Experiment: Study of a complex ion equilibrium

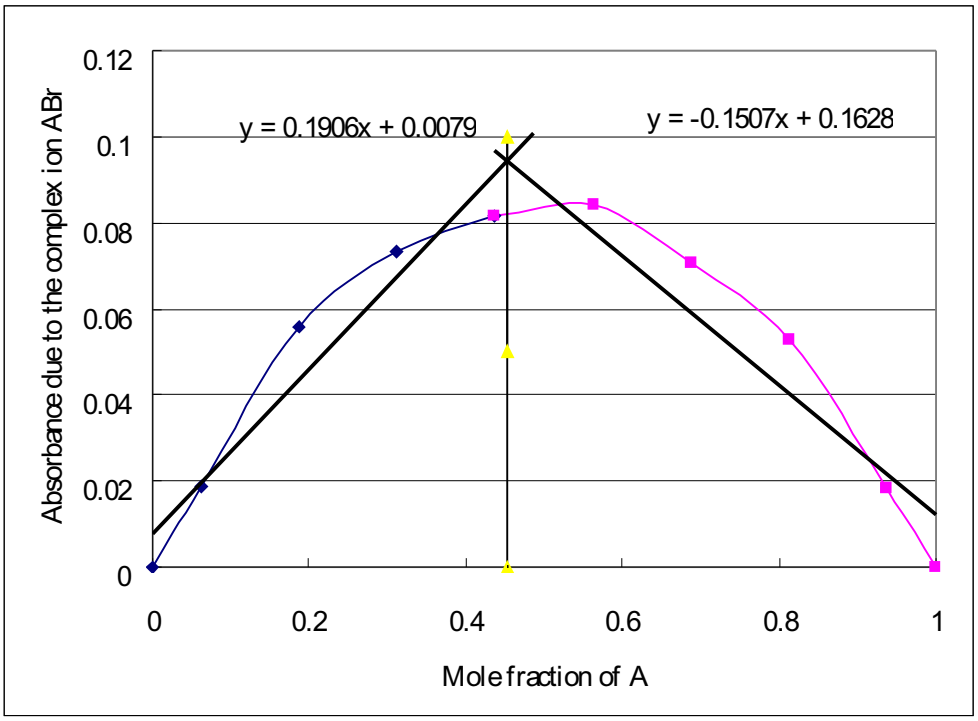
Aim: To determine the formula and formation constant of iron (III) thiocyanate ion by sprectrophotometry

Procedure:

Please refer to the lab manual

Result:

solution number	1	2	3	4	5	6	7	8	9	10
volume of solution A used /mL	0	1	3	5	7	9	11	13	15	16
$i = [A]_{initial}$ / M	0	0.00012	0.00036	0.0006	0.00084	0.00108	0.00132	0.00156	0.0018	0.00192
Total absorbance	0	0.019	0.057	0.075	0.084	0.087	0.074	0.057	0.023	0.005
Absorbance due to Fe^{3+} (A_{10} . V_p/V_{10})	0	0.0003125	0.0009375	0.0015625	0.0021875	0.0028125	0.0034375	0.0040625	0.0046875	0.005
Absorbance due to the complex ion AB_n	0	0.0186875	0.0560625	0.0734375	0.0818125	0.0841875	0.0705625	0.0529375	0.0183125	0
mole fraction of A	0	0.0625	0.1875	0.3125	0.4375	0.5625	0.6875	0.8125	0.9375	1
$y = [AB_n]$ / M	0	0.00012	0.00036	0.0004716	0.0005254	0.0005406	0.0004531	0.0003399	0.0001176	0
value of *K*	-	-	3.893E+12	4327.8564	3010.2702	3347.4912	3558.3531	13884.485	29025.856	-



Calculations:

Concentration of solution A = $[A]_{in}$ = 0.003M

Concentration of solution B = $[B]_{in}$ = 0.003M

Let the initial concentration of A be i,

the initial concentration of B be c-i.

the concentration of AB_n be y when equilibrium is established

$$A + nB \rightarrow AB_n$$

$$[AB_n]_{eq} = y$$

$$[A]_{eq} = i-y$$

$[B]_{eq} = c\text{-}i\text{-}ny$

Equilibrium constant $K = y/ [(i\text{-}y)(c\text{-}i\text{-}ny)^n]$

Taking solution number 3 for full calculation

Initial concentration of A (i) = $[A]_{soln\ 3}$ × vol of A in soln. 3 / total volume of soln

$= 0.003 \times 3/25$

$= 3.6 \times 10^{-4}$ M

Total absorbance for solution 3 = A(total) = 0.057A

Absorbance due to Fe^{3+} = Total absorbance of solution 10 ×3/16

$= 0.00\ 5 \times 3/16$

$= 9.375 \times 10^{-4}A$

Absorbance due to the complex ion AB_n = A(total) – $A(Fe^{3+})$

$= 0.0\ 57 - 9.375 \times 10^{-4}$

$= 0.0\ 5606A$

Mole fraction of A in solution 3 = $M_AV_A / (M_BV_B + M_AV_A)$

$= 0.003 \times 3 / (0.003 \times 13 + 0.003 \times 3)$

$= 3/16$

$= 0.1875$

From the graph of absorbance against mole fraction,

Maximum occurs at mole fraction of A:

$$i_{max}/c = X_{max} = 0.4538 = 1/(n+1)$$

$$n = 1.2036$$

$$n \sim 1$$

Therefore, the formula of the complex is $Fe(NCS)^{2+}$

Assume that Fe^{3+} in solution 2 goes to complete ion in this case, due to large excess of ligands:

By Beer's Law,

$y = [AB_n]_{eq} = 0.003 \times 1/25$

$= 1.2 \times 10^{-4}$ M

b = 1cm

$\varepsilon = A/yb$

$= 0.019/1.2 \times 10^{-4}$

$= 158.3333 \text{ mol}^{-1}\text{dm}^3\text{cm}^{-1}$

For solution 3,

$y = A/\varepsilon b$

$= 0.056/158.33$

$= 3.5368 \times 10^{-4} M$

$c = i/ X$

$= 3.6 \times 10^{-4}/0.1875$

$= 1.92 \times 10^{-3} M$

$K = y / [(i-y)(c-i-ny)^n]$

$= 3.5368 \times 10^{-4} / (3.6 \times 10^{-4} - 3.5368 \times 10^{-4})(1.92 \times 10^{-3} - 3.6 \times 10^{-4} - 3.536 \times 10^{-4})$

$= 46390.6968 mol^{-1}dm^3$ (rejected)

The 3rd, 8th and 9th value of the K is also rejected sinc e it is too large compared with the other data.

The mean of K is $3561.00 mol^{-1}dm^3cm^{-1}$ and the standard deviation of K is $558.86 mol^{-1}dm^3cm^{-1}$