

**Host-guest interaction between cyclen based macrotricyclic ligands and phosphate anions. A potentiometric investigation.**

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**Electronic Supplementary Material.**

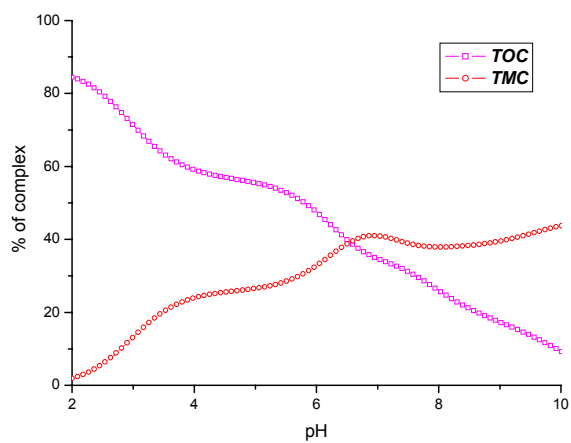
### (Macrotricycles : Orthophosphate) systems

Logarithm recognition constants,  $\log K_{alh}$ ,

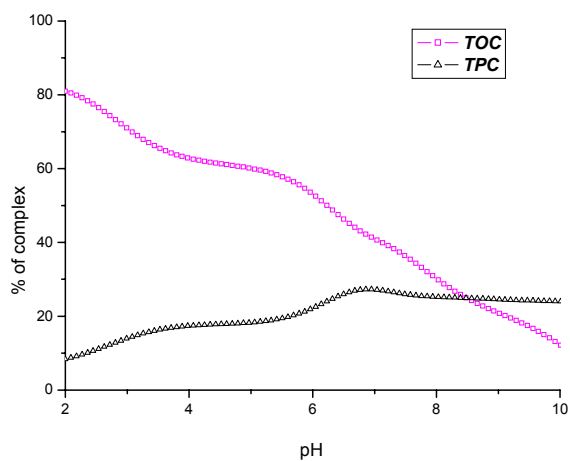
orthophosphate	<i>TOC</i>	<i>TMC</i>	<i>TPC</i>
A+L+2H=ALH <sub>2</sub>	24,35	24,43	24,14
AH+LH=ALH <sub>2</sub>		2,82	3,37
A+L+3H=ALH <sub>3</sub>	33,44(9,09)	33,06 (8,62)	32,84(8,70)
AH+LH <sub>2</sub> =ALH <sub>3</sub>		2,98	3,37
A+L+4H=ALH <sub>4</sub>	41,48(8,04)	40,59 (7,53)	40,4(7,56)
AH+LH <sub>3</sub> =ALH <sub>4</sub>		3,59	3,64
A+L+5H=ALH <sub>5</sub>	48,24(6,76)	47,82 (7,23)	47,42(7,02)
AH+LH <sub>4</sub> =ALH <sub>5</sub>			4,02
AH <sub>2</sub> +LH <sub>3</sub> =ALH <sub>5</sub>		3,60	
A+L+6H=ALH <sub>6</sub>	54,74(6,5)	53,92 (6,10)	53,54(6,12)
AH <sub>2</sub> +LH <sub>4</sub> =ALH <sub>6</sub>		3,94	3,37
A+L+7H=ALH <sub>7</sub>	57,85(3,11)		55,96(2,42)
AH <sub>2</sub> +LH <sub>5</sub> =ALH <sub>7</sub>		4,92	3,17

$I = 0,1 \text{ M (NaCl)} ; T = 298 \text{ K}$

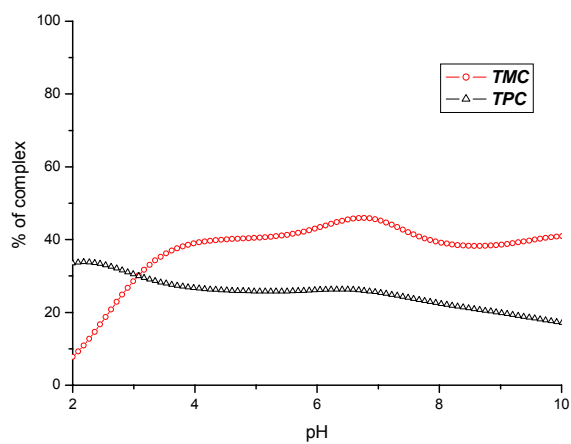
### Competition systems between two ligands for orthophosphate



