*Thermochimica Acta*, 66 (1983) 351–355
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands



## Note

# pH-METRIC STUDIES ON Cd(II)-, Pb(II)-, Al(III)-, Cr(III)- AND Fe(III)-*p*-NITROBENZALDEHYDE THIOSEMICARBAZONE SYSTEMS

S.S. SAWHNEY and R.M. SATI

*Department of Chemistry, D.A.V. (P.G.) College, Dehra Dun 248001 (India)*

(Received 7 January 1983)

In an earlier communication [1] we reported the stability and thermodynamics of Cu(II)-, Ni(II)-, Co(II)-, Mn(II)-, and Zn(II)-*p*-nitrobenzaldehyde thiosemicarbazone systems. The present note concerns the interaction of *p*-nitrobenzaldehyde thiosemicarbazone (*p*-N · BzH · THSMC) with Cd(II), Pb(II), Al(III), Cr(III) and Fe(III) which has been investigated in solution pH-metrically with a view to determining the stoichiometry, stability and thermodynamics of these systems.

## EXPERIMENTAL

All the chemicals used were of Analar quality. The metal nitrate/chloride solutions were prepared in double distilled water and standardized by standard method. The *p*-nitrobenzaldehyde thiosemicarbazone was prepared according to the method of Pandey [2]. The pH values of the solutions were recorded using a Beckman H-2 pH meter, equipped with a glass and calomel electrode assembly, and standardized with standard buffers. The solutions (in 50% acetone–water): $4 \times 10^{-3}$ M $HNO_3$/HCl, $1 \times 10^{-1}$ M $KNO_3$/KCl; $4 \times 10^{-3}$ M $HNO_3$/HCl, $1 \times 10^{-1}$ M $KNO_3$/KCl, $1 \times 10^{-3}$ M *p*-N · BzH · THSMC; $4 \times 10^{-3}$ M $HNO_3$/HCl, $1 \times 10^{-1}$ M $KNO_3$/KCl, $1 \times 10^{-3}$ M *p*-N · BzH · THSMC, $2 \times 10^{-5}$ M metal, were titrated with 0.1 N NaOH (in 50% acetone–water). The pH values were corrected for non-aqueous media according to the method of Van Uitert and Haas [3]. Correction due to volume was also applied. The shapes of the curves were as usual.

## RESULTS AND DISCUSSION

The acidic nature and protonation constant (log ${}^{P}K^{H} = 11.20$ and 10.25 at 28 and 38°C, respectively) of *p*-N · BzH · THSMC (50% acetone–water media and $\mu = 0.1$ KCl) have been explained previously. The free ligand exponent

0040-6031/83/$03.00 

TABLE 1

Stability constants and thermodynamic functions of some metal complexes of *p*-nitrobenzaldehyde thiosemicarbazone.

| System | Temp. (°C) | Method [a] | log $k_1$ | log $k_2$ | log $k_3$ | log $k_1/k_2$ | log $\beta_2$ | $\Delta G^0$ (kcal mole$^{-1}$) | $\Delta H^0$ (kcal mole$^{-1}$) | $\Delta S^0$ (cal mole$^{-1}$ °C$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd(II) | 28 | A | 10.50 | 7.50 | | 3.00 | 18.00 | | | |
| | | B | 10.46 | 6.45 | | | 16.91 | | | |
| | | C | 10.45 | 6.50 | | | 16.95 | | | |
| | | D | 11.12 | 7.22 | | | 18.34 | | | |
| | | Mean | 10.63 | 6.92 | | | 17.55 | −24.71 | | |
| | 38 | A | 10.90 | 7.50 | | 3.40 | 18.40 | | | |
| | | B | 10.83 | 7.07 | | | 17.90 | | | |
| | | C | 10.95 | 7.20 | | | 18.15 | | | |
| | | D | 11.11 | 7.72 | | | 18.83 | | | |
| | | Mean | 10.95 | 7.37 | | | 18.32 | −26.07 | 32.98 | 189.87 |
| Pb(II) | 28 | A | 9.90 | 6.00 | | 3.90 | 15.90 | | | |
| | | B | 10.48 | 6.05 | | | 16.53 | | | |
| | | C | 10.35 | 6.00 | | | 16.35 | | | |
| | | D | 11.30 | 6.23 | | | 17.53 | | | |
| | | Mean | 10.50 | 6.07 | | | 16.58 | −22.84 | | |
| | 38 | A | 11.10 | 6.00 | | 5.10 | 17.10 | | | |
| | | B | 10.93 | 6.53 | | | 17.46 | | | |
| | | C | 11.00 | 6.30 | | | 17.30 | | | |
| | | D | 11.11 | 7.72 | | | 18.83 | | | |
| | | Mean | 11.03 | 6.64 | | | 17.67 | −25.15 | 46.69 | 230.99 |

