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### Evaluation of Stability Constants of Mixed Ligand Complexes pH-metrically

S. RAMAMOORTHY & M. SANTAPPA  
Department of Physical Chemistry, University of Madras  
Madras 25

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pH-metric evaluation of stability constants of mixed ligand systems, metal ion-ligand<sub>1</sub>-ligand<sub>2</sub> is described. The method involves primarily the identification of the mixed complex and determination of the course of equilibria for its formation from the shifts in the precipitation points as compared with those for individual simple complexes, metal ion-ligand. Equations for the determination of stability constants of the mixed complexes involving up to three ligands have been derived.

**METHODS** of evaluation of stability constants of 1:1 complexes of metal ions-ligand are well known. The evaluation of the former for mixed ligand systems metal ion-ligand<sub>1</sub>-ligand<sub>2</sub> is preceded by the identification of the mixed complex and determination of the course of the equilibria

for its formation from the shifts in the precipitation points as compared to corresponding individual, M-ligand<sub>1</sub> and M-ligand<sub>2</sub> systems and superimposition of the titration curves. In the titration of metal ion-mixed ligand system against standard sodium hydroxide solution, most probable equilibria may be concluded from a comparison of shapes and positions of the titration curves and superimposing the 1:1:1 mixed ligand titration curves on the titration curves of 1:1 M-L and M-L' systems. The stability constant ( $K_{MLL'}$ ) of the mixed complex (MLL') may then be calculated either by method I (stepwise) or method II (simultaneous).

*Method I (for stepwise equilibria)*—The formation of the mixed complex MLL' by two successive steps may be simply compared to the formation of 1:2 complex,  $ML_2$  and hence a general equation for the stability constant  $K_{MLL'}$  of the mixed complex formed by successive equilibria may be derived by replacing  $M(=L)$  by  $ML$  or  $ML'$  in the equation

$$K_{ML} = \frac{\{T_M - ([L].X)\}}{([L]^2.X)}$$

TABLE 1 — EQUATIONS FOR THE CALCULATION OF STABILITY CONSTANTS FOR MIXED COMPLEXES

System	Stability constants	( $T_M = T_L = T_{L'} = T_{L''}$ )	X =
MONOBASIC ACIDS			
Type (1)	$K_{MLL'} = \frac{(T_M - (\frac{1}{2})[A] \cdot X)}{(\frac{1}{2})^2 [A]^2 \cdot X}$	$\frac{2T_M + P - T_{OH} - [H^+]}{2[H^+]} \cdot \frac{1}{K_1 + K_1'}$	$1 + \frac{2[H^+]}{K_1 + K_1'}$
Type (2)	$K_{MLL'L''} = \frac{(T_M - (\frac{1}{3})[A] \cdot X)}{(\frac{1}{3})^3 [A]^3 \cdot X}$	$\frac{3T_M + P - T_{OH} - [H^+]}{3[H^+]} \cdot \frac{1}{K_1 + K_1' + K_1''}$	$1 + \frac{3[H^+]}{K_1 + K_1' + K_1''}$
DIBASIC ACIDS			
Type (1)	$K_{MLL'} = \frac{(T_M - (\frac{1}{2})[A] \cdot X)}{(\frac{1}{2})^2 [A]^2 \cdot X}$	$\frac{4T_M + P - T_{OH} - [H^+]}{2[H^+]} \cdot \frac{1}{(K_2 + K_2') + (K_1 K_2) + (K_1' K_2')}$	$1 + \frac{2[H^+]}{(K_2 + K_2')} + \frac{2[H^+]^2}{(K_1 K_2) + (K_1' K_2')}$
Type (2)	$K_{MLL'L''} = \frac{(T_M - (\frac{1}{3})[A] \cdot X)}{(\frac{1}{3})^3 [A]^3 \cdot X}$	$\frac{6T_M + P - T_{OH} - [H^+]}{3[H^+]} \cdot \frac{1}{(K_2 + K_2' + K_2'') + (K_1 K_2) + (K_1' K_2') + (K_1'' K_2'')}$	$1 + \frac{3[H^+]}{(K_2 + K_2' + K_2'')} + \frac{3[H^+]^2}{(K_1 K_2) + (K_1' K_2') + (K_1'' K_2'')}$
MONOBASIC + DIBASIC ACIDS			
Type (1) metal ion-mono-basic-dibasic acid	$K_{MLL'} = \frac{(T_M - (\frac{1}{2})[A] \cdot X)}{(\frac{1}{2})^2 [A]^2 \cdot X}$	$\frac{3T_M + P - T_{OH} - [H^+]}{2[H^+]} \cdot \frac{1}{K_2 + K_1' + \frac{2[H^+]^2}{K_1 K_2}}$	$1 + \frac{2[H^+]}{K_2 + K_1'} + \frac{[H^+]^2}{K_1 K_2}$
Type (2) metal ion-mono-basic-mono-basic-dibasic acids	$K_{MLL'L''} = \frac{(T_M - (\frac{1}{3})[A] \cdot X)}{(\frac{1}{3})^3 [A]^3 \cdot X}$	$\frac{4T_M + P - T_{OH} - [H^+]}{3[H^+]} \cdot \frac{1}{(K_2 + K_1' + K_1'') + \frac{2[H^+]^2}{K_1 K_2}}$	$1 + \frac{3[H^+]}{K_2 + K_1' + K_1''} + \frac{[H^+]^2}{K_1 K_2}$
Type (2) metal ion-mono-basic-dibasic-dibasic acids	$K_{MLL'L''} = \frac{(T_M - (\frac{1}{3})[A] \cdot X)}{(\frac{1}{3})^3 [A]^3 \cdot X}$	$\frac{5T_M + P - T_{OH} - [H^+]}{3[H^+]} \cdot \frac{1}{K_2 + K_2' + K_1'' + \frac{4[H^+]^2}{(K_1 K_2) + (K_1' K_2')}}}$	$1 + \frac{3[H^+]}{K_2 + K_2' + K_1''} + \frac{2[H^+]^2}{(K_1 K_2) + (K_1' K_2')}$

