

Infrared Spectra of Alkali Metal Salts

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Abstract: In continuation to our project for exploring the mechanism of selective absorption of alkali metals by plants as well as the possible role of alkali metals cations in plant metabolism Chemistry of alkali metals would facilitate fuller understanding of the mechanism. The study of the Coordinator Chemistry of these metals has been undertaken..

Keywords : -hydroxyacetophenone – 2 , 4 – dinitrophenyl , hydrazone salicylaldehyde, anthranilic acid, Picolinic acid and Quinaldinic acid

Introduction

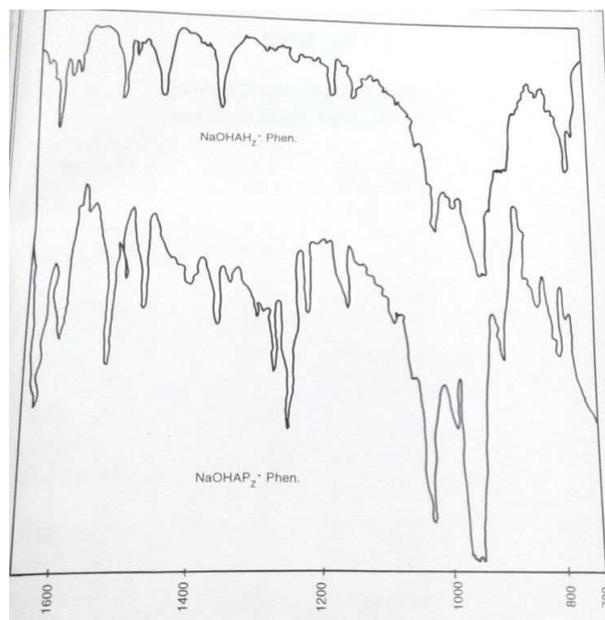
We have described the preparation of a large number of mixed ligand alkali complexes involving potential chelating ligand, having oxygen and nitrogen as the donor atoms.

It has been observed that the chelating ability of hydrazone decreases in the order : O- hydroxyacetophenone hydrazone > O- hydroxyacetophenone phenylhydrazone > O- hydroxyacetophenone – 2, 4 – dinitrophenylhydrazone. Thus substituted hydrazones become more selective in their behaviour towards alkali metal cation.

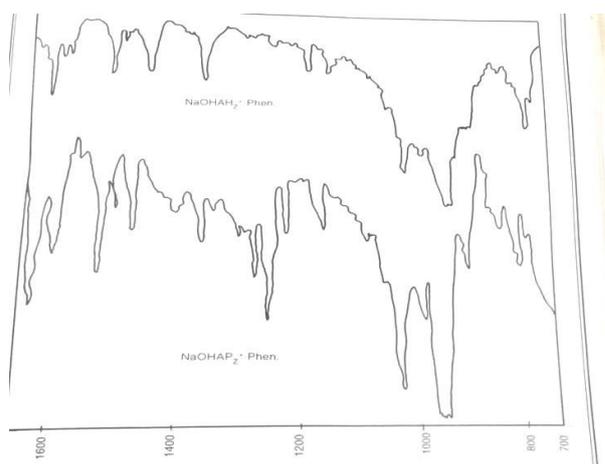
INFRARED SPECTRA :

The Infrared measurements of all the compounds have been carried in the region $4000 - 650 \text{ cm}^{-1}$ in Nujol mulls. The principal bands in the spectra of these complexes are given in Table – 7.3.

A comprehensive study of the infrared spectra of 1,10 – phenanthroline metal complexes in the rock salt region was undertaken by Schilt and Taylor¹²⁵, and much of the data concerning assignments of different bands comes their work. They observed that the spectra of the various metal complexes were remarkably similar in their gross features. However, this is not unexpected, since the vibrational frequencies occurring in the rock salt region will arise almost exclusively from the ligand which, being fairly large and complex implies that the spectra will not very markedly with metal ion. This can be observed by comparing the spectrum of $[\text{Cu}(\text{phen})_2]\text{ClO}_4$ with the spectra of 1,10 – phenanthroline complexes of alkali metal salts of few organic acids (Fig. 7.3 and 7.4).



WAVE NUMBER (CM-1)
(Fig. 7.3)



WAVE NUMBER (CM⁻¹)
(Fig. 7.4)

TABLE – 7.2
Physical Properties of Alkali Metal
Complexes of 1,10 – phenanthroline

| Compound | Colour | Melting Point / decomposition / transition temp. (°C) | Conductivity* |
|-----------------------|-------------|---|---------------|
| 1,10 – phenanthroline | White | 115 – 117m | - |
| LiOHAHz.Phen | Pale Yellow | 190d | 4.5 |
| NaOHAHz.Phen | Pale Yellow | 185d | 4.5 |
| KOHAHz.Phen | Pale Yellow | 180d | 6.0 |
| LiOHAPz.Phen | Pale Yellow | 185d | 5.0 |
| NaOHAPz.Phen | Pale Yellow | 180d | 5.5 |
| KOHAPz.Phen | Pale Yellow | 183d | 6.5 |
| LiOHADNPz.Phen | Orange | 180d | 5.0 |
| NaOHADNPz.Phen | Orange | 178d | 6.0 |
| KOHADNPz.Phen | Orange | 170d | 8.0 |

* Molar Conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) of 10^{-3} M solution in N – methyl 2 – pyrrolidone.