| | | | | | | | $\log \beta_3$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Al(III) | 28 | A | 11.10 | 9.90 | 7.30 | 1.20 | 28.30 | | | |
| | | B | 11.23 | 9.98 | 6.28 | | 27.49 | | | |
| | | C | 11.25 | 10.00 | 6.00 | | 27.25 | | | |
| | | Mean [b] | 11.24 | 9.99 | 6.14 | | 27.33 | −37.69 | | |
| | 38 | A | 11.00 | 6.60 | 5.30 | 4.40 | 22.90 | | | |
| | | B | 10.98 | 7.93 | 5.30 | | 24.21 | | | |
| | | C | 10.95 | 7.80 | 5.35 | | 24.10 | | | |
| | | Mean | 10.98 | 7.44 | 5.32 | | 23.74 | −33.79 | −155.49 | −391.32 |
| Cr(III) | 28 | A | 10.50 | 6.00 | 4.90 | 4.5 | 21.40 | | | |
| | | B | 9.71 | 5.71 | 5.07 | | 20.55 | | | |
| | | C | 10.25 | 5.85 | 4.80 | | 20.90 | | | |
| | | Mean | 10.15 | 5.85 | 4.92 | | 20.95 | −28.87 | | |
| | 38 | A | 11.30 | 10.00 | 5.40 | 1.3 | 26.70 | | | |
| | | B | 11.24 | 9.87 | 6.02 | | 27.13 | | | |
| | | C | 11.25 | 9.95 | 6.25 | | 27.45 | | | |
| | | Mean [b] | 11.25 | 9.91 | 6.13 | | 27.29 | −38.84 | 271.58 | 998.14 |
| Fe(III) | 28 | A | 12.00 | 9.40 | 6.70 | 2.6 | 28.10 | | | |
| | | B | 11.40 | 10.00 | 6.75 | | 28.15 | | | |
| | | C | 11.50 | 9.65 | 6.80 | | 27.95 | | | |
| | | Mean | 11.63 | 9.68 | 6.75 | | 28.07 | −38.66 | | |
| | 38 | A | 11.10 | 7.10 | 5.10 | 4.0 | 23.30 | | | |
| | | B | 11.10 | 7.57 | 5.46 | | 24.13 | | | |
| | | C | 11.10 | 7.50 | 5.50 | | 24.10 | | | |
| | | Mean | 11.10 | 7.39 | 5.42 | | 23.84 | −33.92 | −189.77 | −501.13 |

[a] A, Bjerrum's integral method; B, pointwise calculation method; C, graphical method; D, Bjerrum's eqn. (4).
[b] Mean value of methods B and C.

(pL) was calculated using Bjerrum's expression [4]

$$\mathrm{pL} = \log\left[\frac{1 + (\mathrm{H}^+)/K}{T_\mathrm{L} - (\mathrm{ML}) - 2(\mathrm{ML}_2)\ldots N(\mathrm{ML}_\mathrm{N})}\right]$$

where $K = 1/{}^{\mathrm{p}}K^{\mathrm{H}}$ and $(\mathrm{H}^+) = 10^{-\mathrm{pH}}$.

