Stability constants of Iron (II) and lead (II) complexes of anthranillic and sulphanillic acids

*** Yahya Abdul Majid**

Date of acceptance 12/3/2006

Abstract :

Stability constant of complexes formed by Fe^{++} and Pb^{++} ions with Anthranillic acids And sulphanillic acids were established . Results which are obtained indicated that instability of metal ion complexs are in harmony with the ease of disociation of the acids involved.

Overall Enthalpy and Entropy of complex formation were calculated from stability constant measurements at different temperatures, Also experimental results showed that metal ion complex formations with Anthranillic acid are exothermic while those of sulphanillic acid are endothermic.

Introduction

Anthranillic acid or (O – amino benzoic acid) is known to be weaker acid than benzoic acid and a stronger acid than glycine (1). However, metal ion complexes are known for the former (2) and for the later acids (3).

Sulphanillic acid or (P – aminobenzoene sulphonic acid) is less versatil in analytical chemistry than anthranillic acid . It is known to form complexes with silver ions (4) and some lanthanide ions (5).

Preliminary investigations on Anthranillic and sulphanillic metal ion complexes have been made in our laboratory and in all cases a lowering of pH values accompanying the resulting solutions, which in some cases a colour change occur . These observations are clear cases of complex ion formations in solution (6) and these require through investigations.

Experimental

Reagents:-

Standard solutions of lead Nitrate and ferrous sulphates were prepared from B.D.H. Analar grade qualities .

Freshly prepared solutions of Anthranillic acid ,sulphanillic acid and potassium hydroxide were made from AR grades .All solutions were made with deionized waters and the carbonate free alkali solutions were standaredized against pure potassium hydrogen phthalate(7).

Apparatus: -

pH measurements were made using practirionic pH –meter equiped with glass electrode and saturated silver –silver chloride electrode, The pH meter was standardized befor each run against Buffer solutions of known pH values and was checked at the end of each run . The titrant was delivered from a semi micro burette and the pH values recorded as soon as it becomes steady.

---

* Prof. Dr. Chemistry department , college of science for women University of Baghdad

Results:-

Re investigation of the acid dissociation constant of Anthranillic and sulphanillic acids at different temperatures were made , as can be seen in tables (1,2,3) and figure (1).

Representative titration of mixtures of acids and Metal ions with alkali solution are listed in tables (4, 5, 6, 7).

Calculations of chelate formation constants were made according to J. Bjerum' s summation equation (8) and explained fully in previous papers (5,7). Typically results are summarized in table (7) and table (8)

The Logarithm of overall stability constants of complexes are ploted against reciprocal absolute temperature as it can be seen in figure (2),from which thermodynamic properties of the reaction involved are calculated . Results are shown in table (9).

Discussion

Anthranillic acid and sulphanillic acid are bidentate chelating ligands ,each of which with one electron releasing and one anionic site , they may form 1:1 ,1:2 and 1:3 complexxes in solution with metal ions , they could form complexes with Pb $^{++}$ and Fe^{++} ions according to the following equations:

$$M^{2+} + L^{-} \longleftrightarrow (ML)^{+}$$

$$(ML)^{+} + L^{+} \longleftrightarrow (ML_2)$$

$$(ML_2) + L^{-} \longleftrightarrow (ML_3)^{-}$$

Where M^{2+} represents Pb $^{++}$ and Fe^{++} ions , L- represents Anthranilliate or sulphanillate ions .

Evalution of chelate stability requires comparison of the acid dissociation constants of the chelating reagents .

Acid dissociation constants are listed in table (3) indicate a very high order of stability for chelates of Anthranillic acid , they are greater than those of sulphanillic acid . Since , according to Calvin and Wilson (9) , the force holding a hydrogen ion to a moloule are a similar to those that will hold a metal ion to the same molcuale . The High stability of chelates of Anthranillic acid can be explained by the high basicity of its functional groups , Also in accord with Calvin and Wilson . the low stabilities of chelates of sulphanillic acid could well be associated with its high acid dissociation constant ,(PK_{Av} = 4 .52).

