Asian Journal of Chemistry Vol. 11, No. 3 (1999), 1017–1019

NOTE

Thermodynamic Study of Metal Complexes of Mixed Morpholine-thiocyanate and Isothiocyanate

MD. M. ALAM*, A.H. KAZMI, H.K. SINHA[†] and V.P. SINGH[†]
Department of Chemistry
M.G. College, Gaya, India

Thermodynamic study has been made to know the stability of mixed morpholine-thiocyanate and isothiocyanate complexes of Zn^{2+}, Cd^{2+} and Hg^{2+} ions. In this connection, the study based on thermodynamic parameter indicates that (—SCN) complexes of these metals are more stable than (—NCS) complexes.

Previous workers paid much attention to the determination of stabilities of a series of complexes[1–4] and attempts have also been made to assess the stability on the basis of the thermodynamic function ΔF in solution phase[5–7]. But there is almost no record for its applications in solid phase studies.

Hence, the present work has been taken up to use the thermodynamic function ΔF in solid phase studies of —SCN and —NCS complexes of the Zn^{2+}, Cd^{2+} and Hg^{2+} with a view to characterise the stability of these complexes.

TABLE-1
DISSOCIATION PRESSURE OF MIXED MORPHOLINE-THIOCYANATE AND ISOTHIOCYANATE COMPLEXES MEASURED AT DIFFERENT TEMPERATURES

Zn Complexes				Cd Complexes				Hg Complexes			
—SCN		—NCS		—SCN		—NCS		—SCN		—NCS	
T	log (p)	T	log (p)	T	log (p)	T	log (p)	T	log (p)	T	log (p)
308.0	1.0170	297.7	1.0607	308.0	1.1303	304.0	1.2531	303.5	1.0017	295.0	0.9294
313.0	1.1400	303.0	1.2041	313.0	1.2304	308.1	1.3628	308.5	1.1238	303.1	1.1592
318.0	1.2672	308.9	1.3732	318.0	1.3418	312.4	1.4828	313.4	1.2242	309.0	1.3344
323.0	1.3967	314.0	1.5138	323.0	1.3979	318.0	1.6083	318.0	1.3163	314.5	1.4771
328.0	1.4781	319.0	1.6253	328.0	1.4772	323.4	1.7120	323.0	1.3802	318.0	1.5670
333.0	1.5682	324.5	1.7535	333.0	1.5563	328.0	1.7788	328.0	1.4400	322.7	1.6665
337.0	1.6383	326.5	1.8055	—	—	—	—	333.0	1.5066	327.0	1.7528

T (temperature) in Kelvin: log (p) in mm

[†] A.M. College, Gaya, India.

The mixed morpholine —SCN complexes of Zn^{2+}, Cd^{2+} and Hg^{2+} were prepared by standard method using $Ba(SCN)_2$ as starting material and —NCS complexes were prepared with the help of Kauffman and others[8].

TABLE-2

HEATS OF DISSOCIATION (ΔH), FREE ENERGY CHANGES (-ΔF) AND CHANGE IN ENTROPIES (ΔS) OF MIXED MORPHOLINE-THIOCYANATE AND ISOTHIOCYANATE COMPLEXES AT DIFFERENT TEMPERATURES

Complexes	ΔH (kcal/mol)	−ΔF (kcal/mol)			ΔS (e.u./mol.)		
		40°C	50°C	60°C	40°C	50°C	60°C
Zn complexes							
—SCN	11.44	0.76	0.80	0.97	38.9	37.7	27.2
—NCS	11.52	0.29	0.33	—	37.4	36.6	—
Cd complexes							
—SCN	10.04	0.63	0.80	0.99	34.0	25.9	25.7
—NCS	11.66	—	0.36	0.50	—	26.8	26.4
Hg Complexes							
—SCN	9.89	0.65	0.83	1.05	33.6	21.8	21.8
—NCS	12.03	0.33	0.41	—	29.5	28.9	—

The thermodynamic functions of these metal complexes have been calculated by the use of the following equations:

$$-\Delta H = \frac{\log p_1 - \log p_2}{1/T_1 - 1/T_2} \times R \times 2.303 \qquad \text{(i)}$$

$$-\Delta F = RT \log_e p_1/p_2 \qquad \text{(ii)}$$

and

$$\Delta S = \frac{\Delta H - \Delta F}{T} \qquad \text{(iii)}$$

where all the symbols used above have their usual meanings.

