THE STABILITY CONSTANTS OF Co(II) AND PYRIDINE-2-AZO-p-DIMETHYL ANILINE 1 : 1 COMPLEX IN MIXED SOLVENTS*

Shabbir A. Zubairi

Department of Chemistry, Univeristy of Karachi, Karachi 32

Abstract. The stability constants and thermodynamic parameters of 1:1 complex of cobalt(II) and pyridine-2-azo-*para* dimethyl aniline has been studied at three temperatures in alcohol–water mixtures keeping alcohol in low-mole fractions. Effort has been made to explain these results on the basis of structuring–destructuring effect of cosolvent in water. It was found that methanol has ordering effect on bulk solvent up to 3.31% mole fraction.

Much attention has been drawn in recent years towards the study of thermodynamics and kinetics of chemical reactions in mixed solvents.[1-4] Such studies were oriented towards understanding the influence of cosolvent on the structure of bulk solvent. Since change in dielectric constant is an important factor in ion-pair formation.[5-7] The changes in rates and equilibrium constantis were strongly influenced by decrease of dielectric constant.[8] Measurement of stability constant of 1:1 complex of Co(II) and pyridine-2-azo- *para*-dimethyl aniline were made in methanol-water mixtures containing low-mole fractions of methanol to understand the effect of change in bulk solvent structure on the thermodynamic parameters of their reaction. Since a suitable range of pH exists in which the dye is electrically neutral the change of stability constants should not be much effected by the changes in dielectric constant.[3]
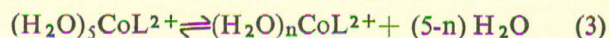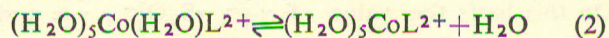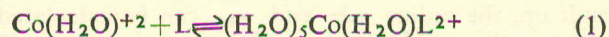
Experimental

Inorganic chemicals of reagent grade were used in the preparation of solution. Cobalt(II) nitrate was used for making solution and was standardized using ion exchange resin. Spectral grade methanol was used in preparation of all solutions. Potassium nitrate was used to adjust ionic strength to 0.1 mole/liter. The ligand and the complex concentrations were measured by Cary-14 spectrophotometer. Due to decomposition of the dye freshly prepared solutions were always used.

Spectra of the solutions of dye at various pH values were recorded in the visible region in different mole fractions of methanol at 15, 25 and 35°C. There were changes in spectra up to 5.6 pH and from there onwards the spectra remained unchanged, at least up to pH 9.0. These findings are in accord to the results reported by Klotz and Ming[9] who proposed that the dye is electrically neutral above pH 6.0. All measurements were made in solutions at pH 5.8–7.0 having ionic strength of 0.1 M in from KNO_3.

Results and Discussion

The complex was found to show maximum absorbance at 540 nm in all solvent compositions under study. Measurements were made at this wavelength and K was calculated according to the method proposed by Klotz and Ming.[9] (Table 1). The enthalpy and entropy changes were calculated at 25°C using Van't Hoff equation (Table 2). It was observed that the values of K, $\triangle H_0$ and $\triangle S_0$ undergo a minimum around 3.3% mole fraction of ethanol after which a rise in these values was observed. This can be considered as an indication of change in bulk solvent structure.[4, 10, 11] Since the mole fractions of the cosolvent are very small, it can therefore, be argued that the metal ion would be solvated by water molecules only and the cosolvent molecules have very little probability of being present in the primary coordination sphere. This system has been shown to abide SN_2 mechanism[12] as proposed by Eigen *et. al.* [6,13,14,15] The following primary steps can be proposed for the formation of 1:1 complex understudy.

$$Co(H_2O)^{+2}+L \rightleftharpoons (H_2O)_5Co(H_2O)L^{2+} \qquad (1)$$

$$(H_2O)_5Co(H_2O)L^{2+} \rightleftharpoons (H_2O)_5CoL^{2+}+H_2O \qquad (2)$$

$$(H_2O)_5CoL^{2+} \rightleftharpoons (H_2O)_nCoL^{2+}+ (5\text{-}n)\,H_2O \qquad (3)$$

Step 1, the Bjerrum ion-pair step, is diffusion-controlled in case of changeless ligand, while steps 2 and 3 are formation of inner sphere complex and ring closure in case of bidentate ligand respectively. In addition to elimination of water from primary coordination sphere the secondary and tertiary solvation spheres would also be distorted and destroyed.[3] The Bjerrum ion-pair constant K_0 is given by

$$K_0 = \tfrac{4}{3}\pi N^0 a^3$$

where N° is Avogadros number and a is the distance of closest approach in Angstrom units. Since the equation is independent of temperature and dielectric constant, i.e. solvent composition, the changes observed in equilibrium constant, $\triangle H_0$ and $\triangle S_0$ must originate from steps 2 and 3 of the mechanistic equations.[3]

STABILITY CONSTANTS OF CO(II) and PYRIDINE-2-AZO-p-DIMETHYL ANILINE 1:1 COMPLEX

TABLE 1. THE STABILITY CONSTANTS AT VARIOUS TEMPERATURES and MOLE FRACTIONS.