High stability of Anthranillic acid complexes could be attributed to ease of chelate formation ., since the two functional groups (- NH_2 - and –cooH) are not far from each other forming six membered ring structure with metal ion , while the functional groups (- NH_2 - and –SO_3H) in sulphanillic acid are far from each other forming eight membered ring structure chelate with metal ions which is of low stability .the general ligand metal complex stability order being Anthranillic acid > sulphanillic acid .

The stability sequence for metal ion studied with Anthranillic acid and sulphanillic acid as ligands has been shown to be in perfect agreement with those of E. D.T. A (10) and sebacic acid as ligands , The general metal complex stability oder being Fe^{++} > Pb $^{++}$.

Effect of Temperature on dissociation of the acids

When a reaction is an endothermic one , that is if Δ H is positive , its equilibrium constant increases as temperature increase.

From the point of Lechate lier ' s principale , an increase of temperature is astress that is partially relived by the occurrence of a net reaction that proceeds with absorption of heat by the system.

In the present problem , temperature rise affect dissociation of the acids . Results are shown in table (2) and fig (1) .

The enthalpy of reaction was determind from Vant's Hoff plot of Log K against $\frac{1}{T}$ and it was found to be (17:16 and 4. 12) K.cal/mol for Anthranillic acid and sulphanillic acid resprectively .

The over all change in entropy of dissocation was calculated for these acids from the following thermodynamic functions and were found to be (-17 . 00 and -13. 52)cal/deg for Anthranillic acid and sulphanillic acid reprectively .

Fom thermodynamics ;

$\Delta G = -RT \ln k$ ....(1)

And $\Delta G = \Delta H - T\Delta S$ ....(2)

Where ΔG , ΔH and ΔS are the change s in free energy , enthalpy and entropy of reaction respectively , k being the stability constant .

Negative enthalpy change observed in these dissociations of the acids at high temperatures , and more water molecules were captured by the hydrogen ions that set free during ionization of the acids.

Effect of Temperature on stability of complexes

Vant's Hoff plots between Log β_3 against 1/T for all complex Systems studied give an overall Enthalpies of complex formation . Applying equation (1) and (2) to these systems , an overall entropy changes are obtained .

Results presented in table (9) and figure (2) indicate clearly that complex formation reaction involving anthranilliate ions are allwayes exothermic , while complex formation reaction with sulphanilliate ions are allways endothermic . Also a decreased in entropies were found with the first system while an increase in entropies were found with the latter system.

Hard – soft Interactions

The relationship between stability constant of complexs and the characteristic properities of their constants were established by pearson $^{(12)}$, he forwarded the interpretation of hard interaction as electosatic and soft one as covalent , parallels the two parameter system of Drago and wayland $^{(13)}$ for Lewis acid –base interactions. Such an interpretation Led Misono $^{(14)}$ to the development of an analogous system for coordination compounds.

$PK = -\text{Log} = \alpha X + \beta Y + \gamma$ ....(3)

Where K is the "instability constant" of the complex ,(X) and (Y) are parameter of the metal ion , and (α) and (β) those of the ligand .The parameter (γ) is characteristic of the ligand and is used to adjust the PK 'S ,so that all lie on the same scale . This equation provides an insight into the nature of the bonding between acids and bases . The (Y) parameter is considered to be a measure of softness : hard ion have values below 2 .8 , soft ions have values greater than 3 .2 and border lines species are (2.8 -3.2) .

The analogous ligand parameter (β) ,like wise show the expected increase in value from hard to soft species .

Softness parameter (Y) for ions under consideration have values of 5 .321 , and 4.361 for Pb $^{++}$ and Fe^{++} ions respectively , indicating that Fe^{++} ion is more hard acid than Pb^{++} which is a border line species .

The analogous parameter (β) for the two acids (as ligands) be under investigation can be seen from table (10) show an increase in value from hard base (i .e Anthranillic with $\beta = -0.564$) to a less hard base (i.e sulphanillic-with $\beta = +0.178$).

The (α)and (X) parameters were interpretated by Misono as hardness.