For the calculation of ΔH and ΔF the dissociation vapour pressures of these complexes at the different temperatures have been measured with the help of apparatus and method used by Sinha and Ray[9] and results obtained have been recorded in Table-1. With the help of Table-1, the values of ΔH, −ΔF and ΔS were obtained and these values were tabulated in Table-2.

The values of ΔH, −ΔF and ΔS have been obtained with the help of equations (i), (ii) and (iii). The results were computed and quoted in Table-2. From the observation of this table, it is clear that in the case of (—SCN) complexes, order in ΔH values in metal complexes is $Zn > Cd > Hg$; whereas in the case of (—NCS), order in metal complexes is $Zn < Cd < Hg$. On the above trend, the previous workers[1–4] tried metal complexes is to propose the order of stability of complexes, but they failed to do so. But this value was utilised to determine other thermodynamic functions like −ΔF and ΔS which might throw light on the stability of their complexes. But again, they could not arrive on a definite conclusion on the basis of ΔS values as ΔS values do not indicate any meaningful significance for the assessment of comparative stability of (—SCN) and (—NCS) complexes of Zn, Cd and Hg. After that special attention was focused on the

–ΔF values recorded in the table which reveal the interesting point in the complexes of (—SCN) and (—NCS) of Zn, Cd and Hg. In the case of (—NCS) complexes of Zn, Cd and Hg, –ΔF values are found to be approximately half at 50°C as compared to (—SCN) complexes. Almost similar trend has been observed at temperatures 40° and 60°C. Hence the interpretation of the above results may be explained due to more co-ordinating power of ΔS in (—SCN) and less coordinating power of N in (—NCS). This can also be explained on the basis of appearances of two lone pairs of electrons on sulphur $(-\underset{\bullet\bullet}{\overset{\bullet\bullet}{S}}-C\equiv N)$ and one lone pair of electrons on nitrogen $(-\overset{\bullet\bullet}{N}=C=S)$. Now we are in a position to say that the values of –ΔF may be taken to predict the stability of thiocyanate and isothiocyanate mixed morpholine complexes of Zn, Cd and Hg; the same principle was adopted by Bhattacharya and others[10] for the assessment of stability of complexes found in solid phase. In our present work, –ΔF values of (—SCN) complexes are higher than that of (—NCS) which shows that (—SCN) complexes are more stable than that of (—NCS).

REFERENCES

1. W. Biltz and G.F. Hutting, *Z. Anorg. Allg. Chem.*, **109**, 89 (1919).
2. W. Biltz and W. Fischer, *Z. Anorg. Chem.*, **129**, 1 (1923).
3. W. Biltz and G. Messer Kneet, *Z. Anorg. Chem.*, **129**, 14 (1923).
4. E.B. Singh and D.C. Sinha, *J. Indian Chem. Soc.*, **46**, 10 (1969).
5. J. Bjerrum, Metal Ammines Formation in Aqueous Solution, Hasse & Sons, Copenhagen (1941).
6. F.J.C. Rossetti, in: J. Lewis and R.C. Wilkens (eds.), Modern Coordination Chemistry, Interscience, New York (1960).
7. M. Calvin and R. Bales, *J. Am. Chem. Soc.*, **68**, 953 (1946).
8. B. Georg Kauffman, A. Richard Albers and L. Fred Harlan, in: Robert W. Parry (Univ. of Utah) (ed.), Inorganic Synthesis, Vol. 12, McGraw-Hill, New York, p. 251.
9. P.C. Sinha and R.C. Ray, *Trans. Faraday Soc.*, **44**, 790 (1948).
10. G.C. Bhattacharya, H.C. Das Gupta and A. Chatterjee, *Indian J. Chem.*, **15A**, 1039 (1977).

(*Received*: 22 May 1999; *Accepted*: 1 June 1999) AJC-1733