(a)



(b)



(c)

(a) *TMC : TOC*

(b) *TOC : TPC*

(c) *TMC : TPC*

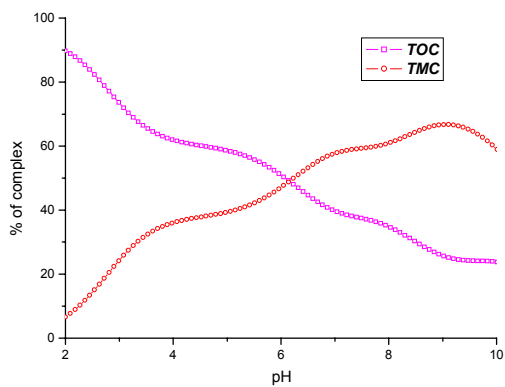
## (Macrotricyclic : pyrophosphate) systems

Logarithm recognition constants,  $\log K_{alh}$ ,

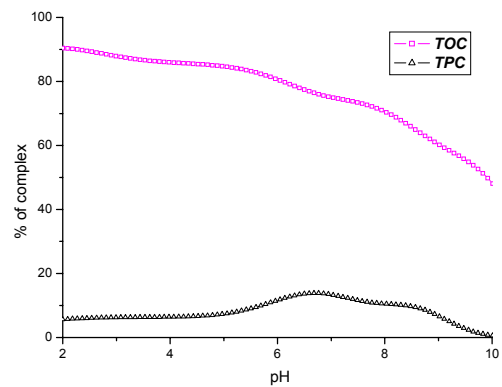
pyrophosphate	TOC	TMC	TPC
A+L+H = ALH	13.86	14,33(9,50)	
A+LH = ALH	3,72	4,66	
A+L+2H=ALH <sub>2</sub>	23.04(9,18)	23,24(8,91)	21,56)
A+LH <sub>2</sub> =ALH <sub>2</sub>	3,97	4,82	3,14
A+L+3H=ALH <sub>3</sub>	31.81(8,77)	31,38(8,14)	29,74(8,18)
AH+LH <sub>2</sub> =ALH <sub>3</sub>	4,39	4,73	2,97
A+L+4H=ALH <sub>4</sub>	39.38(7,57)	38,9(7,52)	37,33(7,59)
AH+LH <sub>3</sub> =ALH <sub>4</sub>	4,53	4,99	3,27
A+L+5H=ALH <sub>5</sub>	46.13(6,75)	45,72(6,82)	44,3(6,97)
AH+LH <sub>4</sub> =ALH <sub>5</sub>	5,12	4,96	3,63
A+L+6H=ALH <sub>6</sub>	51.99(5,86)	51,35(5,63)	49,70(5,40)
AH <sub>2</sub> +LH <sub>4</sub> =ALH <sub>6</sub>	4,93	4,54	2,98
A+L+7H=ALH <sub>7</sub>	54.91(2,92)		52,48(2,78)
AH <sub>2</sub> +LH <sub>5</sub> =ALH <sub>7</sub>	5,72		3,43

$I = 0,1 \text{ M (NaCl)} ; T = 298 \text{ K}$

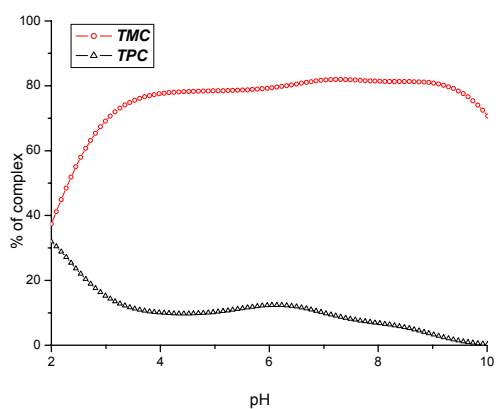
### Competition systems between two ligands for pyrophosphate



(a)



(b)



(c)

(a) *TMC* : *TOC*

(b) *TOC* : *TPC*

(c) *TMC* : *TPC*

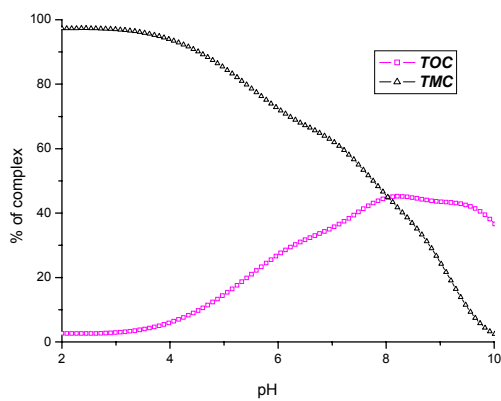
## (Macrotricycles : triphosphate) systems