Separation of the metal curves from the ligand curve, indicative of the participation of the anion of *p*-N · BzH · THSMC, was observed. To avoid hydrolysis of the metal, five-fold ligand-to-metal-ion was maintained. The metal–ligand curves ($\bar{n}$ vs. pL) were complete at both ends. For metal–*p*-N · BzH · THSMC systems the stability constants were calculated using Bjerrum's half integral method, pointwise calculation method and graphical method, using eqns. (1) (2) and (3) and Bjerrum's eqn. (4) (for $N = 2$). For systems where $\log k_1/k_2$ was less than 2.5 (Table 1), the half integral method could not be applied.

$$\log k_1 = \mathrm{pL} + \log \bar{n}/(1 - \bar{n}) \tag{1}$$

$$\log k_2 = \mathrm{pL} + \log(\bar{n} - 1)/(2 - \bar{n}) \tag{2}$$

$$\log k_3 = \mathrm{pL} + \log(\bar{n} - 2)/(3 - \bar{n}) \tag{3}$$

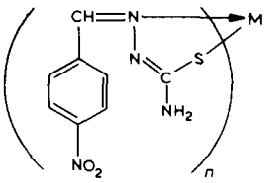
$$\frac{\bar{n}}{\bar{n} - 1}\frac{1}{(\mathrm{L})} + k_1 + \frac{(\bar{n} - 2)(\mathrm{L})}{\bar{n} - 1}k_1k_2 = 0 \tag{4}$$

Table 1 contains the stability data and thermodynamic functions of the systems. It is seen that the values of the stepwise formation constants of Cd(II)-, Pb(II)- and Cr(III)-*p*-N · BzH · THSMC systems increase with increase in temperature, which indicates that high temperatures are favourable for complexation because of the increase in number of collisions with the increase in kinetic energy of the molecules, and hence the stability of the systems is increased. For these systems $\Delta H^0$ values are positive, indicating the endothermic nature of the reactions, and supporting the aforesaid experimental fact. With negative $\Delta \mathrm{H}^0$ values, the reactions between Al(III), and Fe(III) with *p*-N · BzH · THSMC are exothermic, a fact supported by the decrease in the values of stepwise formation constant with rise in temperature. The free energy of formation ($\Delta G^0$) for Cd(II)-, Pb(II)- and Cr(III)-*p*-N · BzH · THSMC complexes has more negative values with rise in temperature, indicating that the reactions are spontaneous processes. The reverse has been observed in Al(III)- and Fe(III)-*p*-N · BzH · THSMC systems. The entropy ($\Delta S^0$) values are positive for Cd(II)-, Pb(II)-, and Cr(III)-*p*-N · BzH · THSMC systems, indicative of favourable entropy for complexation. For other systems, the $\Delta S^0$ value is negative.

The formation curves of the systems being studied reveal that the $\bar{n}$ approaches 2 for Cd(II)- and Pb(II)-*p*-N · BzH · THSMC systems which indicates the existence of 1 : 1 and 1 : 2 complexes in solution. For Al(III)-, Cr(III)- and Fe(III)-*p*-N · BzH · THSMC systems, this value approaches 3, indicating the presence of 1 : 1, 1 : 2, and 1 : 3 complexes in solution. The

above findings were further supported by titrating the different sets having 0 : 1, 1 : 1, 1 : 2, 1 : 3, and 1 : 4 (metal–ligand) ratios with NaOH; these titrations show that reaction between metal and ligand in solution occurs with the liberation of protons, limiting conditions being reached with 1 : 3 mixtures for Cd(II)- and Pb(II)-*p*-N · BzH · THSMC systems and 1 : 4 mixtures for Al(III)-, Cr(III)- and Fe(III)-*p*-N · BzH · THSMC systems.

The possible structures of metal complexes of *p*-N · BzH · THSMC, the explanation of which has been given previously [1], may be written as:




where $n = 2$: M = Cd(II), and Pb(II); $n = 3$: M = Al(III), Cr(III) and Fe(III).

ACKNOWLEDGEMENTS

This work has been carried out under the auspices of the Council of Scientific and Industrial Research, New-Delhi, India. The provision of research facilities by the Principal, D.A.V. (P.G.) College, Dehra Dun, is also acknowledged.

REFERENCES

1 S.S. Sawhney and R.M. Sati, Thermochim. Acta, 61 (1983) 365.
2 U.N. Pandey, J. Indian Chem. Soc., 54 (1977) 579.
3 L.G. Van Uitert and C. Haas, J. Am. Chem. Soc., 75 (1953) 451.
4 J. Bjerrum, Metal Ammine Formation in Aqueous Solution, P. Haase and Son, Copenhagen, 1941, p. 298.