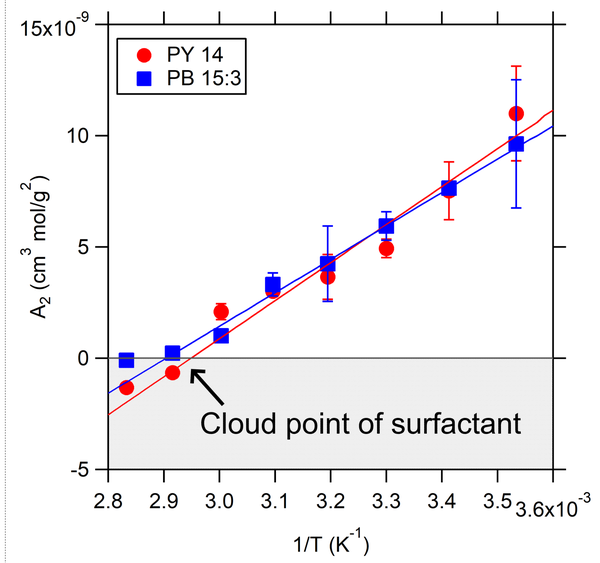
$$\langle N_i(n_{i-1})dn_{i-1} + z_{i(i-1)}dN_i(n_{i-1})\rangle_t = 0$$

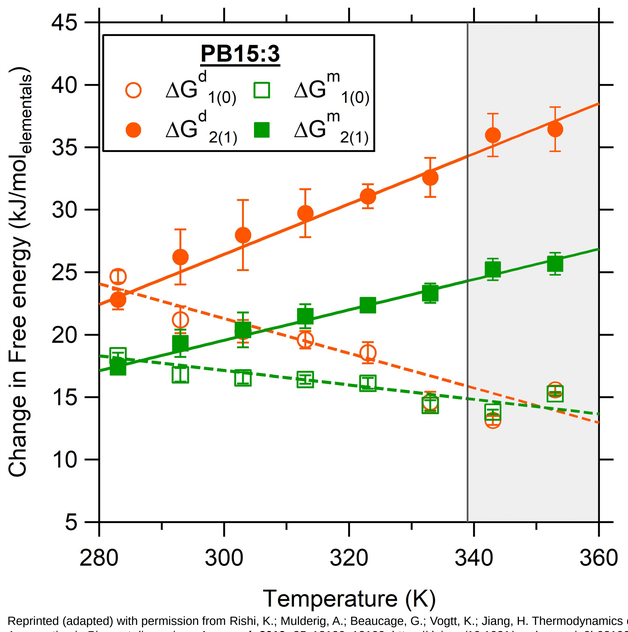
Change in the # of subunits

Degree of aggregation

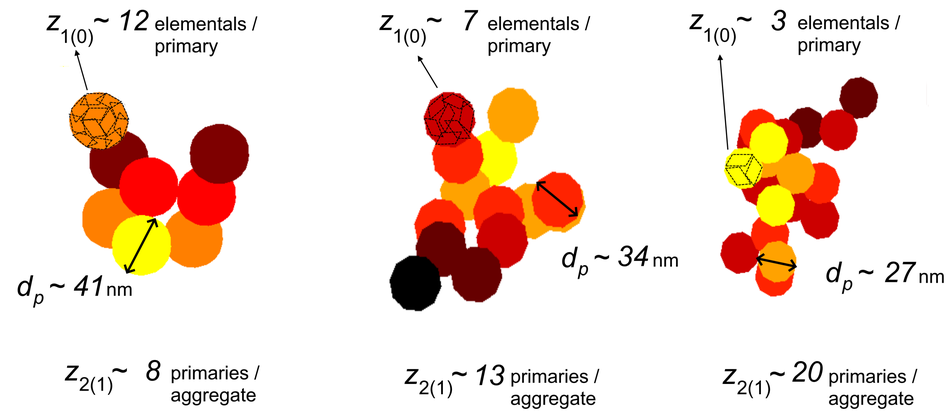
Change in aggregation #

$$G_{i(i-1)} = RT\ln\left(z_{i(i-1)}\right)$$





Thermodynamics of aggregation



References

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