Logarithm recognition constants,  $\log K_{alh}$ ,

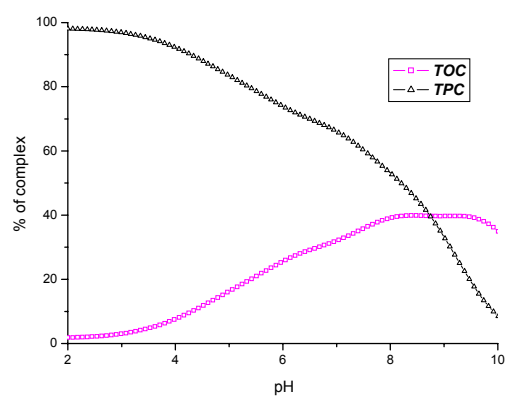
Triphosphate	<i>TOC</i>	<i>TMC</i>	<i>TPC</i>
A+L+H = ALH	13,58		12,45
A+LH = ALH		3,44	2,68
A+L+2H=ALH <sub>2</sub>	22,73(9,15)	22,05	22,31(9,86)
A+LH <sub>2</sub> =ALH <sub>2</sub>		3,66	3,89
A+L+3H=ALH <sub>3</sub>	31,39(8,66)	30,46(8,41)	30,89(8,58)
AH+LH <sub>2</sub> =ALH <sub>3</sub>		4,34	4,49
A+L+4H=ALH <sub>4</sub>	38,94(7,55)	38,43(7,97)	38,74(7,85)
AH+LH <sub>3</sub> =ALH <sub>4</sub>		4,46	5,05
A+L+5H=ALH <sub>5</sub>	45,86(6,92)	45,68(7,25)	45,89(7,15)
AH+LH <sub>4</sub> =ALH <sub>5</sub>		5,22	5,59
A+L+6H=ALH <sub>6</sub>	51,32(5,46)	52,28(6,60)	52,27(6,38)
AH <sub>2</sub> +LH <sub>4</sub> =ALH <sub>6</sub>		4,94	6,23
A+L+7H=ALH <sub>7</sub>	53,75(2,43)	57,49(5,21)	57,11(4,84)
AH <sub>2</sub> +LH <sub>5</sub> =ALH <sub>7</sub>		5,24	8,74
A+L+8H=ALH <sub>8</sub>			
A+LH <sub>2</sub> =ALH <sub>8</sub>			

$I = 0,1 \text{ M (NaCl)} ; T = 298 \text{ °K}$

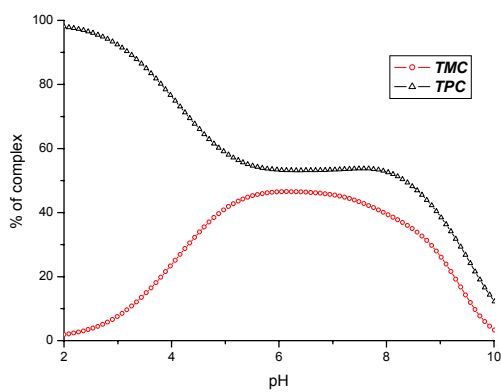
### Competition systems between two ligands for triphosphate



(a)



(b)



(c)

