Supramolecular Chemistry-I

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Week - 01

Lecture - 04

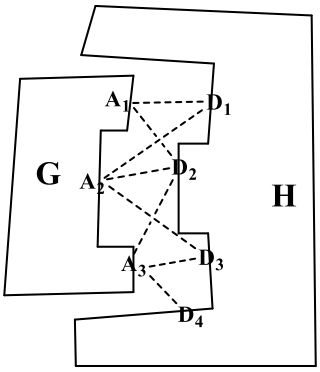
Good morning. So, as we take it from the last talk I had. Today what I am going to do will be called multi-site host guest interactions. We can study molecular recognition by thermodynamics. The concept of pair-wise interactions is of importance here.
As we had shown earlier schematically, strong host-guest complexation occurs due to multi-site interactions between the partners. The following equations can be written:

$$H + G \rightleftharpoons H\bullet G \qquad (1)$$

$$\mathbf{K_a = [H\bullet G]/[H][G]} \qquad (2)$$

$$\Delta G^o = -RT\ln K_a \qquad (3)$$

This treatment of complex formation we know. Now, we have multi-site interactions between a host and a guest.



This is a schematic illustration of pair-wise multisite host-guest interactions. We know that all kinds of interactions are possible. There are actually thousands of this A_iD_j interactions (i and j are integers) possible. Consequently the total binding energy constant in this case can be derived as follows:

So, how we express K_{ij}? We can express K_{ij} as follows:

$$R\text{–}A_i + R'\text{-}D_j \rightleftharpoons R\text{–}A_i\text{---------}D_j\text{–}R' \quad (\mathbf{K_{ij}})$$

So, $K_{ij}\ (M^{-1}) = [\ R–A_i\text{----}D_j–R'\ ]/\ [R–A_i]\ [R'\text{-}D_j]$

Therefore, we can write

$$R–A_1 + R'\text{-}D_1 \rightleftharpoons R–A_1\text{---------}D_1–R' \quad (\mathbf{K_{11}})$$

$$R–A_1 + R'\text{-}D_2 \rightleftharpoons R–A_1\text{---------}D_2–R' \quad (\mathbf{K_{12}})$$

$$R–A_2 + R'\text{-}D_2 \rightleftharpoons R–A_2\text{---------}D_2–R' \quad (\mathbf{K_{22}})$$

etc.,

For this, $K_t = K_{11}\, K_{12}\, K_{22}$ …….. Eqn. (1)

Now, total constant has the dimension, M^{-1} and also each K_{ij} has the dimension, M^{-1}

Therefore, on the right side of this equation (1) has the dimension M^{-n} and on the left side is M^{-1}. So, that is a problem in an equation; if you have different dimensions on the left and right you cannot equate them. So, there is a major problem alright. To surmount this problem, we have to go dimensionless. But, how to go dimensionless? Suppose we are discussing these host and guest, each are interacting in one molar aqueous solution, alright? Therefore, the molar fractions will be 1/55.6 Ok? Because we are talking about 1 molar solution. So, water has 55.6 moles in 1 litre volume. And, we have to divide 1 upon 55.6 to make the concentration dimensionless. Remember, we are neglecting 1 molecule of the host and the guest with respect to 55.56 moles. So, therefore, I can write now instead of the usual concentration that we write we will express concentrations as ratio of molar fractions. So, I can write the total equation as follows:

$$K_{ij}\ (M^{-1}) = [\ R–A_i\text{----}D_j–R'\ ]/\ [R–A_i]\ [R'\text{-}D_j]$$

$$= (\{[\ R–A_i\text{----}D_j–R'\ ]/55.6)(1/55.6)\}/\ ([R–A_i]/55.6)\ ([R'\text{-}D_j]\ /55.6)$$

$$= X_{R–Ai\text{----}Dj–R'}\,(1/55.6)/\ X_{R–Ai}X_{R'\text{-}Dj}$$

$$= K_{ij}^{\,x}/55.6$$

Now, we can write $K_t^{\,x} = K_{11}^{\,x}\, K_{12}^{\,x}\, K_{13}^{\,x}$……..

On the other hand, $K_t^{\,x} = 55.6\ K_t$

So, $K_t = (55.6)^{n-1}\ K_{11}\, K_{12}\, K_{22}$……..

This equation we have derived assuming complete additivity of these interactions and it is a dimensionless quantity. So, we can get the K_t value from individual pair wise

interaction, $K_{ij.}$ There are many pair-wise interactions in the host-guest complex. If say 100s interactions are there. So, K_t becomes,

$$K_t = (55.6)^{100-1} K_{11} K_{12} K_{22}.....$$

This means, K_t becomes substantial. So, that is the basic principles of host and guest host complexation. This is reality because host and guest combine over a large surface area making "n" number of interactions possible.

It must be kept in mind that I have not talked about entropy. Now, what will happen when host and guest combine there is a change in entropy, but in this case but entropy is less much significance compared to the ΔH values. So, ΔG we can get fairly accurately or we can know that we are quite Ok. From next lecture onwards, I shall start with what is known as supra-molecular synthons. Thank you.