

Formation Constants of Cobalt (II) and Murexide 1:1 Complex in Methanol-Water Mixture.

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(Received 28th Feb. 1980)

Summary: The formation constant of Cobalt(II) and Murexide (1:1) complex were obtained spectrophotometrically in water and 1.8, 3.7, 5.7, 7.8, and 10.1 mole percent of methanol in water at 294^o, 298^o, 304^o, and 309^o K. The enthalpies and entropies were calculated and the data was explained in terms of ordering-disordering effect of co-solvent on bulk solvent water.

Introduction:

It is a well recognised fact that the composition of the medium profoundly effect ionic reactions. Solution kinetics (1,2) and equilibrium studies (3,4) in alcohol-water mixture as well as the physical characters of this binary liquid system have mostly been explained in terms of ordering-disordering effect of alcohol in water (5). Attempts to explain the thermodynamic and kinetic data of complex formation in terms of singular solvent property like dielectric constant, dipole moment or basicity have not been very successful (6). It has been proposed that the maximum covalent effect is observed in the region of low mole fractions of alcohols in alcohol-water binary solvent system (5).

This study reports the effect of the presence of methanol in low mole fractions on the formation constants of cobalt (II) and murexide 1:1 complex. The changes in thermodynamic parameters have been explained in terms of ordering effect of methanol on bulk solvent.

Experimental

Since the ligand and the complex show substantially different spectrum in the visible region, spectrophotometric method was used to determine the formation constants. All observations were recorded on SP-500 series-2 Pye Unicam Spectrophotometer.

Cobalt Nitrate analar of E. Merck was used without further purification. Methyl alcohol of E. Merck 99.5% G.R., was kept dry on molecular seive (3A^o) and was used as such for preparation of all solvent system.

Ammonium perpurate of Hopkins & Williams was used as source of Murexide ions. Freshly prepared solu-

tions were used since the ligand tends to decompose slowly. The ligand solution concentration was always checked spectrophotometrically. The ionic strength of all solutions was adjusted to 0.1 M with KNO₃. All observations were made in solutions of pH 5.0 to 5.5, since at this pH the ligand is in the form of H₂L⁻(4). The pH was adjusted by NaOH and HNO₃ solutions using Pye Unicam pH meter model 290. The total ligand concentration was maintained at 4 × 10⁻⁵ M, and the metal ion concentration was varied between 1 × 10⁻³ to 1 × 10⁻² in each experiment. Water from constant temperature bath was circulated through cell holder to maintain required temperature. The temperature stability of cell holder was ± 1^oC. The spectra of the ligand and complex in visible region was practically unaltered within the range of temperature and methanol concentration under study.

Results and Discussion:

Since both the ligand and complex absorb substantially between 400 and 500 nm, all observations were recorded at 420, 440 and 460 nm, where extinction coefficients have maximum differences. The molar extinction coefficients of the ligand were 900, 2250 and 5040 and those of complex were 8100, 11760 and 14950 at 420, 440 and 640 nm respectively. The concentration of complex was calculated using the relation:

$$A_T = \epsilon_{ML} X + \epsilon_L (L_0 - X)$$

where A_T total absorbance recorded at a given wave

length, ϵ_{ML} & ϵ_L are the extinction coefficients at the given wave length, X is the concentration of the complex and L_0 , is total concentration of ligand. From this data K were calculated since the total concentration of ligand, L_0 , and that of metal ion M_0 are known, using the following relations:

$$K = \frac{X}{(L_0 - X)(M_0 - X)} \quad (2)$$

Due to large excess of Co(II) only 1:1 complex for-

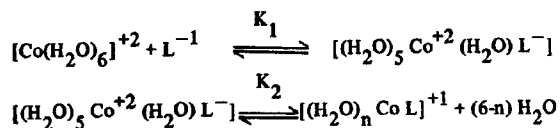
mation was possible. No spectral shifts due to the presence of M_2L were detected. The pH was maintained between 5.0 to 5.5. The formation constant thus obtained are given in Table I. In all cases an increase in the values of K was observed upto about 3.70 mole percent of metanol followed by a decline with a minima at about 6 mole percent and thereafter a steady rise. The ΔG° values show corresponding decrease upto 3.70 mole percent followed by slight increase at 5.7 mole percent and as concentration of alcohol further increases there is a steady decline in the value of ΔG° .

The K values under discussion refer to overall equilibrium constant of two reactions i.e.

Table 1.