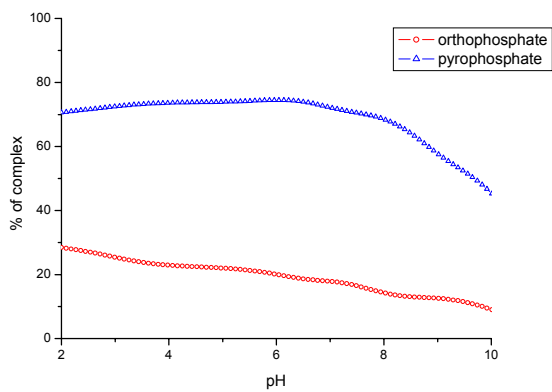
(a) *TMC* : *TOC*

(b) *TOC* : *TPC*

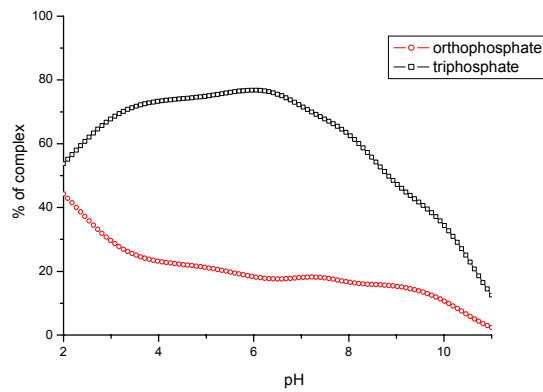
(c) *TMC* : *TPC*

## Macrotricycles selectivity

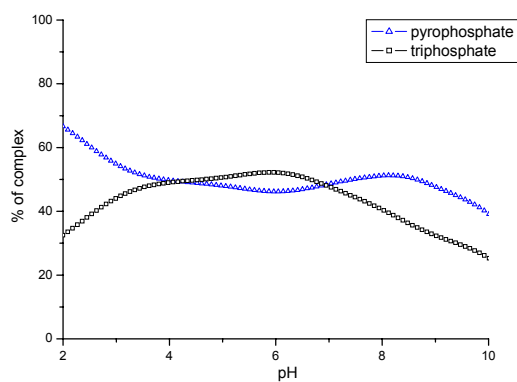
• **TOC**



(a)



(b)



(c)

