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NOTE

Complexes of Silver Ion with Pyridines and Some Amines in Acetonitrile

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In the present work, we report the interaction of silver ions with pyridines and some amines in non-aqueous medium with lower dielectric constant like acetonitrile.

Solutions of coordination complexes in semipolar and nonpolar solvents become subject to rational consideration. The use of water as a solvent for inorganic salts is reduced to that of the special case of a substance combining high dielectric constant with high base strength. With this conceptual background it was decided to study the interaction of silver ions with pyridines and some amines in a non-aqueous medium with lower dielectric constant like acetonitrile. Such complexes have been frequently used as catalysts or intermediates in the synthesis of new organic and organometallic compounds. The silver ion complexes were studied by the potentiometric method and the data have been analysed to obtain stability constants of the complexes. These data have been compared with literature information on such complexes in an aqueous medium.

Commercially available acetonitrile (S. Merck) was purified by first refluxing with P_2O_5 for 1 h and then subsequently fractionating in a column packed with cut-glass rings. The major fraction obtained was then redistilled over a few pellets of potassium hydroxide under an atmosphere of nitrogen. The fraction boiling at 80°C (722.5 mm Hg) was collected and used in the present work (RI 1.3414, 25°C). Samples of pyridines and amines were readily available in the laboratory and were purified by standard procedures.[1] Solutions of the ligands in acetonitrile were prepared by dissolving approximate quantities by volume and then standardising the solution by titration against standard perchloric acid.[2] Solutions of silver nitrate in acetonitrile were obtained by dissolving weighed quantities of the salt BDH AR in the solvent.

Actual complexation studies were carried out by titrating 25 mL of the silver nitrate solution, taken in a beaker immersed in a thermostat maintained at 25 ± 0.1°C, with the ligand solution. The change in metal ion concentration was followed using the electrochemical combination

$Ag \mid Ag^+$ (dissolved in CH_3CN) $\|$ Double junction Reference electrode

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The silver electrode was of an analytical grade silver metal rod which was polished with emery paper, washed with dilute nitric acid and distilled water before use every time. The double junction reference electrode was an Orion Type 90–02 (M/s Orion Research Inc., USA). The outer chamber of this electrode was filled with 0.1 M sodium perchlorate solution in acetonitrile. The EMF of the cell was measured by a Phillips Multimeter Model PM 2522 having an accuracy of ± 0.1 mv.

All experiments were carried out under an atmosphere of purified nitrogen gas and the solutions in the beaker were stirred with a glass paddle stirrer attached to a small electric motor. The results are given in Tables-1 and 2.

TABLE-1
MAXIMUM DEGREE OF COMPLEX FORMATION ($\bar{n}$) FOR THE LIGANDS WITH THE SILVER ION AT 25°C

Ligand	$\bar{n}$
Pyridine	0.77
α-Picoline	1.09
β-Picoline	0.79
γ-Picoline	0.72
Diethylamine	1.06
Disopropylamine	1.00
Triethanolamine	0.55
o-Phenylene diamine	0.64

TABLE-2
STABILITY CONSTANTS OF COMPLEXES OF PYRIDINES AND SOME AMINES WITH SILVER IONS IN ACETONITRILE AT 25°C

Ligand	log K (Acetonitrile)	log K (Aqueous)
Pyridine	1.82	2.06
α-Picoline	2.14	2.33
β-Picoline	1.91	2.25
γ-Picoline	2.11	2.18
Diethylamine	2.95	2.98
Diisopropylamine	3.40	—
Triethanolamine	1.90	2.30
o-Phenylene diamine	2.18	—

The electrode combination showed Nernstian response in acetonitrile containing silver ions with a mean value of the Nernst's slope as 60.74 mv/°C. With all the ligands used in the present work, the value of the maximum degree of formation was established using the equation[3],

$$\bar{n} = -\,[d \log C_M / d \log C_L]_L \qquad (1)$$

These results of n values are summarised in Table-1 which clearly indicates that only a 1 : 1 complex (M : L) is formed in solution.

The ratio of the ligand to metal ion in these determinations was particularly kept high, *i.e.*, beyond 10, depending upon the experimental convenience.

Since only a 1 : 1 complex is present in solution, the mass balance equations for the metal ion and ligand in solution are

$$T_M = C_M + \beta_1 \cdot C_M \cdot C_L \qquad (2)$$

and

$$T_L = C_L + \beta_1 \cdot C_M \cdot C_L \qquad (3)$$

where the C's represent the free concentrations in moles (g ions per litre) of the various species in solution at equilibrium and the T's represent the total concentrations in moles (g ions per litre). It hence follows that

$$C_L = T_L - (T_M - C_M) \qquad (4)$$

Since C_M is measured by the electrode combination, values of C_L for various values of T_M and T_L at various stages of titrations can be calculated, thereby permitting computation of the degree of formation $\bar{n}$ using the formula indicated above.

Further since values of $\bar{n}$ at different concentrations of free ligand in solution C_L are available, values of log β_1 were calculated using the equation[3],

$$\log \beta_1 = \log [\bar{n}/(1 - \bar{n})] - \log C_L$$

The results of these log β_1 so obtained are an average of two independent determinations and are summarised in Table-2, which also compares similar literature data on these complexes in an aqueous medium[4].

The results in Table-2 indicate that generally the stability constants of the complexes of the silver ions with the pyridines and amines in acetonitrile are lower compared to the corresponding values in an aqueous medium. The trend in the series pyridine, α-picoline, β-picoline and γ-picoline follows the trend required by electron density considerations. The trend in the values of stability constants parallel the trend in an aqueous medium although the change is not as sharp as in aqueous medium.

REFERENCES

1. D.D. Perrin, W.L.L.F. Armarago and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press Ltd., London (1966).
2. J. Mitchell, Organic Analysis, Vol III, Interscience, London, p. 145 (1956).
3. M.T. Beck, Chemistry of Complex Equilibria, D. Van Nostrand Reinhold Company, London (1970).
4. R.M. Smith and A.E. Martell, Critical Stability Constants, Vol. 2: Amines, Plenum Press, London (1975).

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