Mole fractions of MeOH %	K		
	15°C	25°C	35°C
0·0	$6·1 \times 10^3$	5×10^3	$4·5 \times 10^3$
1·84	$5·57 \times 10^3$	$4·4 \times 10^3$	$3·54 \times 10^3$
3·31	$5·2 \times 10^3$	$4·0 \times 10^3$	$3·14 \times 10^3$
4·7	$5·7 \times 10^3$	$4·6 \times 10^3$	$3·8 \times 10^3$
12·0	$6·2 \times 10^3$	$5·1 \times 10^3$	$4·4 \times 10^3$

Temperature stability $\pm 0·1$°C; Standard deviation $\pm 5\%$

TABLE 2. THERMODYNAMIC PARAMETERS AT VARIOUS MOLE FRCTIONS.

Mole fraction of MeOH%	$-\triangle H_o$ kcal/mole	$\triangle S_o$ c.u.
0·0	2·60	25·2
1·84	3·70	28·0
3·31	4·30	29·8
4·75	3·70	28·2
12·0	2·70	25·4

Standard deviation $\triangle H_o = \pm 3\%$; Standard deviation $\triangle S_o = \pm 7\%$.

Steps 2 and 3 involve elimination of water molecules from the solvation spheres and primary coordination sphere. Since it can be safely assumed that the reaction mechanism and metal–ligand bond strength remains independent of bulk solvent in low-mole fractions of methanol,[3,8] the changes in the $\triangle H_o$ value as a function of mole fractions of methanol would really reflect the changes in the metal ion–water bond strength.

It has been shown that dipolar and protic solvents have ordering–disordering effect on water when added in small mole fractions.[4,17,18] The results obtained from this study indicate that methanol imposes order on the bulk up to about 3.31% mole fraction, after which the system tends to go to disorder again. Probably another maxima occurs around 30% mole fraction as pointed out by some authors.[4] However, the region of small mole fractions included in this study has not been studied. These results are in accordance with the studies in dioxane–water[17] and methanol–water systems.[17,18]

References

1. G. Atkinson and S. K. Koss, J. Phys. Chem., **69**, 128 (1965).
2. N.S. Angerman and R. B. Jordan, Inorg. Chem., **8**, 2579 (1969).
3. H. P. Bonnetto, R. Balmer and E. F. Caldin, J. Chem. Soc. (A), 2198 (1971).
4. F. Frank and D. J. G. Ives, Quart, Rev. Chem. Soc., **20**, 1 (1966).
5. P. Debye, Trans. Electrochem. Soc., **28**, 265 (1942).
6. M. Eigen, Z. Phys. Chem., **1**, 176 (1954).
7. R. M. Fuoss, J. Am. Chem. Soc., **80**, 5059 (1958).
8. R. G. Pearson and P. Ellgen, Inorg. Chem., **6**, 1379 (1967).
9. Klotz and M. W. C. Loh Ming, J. Am. Chem. Soc., **75**, 4159 (1953).
10. H. S. Frank and M. W. Evans, J. Chem. Phys. **13**, 507 (1945).
11. E. M. Arnett, *Phycochemical Processes in Mixed Aqueous Solvents* edited by F. Frank (Hinemann, London, 1967).
12. S. A. Zubairi, Ph.D. Dissertation., University of Houston, Houston, Texas (1973).
13. M. Eigen and K. Tamm, Z. Electrochem., **66**, 93 (1962).
14. M. Eigen and K. Tamm, Ibid, **66**, 107 (1962).
15. M. Eigen and L. De Macyer, *Technique in Organic Chemistry*, edited by S. Friers, E. Lewis and Weissberg (Interscience, New York, 1963), vol. VIII, part 2, p.
16. C. T. Lin, Ph.D., Dissertation, University of Houston, Houston, Texas (1970).
17. D. R. Under down, Dissertation, University of Houston, Houston, Texsas (1972)
18. P. K. Chettapodhyaya and J. F. Coltzee, Inorg. Chem., **113**, 12 (1973).