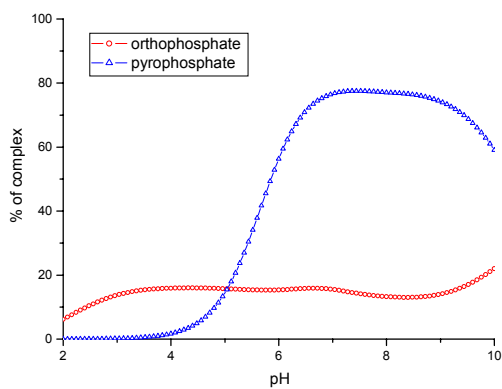
(a) orthophosphate : pyrophosphate

(b) orthophosphate : triphosphate

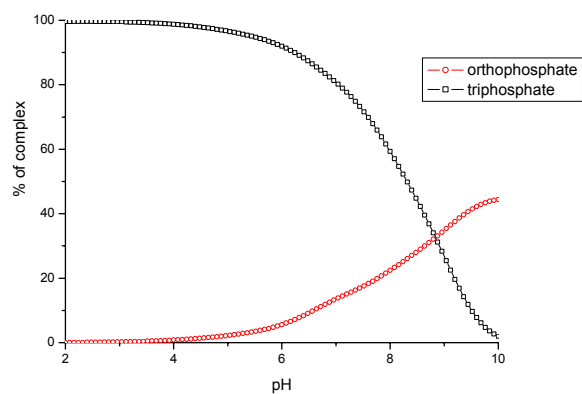
(c) pyrophosphate : triphosphate



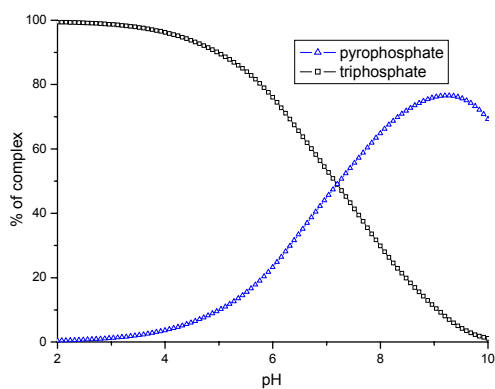
• **TMC**



**(a)**



**(b)**



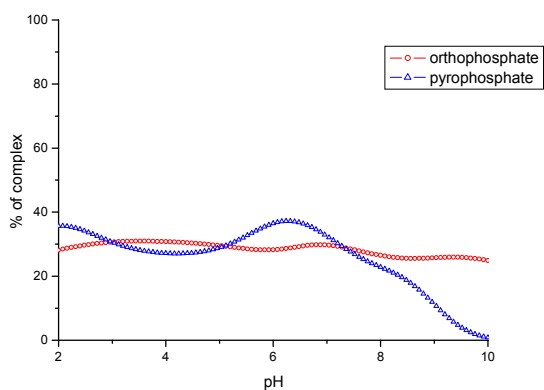
**(c)**

**(a) orthophosphate : pyrophosphate**

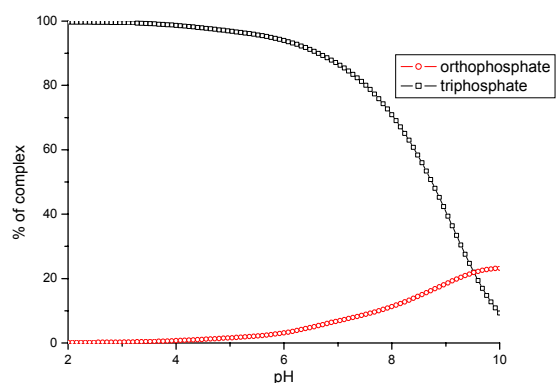
**(b) orthophosphate : triphosphate**

**(c) pyrophosphate : triphosphate**

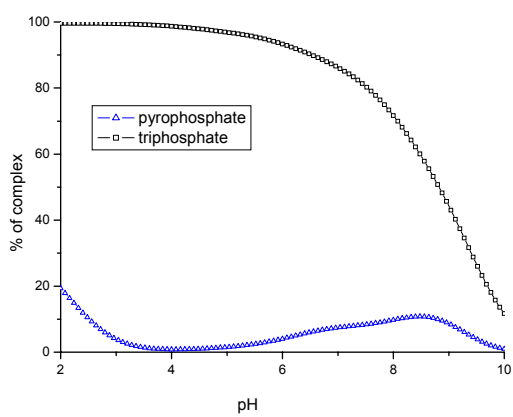
• **TPC**



**(a)**



**(b)**



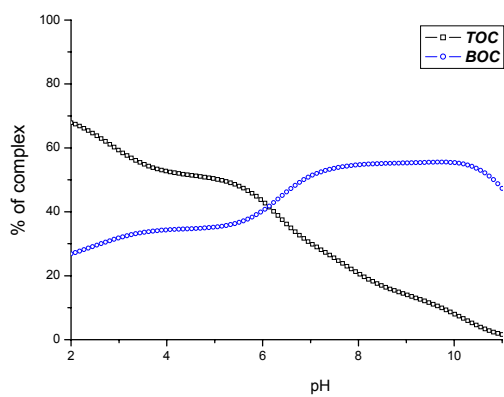
**(c)**

**(a) orthophosphate : pyrophosphate**

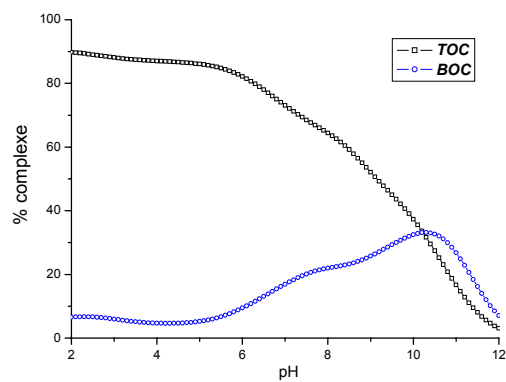
**(b) orthophosphate : triphosphate**

**(c) pyrophosphate : triphosphate**

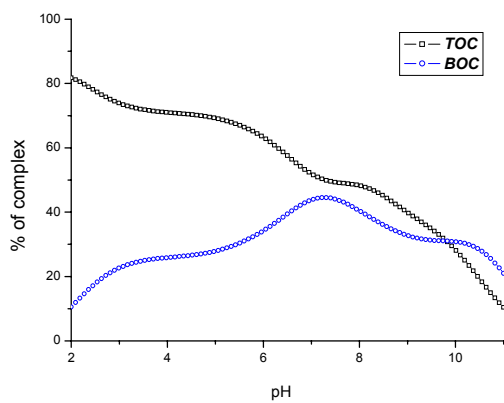
## Competition: bismacrocycles / macrotricycles



(a)