Table (1)

Acid dissociation constant of sulphanillic acid at 30°c

15 ml 0.05 Msulphanillic acid +32.5 ml distilled water

Temp = 30°c , [KOH] = 0.1 M

1	2	3	4	5	6	7	8
Ml KOH 0.1 M	*PH*	Stoicheometric concentrations		POH=14-PH $[OH^-]$	$\frac{[BH^+]+[OH^-]}{[B]-[OH^-]}$	Log_{10} colomn 6	Pka=PH+ COLOUMN 7
		$[BH^+]$	*[B]*				
0.00	2.83	0.0158	0	-	-	-	-
0.05	2.86	0.01462	1.041×10^{-3}	7.244×10^{-12}	14.044	1.1474	4.0074
1.00	2.94	0.01344	2.0618×10^{-3}	8.709×10^{-12}	6.562	0.817	3.757
1.50	3.00	0.01228	3.0612×10^{-3}	1×10^{-11}	4.0114	0.6033	3.603
2.00	3.06	0.011148	4.04×10^{-3}	1.1481×10^{-11}	2.759	0.4408	3.5008
2.50	3.13	0.010036	5.0×10^{-3}	1034×10^{-11}	2.007	0.3026	3.4326
3.00	3.12	0.008947	5.94×10^{-3}	1.621×10^{-11}	1.5062	0.17789	3.3878
3.50	3.31	0.00788	6.862×10^{-3}	2.047×10^{-11}	1.4466	0.1603	3.470
4.00	3.44	0.0681	7.767×10^{-3}	2.754×10^{-11}	0.86778	-0.0571	3.382
4.50	3.58	0.00580	80653×10^{-3}	3.9019×10^{-11}	0.6703	-0.1737	3.406

PKa Average = 3.5488

$Ka = 2.826 \times 10^{-4}$

Table (2)

Variation of acid dissociation constant with temperature

Anthranillic acid

Temp	$\frac{1}{T}$	Ka
25	3.35×10^{-3}	1.076×10^{-7}
30	3.30×10^{-3}	2.0×10^{-7}
35	3.24×10^{-3}	2044×10^{7}
38	3.21×10^{-3}	3.28×10^{7}
40	3.19×10^{-3}	3.98×10^{-7}
42	3.17×10^{-3}	4075×10^{-7}

Sulphanillic acid

Temp	$\frac{1}{T}$	Ka
24	3.36×10^{-1}	1.72×10^{-4}
30	3.30×10^{-1}	2.82×10^{-4}
35	3.24×10^{-3}	2.29×10^{-4}
38	3.21×10^{-3}	2.63×10^{-4}
40	3.19×10^{-3}	2.63×10^{-4}

Table (3)

Acid dissociation constants

Acid	Temp °c	PKNH	PK_{COOH}	PK_{SO_3H}	$PK_{Average}$
Anthranillic acid	30	7.24	6.07	-	6.97
Sulphanillic acid	30	5.48	-	3.55	4.52

Table (4)

Titration of 0.015 M Anthranillic acid and 0.005M $Pb(NO_3)_2$ solution with standard KOH solution at different temperatures

Ml KOH 0.1M	PH of mixtures at different temperatures				
	24 °c		*35 °c*	*38 °c*	*42 °c*
0 .00	3.37		3.50	4.33	3.00
0.5	3.50		3.66	4.52	3.22
1.0	3.68		3.83	4.67	3.43
1.5	3.84		3.98	4.86	3.59
2.0	3.99		4.13	4.93	3.76
2.5	4.13		4.26	5.14	3.91
3.0	4.22		4..33	-	4.05
3.5				-	4.18
4.0				-	4.27
4.5				-	-

Table (5)

Titration of 0.015 M sulphanillic acid and 0.005M $Pb(NO_3)_2$ solution with standard KOH solution at different temperatures

Ml KOH 0.1M	PH of mixtures at different temperatures			
	24 °c	30 °c	35 °c	38 °c
0.00	2.5	2.59	2.76	2.78
0.50	2.51	2.60	2.82	2.85
1.00	2.57	2.66	22.88	2.89
1.50	2.63	2.71	2.93	2.95
2.00	2.70	2.78	2 099	2.99
2.50	2.77	2.84	3.04	3.04
3.00	2.84	2.91	3.08	3.09
3.50	2.91	2.99	3.13	3.16
4.00	2.98	3.06	3.22	3.20
4.50	3.05	3.14	3.28	3.26

Table (6)

Titration of 0.015M Anthranillic acid with 0.005M $FeSO_4$ solution with standard KOH solution at different temperatures .