X_0 % alcohol	Temp. °K	$K/10^2 \text{ mol}^{-1} \text{ dm}^3$	$\Delta G^\circ/\text{KJ mol}^{-1}$	$\Delta H^\circ/\text{KJ mol}^{-1}$	$\Delta S^\circ/\text{KJ mol}^{-1} \text{ K}^{-1}$
0.00	294	3.75 ± 0.26	-14.44	-6.65 ± 1.46	21.34 ± 3.77
	298	2.76 ± 0.30	-13.89		
	304	1.77 ± 0.27	-13.26		
	309	0.76 ± 0.09	-11.09		
1.80	294	4.02 ± 0.23	-14.60	-3.72 ± 0.59	33.89 ± 2.01
	298	2.78 ± 0.27	-13.89		
	304	2.48 ± 0.25	-13.89		
	309	1.84 ± 0.22	-13.14		
3.70	294	4.27 ± 0.24	-14.77	-2.97 ± 0.84	38.07 ± 1.34
	298	3.38 ± 0.11	-14.39		
	304	3.23 ± 0.45	-14.56		
	309	2.63 ± 0.30	-14.27		
5.70	294	3.65 ± 0.43	-14.39	-2.76 ± 0.25	37.66 ± 1.46
	298	3.15 ± 0.20	-13.81		
	304	2.42 ± 0.30	-13.85		
	309	2.40 ± 0.25	-13.85		
7.80	294	3.72 ± 0.30	-14.44	-2.97 ± 0.17	37.11 ± 1.46
	298	3.51 ± 0.30	-14.48		
	304	2.69 ± 0.22	-14.10		
	309	2.13 ± 0.25	-13.72		
10.10	294	5.23 ± 0.40	-15.23	-3.05 ± 0.17	37.45 ± 4.48
	298	4.50 ± 0.50	-15.10		
	304	3.47 ± 0.20	-14.73		
	309	0.95 ± 0.10	-11.67		

Note:— i) X_0 % is mole fractions per 100 mole of solvent.
 ii) All K values obtained at 0.1 ionic strength in KNO_3 .
 iii) Errors refer to internal standard deviation with in data.



where K_1 is the equilibrium constant for ion-pair formation while K_2 for elimination of water molecules and formation of inner sphere complex. The ΔH° and ΔS° values calculated from overall equilibrium constant would be the sum of the enthalpies and entropies of these two steps, and these quantities would ultimately govern the overall equilibrium constant and its trends of changes in different solvents. All ΔH° values are negative, indicating greater stability of complex as compared to metal ion hydrate and free ligand. However, there is a positive change in ΔH° values upto 5.70 mole percent of approximately 2.76 KJ (Table 1). In the given temperature range the change in dielectric constant is less than 4.0 (7) which can not fully account for the observed change in the ΔH° values nor does the changes of K values abide by the trend expected from Fross equation for ion pair formation (8). This indicates that ΔH° values are presumably more influenced by changes in K_2 rather than in K_1 , since K_1 is expected to be more dependent on dielectric constant. The ΔH° observed should then be a measure of differences in bond formation energy between cobalt (II) and the ligand and the bond dissociation energy between the metal ion and water solvation. The metal ion water bond could become stronger if metal ion is less solvated in methanol-water mixture compared to pure water. This would cause positive changes in ΔH° values as observed (Table 1). If alcohol imposes greater order on bulk water in low mole fractions, as has been pointed out (2, 5, 9, 10), this effect would be expected. Increase in concentration of methanol beyond 5.7 mole percent causes reversal of trend in ΔH° values indicating on set of disorder.

All ΔS° values were positive as expected for chelates. However, since the metal ion, the ligand and the complex are charged species and the dielectric constant is changing on addition of methanol, the interpretation of changes in ΔH° values is difficult (3, 4).

Though it has been pointed out that maximum

effect of co-solvent on bulk solvent water would be observed in low mole fraction region of co-solvent (5) most of the rate and equilibrium studies reported in methanol-water mixtures include alcohol concentration higher than those reported here (2, 9, 10, 11, 12), these studies indicate the maxima or minima in the activation and thermodynamic parameters around 25 mole percent methanol. Probably in this region a larger magnitude of change is observed compared to the one reported here. However, studies on solution thermodynamic of cobalt (II) and pyridine-2-azo-para dimethyl aniline in low mole percent of methanol in water indicate definite ordering of water upto about 6 mole percent methanol and reversal of trend from there on upto about 10 mole percent methanol. (13) This is in good agreement with the finding of this study.

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