Outline of the solution to Problem 1: How to be a good host

10 marks

17 August, 2020

1 Trends

General trend – Down every column, the value of $\log K_{11}$ increases, reaches a peak value, then decreases. Other visible trends:

- Along each row the value of $\log K_{11}$ for potassium ion is the maximum.
- The changes in the values of $\log K_{11}$ are relatively abrupt for ammonium ion.
- The peak comes later as the size of the cation increases.

2 The host

It is an N-pivot lariat aza-crown ether (except for R = H, which is not a lariat ether)

3 Thermodynamic explanation of changes in the value of $\log K_{11}$

Enthalpic changes are caused due to:

- Electrostatic interactions between the cations and the O atoms of the crown ether and the arms (R groups) of the lariat ether.
- Hydrogen bonding between the H atoms of the ammonium ion and the O atoms of the ether.
- Solvation of the cations and the ether residues of the R group by the solvent methanol.
- Conformational changes due to complexation.

Entropic changes are caused due to:

- Desolvation upon complexation
- Conformational flexibility of the crown and loss of degrees of freedom on complexation

4 Explanation of trends

4.1 General trend-

When R=H, the only interaction is the ion-dipole interaction between the cations and the O atoms of the crown or H-bonding between the H atoms of ammonium ion with the O atoms of the crown. As the N of the aza-crown is substituted, the ether groups of the R interact with the cations and confer stability leading to negative enthalpy change. When R has three arms there are two possibilities: the first and second interact, and the third does not, which is not a problem. The second possibility is that the first and third arms interact, and the second one is bent, which is unstable due to steric hindrance. The two possibilities are probabilistic. So as the number of arms increase, the steric C-C or O-O repulsions increase leading to lower binding constant values.

4.2 Along each row the value of $\log K_{11}$ for potassium ion is the maximum-

The K^+ ion has just the optimum size for the 18 crown 6 ether. Thus, the complexation of potassium ions will have the lowest conformational strain (the sodium and calcium ions are smaller, and thus the conformational strain to ensure a good fit will be higher)

4.3 The changes in the values of $\log K_{11}$ are relatively abrupt for ammonium ion-

The tetrahedral shape of the ammonium ion leads to anisotropic interactions. Thus, the different orientations will have different energies, which leads to greater population variation in these microstates, and thus a decrease in entropy when compared to the metal cations which are isotropic as they are spherical charge distributions. Also, as the number of arms of the substituent increases, the number of ether groups increases which leads to a greater degree of hydrogen bonding with the hydrogens of the ammonium cation.

4.4 The peak comes later as the size of the cation increases-

The smaller cations (sodium and calcium) are able to move around slightly in the binding cavity for proper orientation with respect to the -R substitution, hence the optimum complex stabilization energy is maximized for a smaller -R group. K^+ and NH_4^+ ions have a better fit due to larger size and thus reach the peak value later.

Only explanations to **general trends** have been given. Certain specific trends require a more involved discussion.