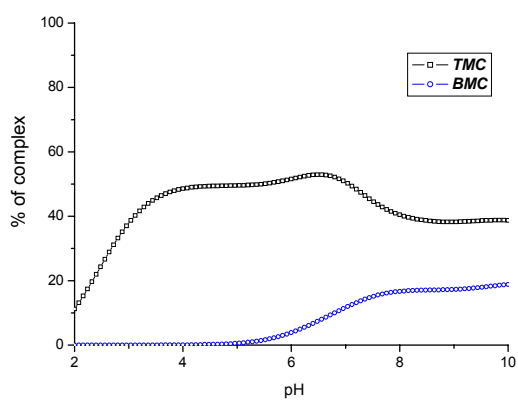


(b)

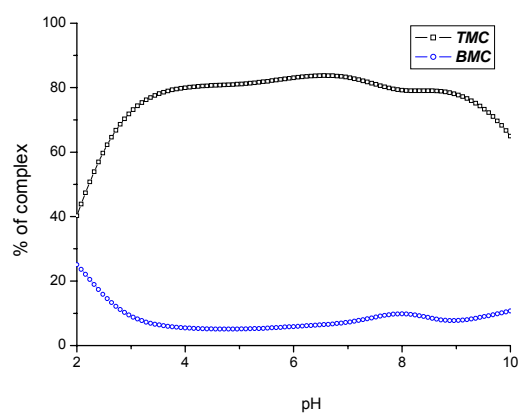


(c)

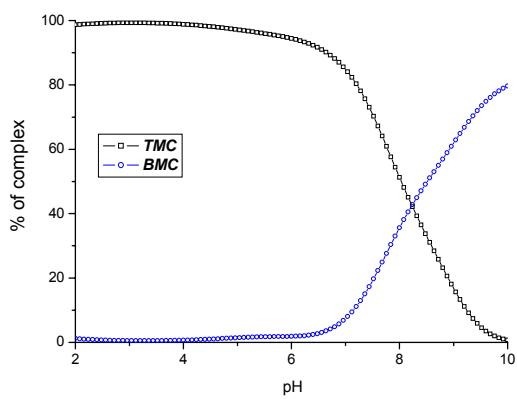
**BOC : TOC / (a) orthophosphate ; (b) pyrophosphate (c) triphosphate**



(a)

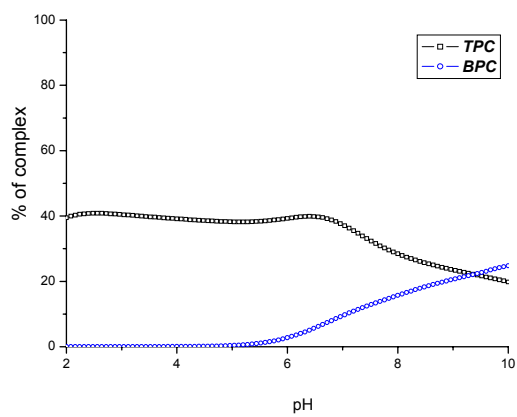


(b)

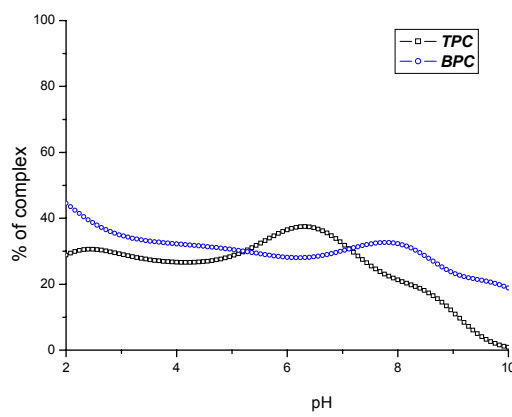


(c)

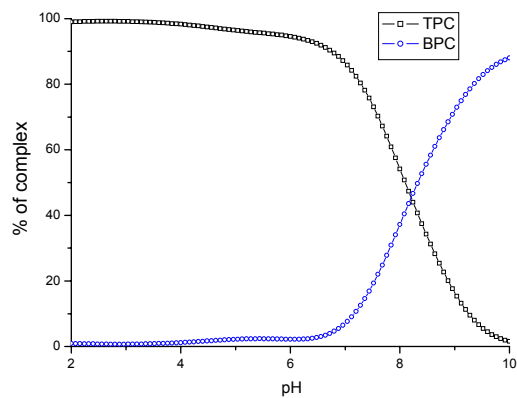
*BMC* : *TMC* / (a) orthophosphate ; (b) pyrophosphate (c) triphosphate



(a)



(b)



(c)

*BPC : TPC* / (a) orthophosphate ; (b) pyrophosphate (c) triphosphate