Ml KOH 0.1M	PH of mixtures at different temperatures	
	24 °c	40 °c
0.00	2.57	2.95
0.50	2.61	3.00
1.00	2.64	2.04
1.50	2.68	2.07
2.00	2.71	2.10
2.50	2.75	2.145
3.00	2.79	
3.50	2.83	
4.00	2.89	
4.50	3.94	

Table (7)

Calculation of stability constant of Fe^{++}/sulphanillate complex

15 ml sulphanillic acid (0.05 M) +5 ml Fe So_4 (0.05M) +27. 5 ml distilled water .

Temprature 24°c , Ka = 1.072×10^{-4} , PKa =3.764

Ml KOH 0.1	PH	$[L]_T$	$[M]_T$ $\times 10^{-3}$	$[KOH]_T$ $\times 10^{-3}$	$[H^+]$	$\frac{[H^+]}{Ka}$	$[L^-]$ $\times 10^{-3}$	$\bar{n}$
0.00	2.74	0.01378	5.263	0.00	1.8197×10^{-3}	10.579	1.493	-
0.50	2.77	0.015625	5.208	1.416	1.896×10^{-3}	9.873	1.492	-
1.00	2.80	0.015464	5.154	2.061	1.584×10^{-3}	9.214	1.455	0.115
1.50	2.82	0.015306	5.102	3.060	1.513×10^{-3}	8.80	1.393	0.324
2.00	2.85	0.015131	5.050	4.040	1.412×10^{-3}	8.212	1.354	0.529
2.50	2.88	0.1500	5.000	5.000	1.318×10^{-3}	7.664	1.306	0.736
3.00	2.92	0.1485	4.950	5.940	1.202×10^{-3}	6. .989	1.276	0.940
3.50	2.97	0.14705	4.807	6.862	1.071×10^{-3}	6.229	1.260	1.163
4.00	3.02	0.014563	4.762	7.766	1.954×10^{-3}	5..552	1.225	1.372
4.50	3.09	0.01442	4.717	8.693	1.812×10^{-3}	4. .725	1.213	1.584

$$\text{Log}\,[L^-] = (PH - PKa) + \text{Log}\,[\,[L]_T - [KOH]\,]$$

$$,\ \bar{n} = \frac{[L]_T - \{\frac{[H]}{Ka} + 1\}\,[L^-]}{[M]_T}$$

Table (8)
Stepwise stability constants of complexes at different temperatures

complexes	Temp °c	β_1	β_2	β_3
Pb^{++} / Anthranillate	24	$6052x10^{11}$	$2.617x10^{11}$	$7.65x10^{8}$
	35	$3.248x10^{10}$	$7.850x10^{9}$	$6.25x10^{6}$
	38	$1.651x10^{7}$	$2.249x10^{7}$	$9.37x10^{4}$
Pb/sulphanillate	24	$2.371x10^{5}$	$4.433x10^{5}$	$4.06x10^{4}$
	38	$2.673x10^{6}$	$1.677x10^{6}$	$3.90x10^{5}$
	42	$1.633x10^{6}$	$2.293x10^{6}$	$2.44x10^{6}$
Fe/Anthranillite	24	$1.604x10^{14}$	$1.123x10^{14}$	$32.90x10^{10}$
	35	$1.78x10^{12}$	-	-
	40	$2.980x10^{11}$	$6.460x10^{11}$	$1.62x10^{8}$
Fe/Sulphanillite	24	$10123x10^{6}$	$8.807x10^{5}$	$2.11x10^{4}$
	35	$1.78x10^{6}$	-	-
	40	$1093x10^{6}$	$4.375x10^{6}$	$1.45x10^{4}$

Table (9)
Thermodynamic proprieties of metal complex formations

complexes	Δ *H Kcal /mole*	Δs
Pb^{++} / Anthranillate	-133.46	-390.5
Fe^{++} /Anthranillate	-73.48	-223.3
Pb^{++}/Sulphanillite	20.00	98.6
Fe^{++} / Sulphanillite	6.00	48.6

parameters , thus (X) is closely related to the electronegativity of the ion (evaluated from the ionization energy necessary to form M^{++}) and measures the tendency of the metal ion to accept electrons from the ligand . Hardness parameter (α) for Anthranillic and sulphanillic acids presented in table (10) indicates clearly that an increase in value from hard base (i .e sulphanillic acid) to less hard base (i.e Anthranillic acid).

