Thermochimica Acta, 92 (1985) 261-263
Elsevier Science Publishers B.V., Amsterdam

CALORIMETRY OF COMPLEXFORMING PROCESSES

Yakubov Kh. M., Offengenden Ye. Ya., Radjabov U.
Tadjik State University, Dushanbe, USSR

Complexforming processes of iron(III) and iron(II) with imidazole, benzimidazole and histidine under 288, 298, 308 and 318 K and ionic strength 1,0M ($NaClO_4$) have been studied by different physico-chemical methods. Has been shown the formation of the next compounds:

1. with imidazole - $FeHIm^{3+}$ ($\varkappa^{o}_{11}$), $FeHImOH^{2+}$ (β^{o}_{111}), $FeHIm(OH)_2^{+}$(β^{o}_{112}), $FeHIm^{2+}$ ($\varkappa^{r}_{11}$), $Fe(HIm)_2^{2+}$ ($\varkappa^{r}_{12}$), $Fe_2(HIm)_2^{4+}$(β^{r}_{202}), $Fe^{III}Fe^{II}(HIm)_2^{5+}$;
2. with benzimidazole - $FeHB^{3+}$, $FeHBOH^{2+}$, $FeHB^{2+}$, $Fe^{III}Fe^{II}(HB)_2^{5+}$;
3. with histidine - $Fe^{III}(H_2His)^{4+}$, $Fe^{III}(HHis)^{3+}$, $Fe_2^{III}(HHiS)_2^{6+}$, $Fe^{II}(HHis)^{2+}$, $Fe_2^{II}(HHis)_2^{4+}$, $Fe_2^{II}(His)_2^{2+}$, $Fe^{III}Fe^{II}(His)_6^{2+}$.

Stability constant values of imidazole and benzimidazole Fe(III) and Fe(II) complexes have been calculated. The values of the formation heat effects of iron imidazole complexes have been determined by the two independent methods -direct calorimetry and temperature coefficient.

The study of biometal complexforming processes with bioligands is of great importance from the practical point of view as well as theoretical. The reactions between iron(II) and iron(III) with heterocyclic compounds such as imidazole (HIm), benzimidazole (HB), histidine (HHis) and their dissociation products apply to such interactions. The determination of their formative thermodynamic characteristics is of great value.

The study of iron(III) and iron(II) complexforming processes with bioligands by the methods of oxidizing potential, spectrophotometry, polarography proceded calorimetry investigations /1,2/.

The formation of different mononuclear, binuclear and heterovalent iron coordination compounds has been shown by the use of aboved methods. Stability constant values of imidazole and benzimidazole complexes are represented in the Table I.

ΔH^{o} values on temperature dependence lgK from 1/T and direct calorimetry method have been determined by us for thermodynamic stability estimation and flow degree of the reaction /3/. Besides composition, fields of existence and stability of the complexes it was neccessary to know procent content of coordination compounds in the solution. These computations were carried out by us on ECM EC-1022 and EC-1050 on the programme RRSU in "Fortran" at different pH and temperatures.

Proceedings of ICTA 85, Bratislava

Table 1. Logarithm values of stability constants of imidazole and benzimidazole complexes

LgK TK	288	298	308	318	Ligand
$\lg \varkappa^{o}_{11}$	5,05	5,20	5,28	5,36	
$\lg \beta^{o}_{111}$	2,54	1,53	1,44	1,92	
$\lg \beta^{o}_{112}$	-	-1,54	0,23	-1,53	imidazole
$\lg \varkappa^{r}_{11}$	4,05	3,51	3,16	2,74	
$\lg \beta^{r}_{202}$	-	-	8,12	5,98	
$\lg \varkappa^{o}_{11}$	2,60	2,69	2,76	2,84	
$\lg \beta^{o}_{111}$	0,61	1,23	0,37	0,32	benzimidazole
$\lg \varkappa^{r}_{11}$	3,52	3,04	2,52	2,16	

It follows from distribution diagramme, that pH increase results to iron(III) aquaion content reduction in the solution and the quantity of $FeHIm(OH)_2^+$ is increased. The quata Fe_2HIm^{3+} reaches its maximum value at pH 3.0. By the temperature increase from 298 to 318 K the content of free incoherent in the complex Fe(III) ion and hydroxocomplex $FeOH^{2+}$ reduces but Fe(II) increases. At elevated temperature and pH 2.5 procent content of $FeHIm^{3+}$ increases from 19 to 71 %. The content of iron(II) complex compound with imidazole $FeHIm^{2+}$ at pH 4.5 is, vice versa, reduced from 87.5 to 49.0 %. Procent quata of the compounds $FeHImOH^{2+}$ and $FeHIm(OH)_2^+$ in the solutions are small and the second is a little more than the first.

Calorimetric experiment was carried out on precision isothermic microcalorimeter of special construction at ligand concentrations and pH corresponding to the regions with maximum output of every complex. ΔH^o calculations were done on the formula:

$$\Delta H^o = \frac{\Delta H_{sm} - \Delta H_p}{\alpha} ,$$

where ΔH_{sm} and ΔH_p were determined as average from 4 – 5 experiments; α - the quata of the forming complexes. ΔH^o values determined by the methods of temperature factor and direct calorimetry are represented in the Table 2. ΔH^o values are in error by ± 2 kDj/mol.

Table 2. ΔH^o values (kDj/mol) of $FeHIm^{3+}$ and $FeHIm^{2+}$ coordination compounds' formation

Complex	method \ TK	288	298	308	318
$FeHIm^{3+}$	Temperature coefficient	17,2	17,2	17,2	17,2
	Calorimetry	-	14,6	16,8	18,4
$FeHIm^{2+}$	Temperature coefficient	-72,7	-72,7	-72,7	-72,7

Thus, in dependence on ligand nature in Fe(III) and Fe(II) aqueous solutions complex compounds different on composition and stability are formed with aboved ligands.

The number of forming complexes is reduced under the transition from imidazole to benzimidazole. Stability of simple compounds is also decreased. It is, obviously, combined with steric hindrances under the formation of iron coordination compounds with benzimidazole.

Under the temperature elevation the stability of the compound FeL^{3+} is increased, but FeL^{2+} decreased. Apparently, under the temperature elevation the bond energy of water with Fe(III) ion falls faster, but with Fe(II) slower than the bond energy of imidazole molecule with central ion.

Under the temperature change ΔH^{o} values determined by calorimetry method is, also, changed and still constant under the method of temperature factor. It indicates, that the first method is more exact for experimental investigations.

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