Consecutive stability constants – statistical considerations

Data for acid dissociation constants of dicarboxylic acids, $HOOC(CH_2)_nCOOH$ in which the two carboxy groups are separated by n methylene groups, are given in Table 1. Also the difference between the two consecutive constants dpK = $pK_1 – pK_2$ is given. Table 2 contains data for acid dissociation constants of the corresponding acids to α,ω-diamines, again with the two acidic groups separated by n CH_2 groups. dpK in this table has the same meaning as in Table 1.

n	pK_1	pK_2	dpK
0	1.28	4.19	2.96
1	2.87	5.70	2.83
2	4.22	5.70	1.48
3	4.35	5.40	1.05
4	4.44	5.44	1.00
5	4.51	5.51	1.00
6	4.52	5.52	.99
7	4.56	5.53	.97
8	4.58	5.54	.96

Table 1: pK-values for dicarboxylic acids $HOOC(CH_2)_nCOOH$ (25 °C).

n	pK_1	pK_2	dpK
2	7.17	9.98	2.83
3	8.71	10.31	1.60
4	9.49	10.67	1.19
5	9.92	10.77	.85
6	10.12	10.80	.68
7	10.16	10.85	.69
8	10.27	10.88	.61
9			
10	10.35	10.94	.59

Table 2: pK-values for α,ω-diamonium ions $H_3N^+(CH_2)_nNH_3^+$ (25 °C).

From the tables it appears that the first pK approaches a value of 4.6 (Table 1) and 10.4 (Table 2). These numbers should be compared to the corresponding pK's of long chained aliphatic monocarboxylic acids (4.85) and monoamonium ions (10.65). The difference is close to 0.3 in both cases. This number on the log-scale of pK's corresponds to the acidity constant K of the di-acid being $10^{0.3}$ = 2 times that of the mono-acid. So, the di-acid appears to betwice as strong as the mono-acid.

The data further reveal that the dpK decreases as the distance between the two acid groups increase (when n becomes larger). It probably indicates that inductive and other effects between the acidic group at one end of the molecule and the acidic group at the other end get smaller. If such interactive effects were totally eliminated due to distance, the two ends of the molecule could be regarded as independent of each other, and the di-acids ought to be twice as strong as mono-acids, simply because the di-acid holds two acid groups and not only one.

Statistically you may argue that there are two chances with equal probability to liberate one proton from the di-acid HBXBH, while there is only one chance (with the same proability) to liberate a proton from ^-BXBH or from HBX (where ^-BXBH is the corresponding base to HBXBH, and X is the separator, making the two H's chemically "invisible" to each other).

In the same way, the base

$^-BXB^-$ becomes twice as strong as either of the bases ^-BXBH or ^-BX. The argument is further, that relative concentrations in the expression for the ratio between K_1 and K_2 can be substituted by the ration between the relative probabilities of forming the two species:

$$\frac{K_1}{K_2} = \frac{[HBXB^-]\cdot[H^+]}{[HBXBH]} \cdot \frac{[HBXB^-]}{[^-BXB^-]\cdot[H^+]} = \frac{2}{1}\cdot\frac{2}{1} = 4; \qquad dpK = 0.6$$

This purely statistical model predicts that dpK equals 0.6, a number which doesn't deviate much from data in the tables. Where data are incomplete such a model could probably serve as a predictive tool to estimate an approximate value from known data.

In systems where stepwise dissociation or uptake of equal ions or molecules is taking place a statistical argument will be possible for the estimation of the value of a consecutive constant. Table 3 presents data for the consecutive constants K_n in the Cd^{2+} - NH_3 system ($n \leq 4$).

n	$\log K_n$	$\log K_n - \log K_{n+1}$
1	2.65	0.55
2	2.10	0.66
3	1.44	0.51
4	0.93	

Table 3 Stability data in the Cd^{2+} - NH_3 system

From the table it is seen, that $\log K_n - \log K_{n+1} = \log(K_n/K_{n+1})$ is close to 0.6 in the all three cases.

The data reflect the feature that consecutive constant decrease rather smoothly (unless other factors are relevant).

Further, it could be argued that: Statistically, the ratio between two adjacent consecutive constants depends on the ratio between the probabilities of taking up one extra ligand as well as the ratio between the probabilities of losing one ligand.

In the above example, let us suppose that Cd^{2+} has 4 coordination sites for ammonia. Then the probability of building $CdNH_3^{2+}$ from Cd^{2+} will be 4/3 the probability of building $Cd(NH_3)_2^{2+}$ from $CdNH_3^{2+}$, because there are 4 and 3 free binding sites (not already occupied by an ammonia), respectively. Now, the ratio between the two probabilities of losing one ligand is 1/2 because there are 1 and 2 ammonia to lose, respectively. The ratio between the stabilities K_1/K_2 could therefore be replaced by the ratio between the probabilities of building the two complexes divided by the ratio between the probabilities of losing one ligand from the two species, in this case 4/3:1/2 = 8/3.

In the same way, K_2/K_3 could be estimated as 3/2:2/3 = 9/4 and K_3/K_4 as 8/3. The corresponding log-values are 0.43, 0.35, and 0.43, respectively. Accordingly, we would expect the decrease in $\log K_n$ to be 0.4 when n increases by 1.

The experimental values (Table 3) are larger due to the fact that the electronic system around Cd^{2+} (and the binding ability) is actually affected to some extent by the substitution of a water molecule by an ammonia. Still, if it is assumed that the maximum coordination number on cadmium(II) is 4 (by the way, it isn't) you could predict an upper limit for $\log K_4$ from the known value of $\log K_3$: 1.44 – 0.43 = 0.99 , which compares rather well with the experimental value 0.93 (Table 3).

In general this type of argumentation means that if the maximum coordination number is N, then K_n/K_{n+1} will as a minimum be $[(N-n+1)/(N-n)]:[n/(n+1)]$ for statistical reasons alone.

Another illustrative example is data of the Nickel(II)-ammonia system found in Table 4

n	**1**	**2**	**3**	**4**	**5**	**6**
$\log\beta_n$(measured)	2.78	5.05	6.70	8.01	8.66	8.74
$\log\beta_n$(statistical)	-	5.18	7.05	8.10	9.05	8.93

Table 4: $\log\beta_n$ in the Ni^{2+}-NH_3-system – experimental data and values predicted from $\log\beta_{n-1}$

Here the statistically predicted upper limit of $\log\beta_n$ (in the row $\log\beta_n$(statistical) of the table) is calculated based upon the maximum coordination number 6, the statistical argument for the minimum ratio between two consecutive constants using and the actual value for $\log\beta_{n-1}$(measured).

As an example $\log\beta_4$(statistical) can be calculated as

$$\log\beta_3 + \log K_3 - \log(K_3/K_4)(\text{statistical}) = 6.70+(6.70-5.05) - 0.25 = 8.10$$

It is seen that the predictions are reasonable when taken relative to $\log\beta_n$.

The irregularity of the 5th step corresponding to

$$Ni(NH_3)_4^{2+} + NH_3 \leftrightarrows Ni(NH_3)_5^{2+}$$

is by no means predictable by this simple model. After all it rely on the assumption that “anything else is unchanged” – and we know very well that this is most often not perfectly true.

In general the statistical argument can be summarised as.

$$\frac{K_n}{K_{n+1}} \geq \frac{(N-n+1)}{(N-n)} \cdot \frac{(n+1)}{n}$$