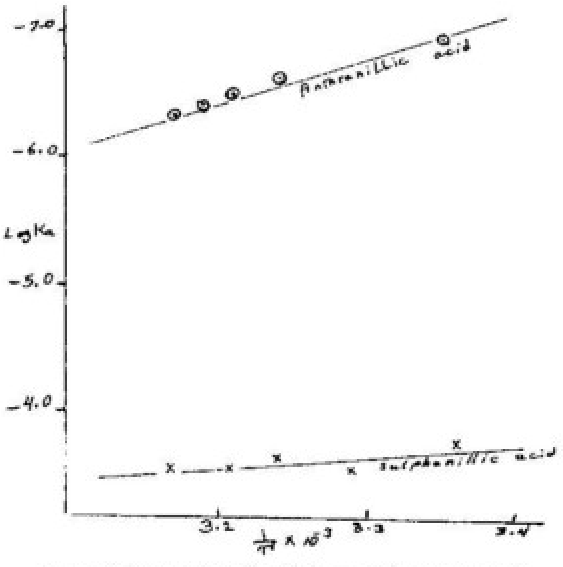
Pearson(12) has classified metal ions as hard acids and soft acids , ligand atoms such as N, O and F are hard bases and those similar to P,S and I are soft bases . The most stable complexes result from hard – hard acid-base and soft –soft acid – base combinations .

According to pearson and Ahrland (15) , acids such as Fe^{2+} and Pb^{2+} ions are border line acid species in the hardness scale , on the other hand calucations of Hadness – softness parameters of these acids and of the ligands Anthanilliate and sulphanillate ions as indicated from table (11) lead to the following results:-

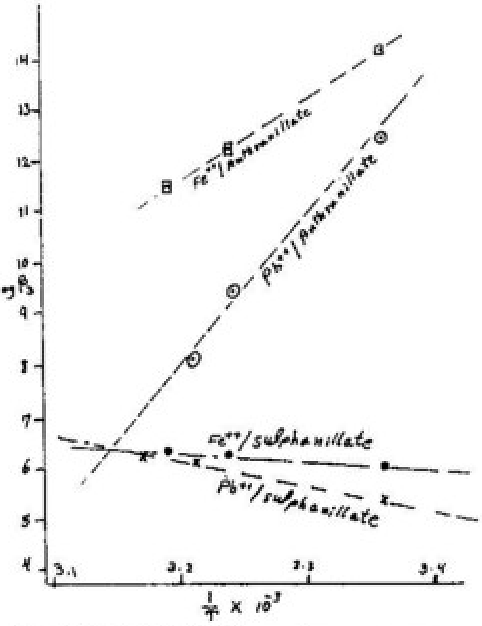
Table (10)
Meson 's Hardness – Softness parameters

Metal complex	- Log K	Metal ion		Ligand		
		X	Y	α	β	γ
Pb^{2+} - Anthranilliate	8.883	3.911	5.321	0.77	0.564	8.8
Fe^{2+} - Anthranilliate	10.462	4.361	3.135	0.770	0.564	8.8
Pr^{3+} - Anthranilliate (5)	7.514	0.90	3.65	0.77	0.564	8.8
Pb^{2+} - Sulphanilliate	4.608	3.911	5.321	0.534	0.178	1.59
Fe^{2+} - Sulphanilliate	4.324	4.361	3.135	0.534	0.178	1.59
Pr^{3+} - Sulphanilliate	2.568	0.90	3.065	0.534	0.178	1.59