$K_1, K_1', K_1''$  = dissociation constants of the three monobasic acids respectively (I).

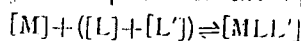
$K_1, K_2, K_1', K_2'$  and  $K_1'', K_2''$  = first and second dissociation constants of three dibasic acids respectively (II).

$K_1, K_1''$  = dissociation constants of monobasic acids,  $K_1, K_2'$  and  $K_1', K_2''$  = first and second dissociation constants of the two dibasic acids respectively.

where  $T_M = [\text{metal ion}]_{\text{total}}$ ,  $[L] = [\text{free ligand}]$  and

$$X = \frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1.$$

**Method 11 (simultaneous equilibria)**—Single ligand systems forming only 1:1 complexes with metal ions seem to be ideal for mixed ligand studies<sup>1,2</sup>. The stability constant ( $K_{MLL'}$ ) may be calculated without the knowledge of individual stepwise stability constants, ( $K_{ML}$ ) or ( $K_{ML'}$ ). That  $[L] = [L']$  is a necessary assumption for the equilibrium



where  $([L] + [L']) = [A]$ , total free ligand concentration and  $[MLL'] = (T_L + T_{L'}) - ([A] \cdot X)$ .

For a system of metal ion-dibasic acid (1)—dibasic acid (2)

$$[MLL'] = T_M - \left\{ \frac{1}{2} \right\} [A] \cdot X \quad (\because T_M = T_L = T_{L'}) \quad \dots(1)$$

$$T_M = 2[H_2L] + 2[H_2L'] + [HL] + [HL'] + [H^+] \quad \dots(2)$$

where  $T_L = [\text{ligand}]_{\text{total}}$  and  $T_{L'} = [\text{ligand}]_{\text{total}}$

$$(2T_L + 2T_{L'}) + P - T_{OH} - [H^+] = 2[H_2L] + 2[H_2L'] + [HL] + [HL'] \quad \dots(3)$$

$P = \text{Initial } [HClO_4]$ ; and  $T_{OH} = [NaOH]$

$\therefore [L] = [L']$ ;  $[H_2L] = [H_2L']$  and  $([L] + [L']) = [A]$ ,

$$K_1 K_2 + K_1' K_2' = \frac{2[H^+]^2[L]}{[H_2L]} = \frac{[H^+]^2[A]}{[H_2L]} \quad \dots(4)$$

Now substituting (4) into (3) and rearranging yields (5)

$$[A] = \frac{(2T_L + 2T_{L'}) + P - T_{OH} - [H^+]}{\frac{4[H^+]^2}{K_1 K_2 + K_1' K_2'} + \frac{2[H^+]}{K_2 + K_2'}} \quad \dots(5)$$

where  $2T_L + 2T_{L'} = 4T_M$

$$K_{MLL'} = \frac{T_M - \left\{ \frac{1}{2} \right\} [A] \cdot X}{\left\{ \frac{1}{2} \right\} [A]^2 \cdot X}$$

if

$$X = 1 + \frac{2[H^+]^2}{K_1 K_2 + K_1' K_2'} + \frac{2[H^+]}{K_2 + K_2'}$$

and

$$\frac{[M]}{X} = [L] = [L'] = \frac{1}{2}[A]$$

Similarly, equations for the stability constants of 1:1:1:1 mixed [metal ion-ligand (1)-ligand(2)-ligand (3)] complexes as well as for various combinations of monobasic and dibasic acids are derived and given in Table 1. The validity of the assumption of equilibria and consequent equations used for the evaluation of stability constants for the mixed complexes proposed by us for the first time (both two ligands as well as three ligand systems) is attested by the constancy in the stability values calculated over a wide range of pH for the systems studied by us and reported earlier<sup>1,2</sup>. Of course other experimental observations such as shift in the precipitation points of the mixed systems compared to those of individual systems and intensification of the colour of the solution were direct evidences for the formation of the mixed complex.

#### References

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