1. When softness parameter (β) of the ligands are compared to each other , Anthranillate ion seem to appear harder base than sulphanilliate ion.
2. Where softness parameter (Y) of the acids (Fe^{++} and Pb^{++} ions) are compared to each other , Fe^{2+} ions appear to be harder acid than Pb^{2+} ions.
3. From the above argument one can predict Fe^{++} / Anthranillate complex to be more stable than Pb^{2+} / Anthranillate complex , a result which is in accord with pearson's rule
4. When hardness parameter (α) of the ligands is considered ,sulphanilliate ion appear to be harder base than Anthraniliate ion .
5. when hardness parameter (X) of theMetal ions is considered ,Fe^{2+} ion seem to be harder than Pb^{2+} ions .
6. From the last statements one can predict Fe^{++} /sulphanilliate complex to be more stable than Pb^{2+} /sulphanillate complex , a result which is also in agood agreement with Pearson's rule.



Figure(1) : effect of temprature on acid dissociation .



Figure(2) : Effect of temprature on stability constants.

Refrences

1. Charles ,D.H and Robert ,C.W.1963.Hand book of chemistry and physics,44ed. The chemical Rubber Puplishing Co.page 1761 .
2. Majid ,Y.A, Zaki , N.S. ,AlMuddaris.M, 1982 . stability constants of some lanthanide and actinide ions with anthranillic acid .Iraqi. J.Sci. 23: 515
3. Yatsimirskii , K. B. and Vasilev V.P. 1960. Instability constant of complex compound . pergamon.
4. Ahrland, S ., chatt, J. , Davis, N, Rand W.A.A. 1958.complexes of P-aminobenzene sulphonic acid with silver ions . J.chem.soc.30: 276.
5. Majid ,Y.A.and Al-Muddaris ,M. 1989. stability constant of some lanthanide and actinide complexes of sulphanilic acid and 8-Hydroxy quinoline . Iraqi J.sci, 30:349.
6. Lewis ,J. and Wilkens ,R.G. 1960 . Modren coordination chemistry ,Interscience. Page 229.
7. Majid ,Y.A. and Zaki , N.S. 1980. studies on thorium glycinate frome stability constants measure ments J.Iraqi.chem.soc. 5: 29

8. Bjerrum, J. 1957. Metal-ammine formation in aqueos solution . Hass P. Copenhagen , page 1941 .

9. Calvin, M. and Wilson, K.W. , 1945 .Forces of Inter action between Ligands and Metal ions . J.chem .soc . 67: 2003.

10.Schwarzen bach, G. ,Gut ,R. and Anderegg ,G. 1954. stability constant of iron (II) and lead (II) complexes with E .D .T. A . Helva -chim– Acta. 37: 937.

11. Wenger, P.E .and Kapetanidis A. 1960 . complexes of iron and lead with sebacid acid .Rec, Trav . chim .79: 569.

12. Pearson , R.G. 1963.Hardness and softenss of chemical species .J.Am.chem.soc. 85: 3533.

13. Drago ,R.S . and Wagland,W, 1965.Two- parameter eystem for acid – base interactions . J.Am.chem.soc.,87 : 3571.

14. Misono ,M,etal, 1967. Development of an logous system for coordination com pounds . J.Inog.Nucl.chem.,29 : 2685.

15.Pearson, R.G, 1968 .Hard and soft acids and basis J.chem.Educ .45 : 581.

ثوابت استقرارية معقدات الحديد الثنائي والرصاص الثنائي مع حامض الانثرانيلك وحامض السلفانيلك

يحيى عبد المجيد العبيدي*

* أ .د. قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد

الخلاصة:

عينت ثوابت الاستقرارية للمركبات المعقدة بين ايونات الحديد (II) والرصاص(II) مع كل من حامض الانثرانيلك وحامض السلفانيلك في المحاليل المائية .

لقد بينت النتائج ان استقرارية المعقدات تتماشى مع النمط الطبيعي لتفكك الحوامض ،فكلما قل تفكك الحامض زادت استقرارية المعقدات الفلزية له.

كذلك بينت التجارب ان تكوين المعقدات الفلزية لحامض الانثرانيلك هي تفاعلات باعثة للحرارة بينما تكوين المعقدات الفلزية لحامض السلفانيلك هي تفاعلات ماصة للحرارة.