Spectra of the complexes have been found to differ from that of an equimolar physical mixture of phenanthroline and the alkali metal salt in that no bands attributable to the free base or its hydrate are observed. From this evidence, it would not be unreasonable to infer that all the phenanthroline in these complexes is coordinated.

The pertinent bands in the IR spectrum of the ligand 1,10 – phenanthroline are 15005, 854 and 738 cm^{-1} . The 1505 cm^{-1} band is the most intense band in the $1650 - 1400 \text{ cm}^{-1}$ region and is attributed to $\nu_{\text{C-C}} + \nu_{\text{C-N}}$ vibration. On complexation, this band shifts to higher frequency by $5 - 10 \text{ cm}^{-1}$ and also exhibits a weak satellite on its low frequency side. Sometime the satellite appears as a shoulder, but mostly as a sharp weak band.

The band in the region $900 - 700 \text{ cm}^{-1}$ are identified with motions of the ring hydrogen atoms giving in phase out – of – the plane of the ring. Particular frequency at which absorption occurs will depend upon the number of adjacent hydrogen atoms around the rings, two of which are equivalent with three hydrogen atoms and one with two adjacent hydrogen atoms.

TABLE – 7.3

IR spectral data of 1,10 – phenanthroline and its Alkali Metal Complexes

| Compound | Selected IR absorption bands (in cm^{-1}) | | |
|-----------------------|--|------------|------------|
| 1,10 – phenanthroline | 1505m | 854s | 738s |
| LiOHAHz.Phen | 1510m, 1495w | 860m, 845s | 745s, 730m |
| NaOHAHz.Phen | 1510m, 1500sh | 865m, 848s | 765s, 735s |
| KOHAHz.Phen | 1510m, 1498w | 860s, 840s | 740s, 730s |
| LiOHAPz.Phen | 1515m, 1500w | 860m, 845s | 740s, 735s |
| NaOHAPz.Phen | 1515m, 1500w | 868m, 848s | 755m, 740s |
| KOHAPz.Phen | 1515m, 1500w | 865m, 845s | 750m, 730m |
| LiOHADNPz.Phen | 1510m, 1495w | 858m, 845s | 740s, 735s |
| NaOHADNPz.Phen | 1515m, 1500w | 865m, 845s | 755s, 740m |
| KOHADNPz.Phen | 1515m, 1495w | 860m, 840s | 750s, 735m |

m = medium s = strong w = weak sh = shoulder

Only two bands are observed : one at 738 cm^{-1} (assigned to out – of – plane motion of the H – atoms on the heterocyclic rings) and the other at 854 cm^{-1} (assigned to out of plane motion of hydrogen atoms on the central ring). On complexation, the multiple splitting of these two bands arise from out – of – plane motions other than those in phase and also probably from overtones of low lying fundamentals in resonance. The splitting of these two bands appears to be metal sensitive.

These facts suggest the coordination of the alkali metals with 1,10 – phenanthroline through the nitrogen atoms of its pyridine fragments.

Our present work shows that hydrogen bonding is not necessary for formation of adducts between a chelating ligand and the alkali metal salt of a chelate ion.

CONDUCTIVITIES :

Molar conductivities of all the complexes were measured in N – methyl – 2 – pyrrolidone at 250°C at a concentration of 10^{-3} M.

The solvent has been calibrated by Banerjee et.al¹⁶ and they have observed that the values of molar conductivities in the range $35 - 40 \text{ cm}^{-1}$ correspond to 1:1 electrolyte. Detail studies^{125,126} of this solvent have shown that significantly different values as obtained with different anions, even for tetra – alkylammonium cations, and that 1:1 electrolytes may give values as low as $25 \text{ ohm}^{-1} \text{ cm}^{-1} \text{ mole}^{-1}$. From the results (Table – 7.2), it is observed that none of the values approach either ideal or 1:1 electrolyte. Low values of molar conductivities of these complexes would seem to indicate neutral complexes. However, low values are also obtained for the simple salts, which may be due to ion-pair formation and the consequent preliminary chelation. The trend $\text{Li} > \text{Na} > \text{K}$ would seem to indicate that the lithium complexes is the strongest in solution.

Significantly high values of molar conductivities of these complexes in N – methyl – 2 – pyrrolidone suggest that they have undergone dissociation in this solvent.

9. N.P. Marullo and R.A. Lloyd : J. Amer, Chem, Soc. : 1966, 88, 1076

STRUCTURE AND BONDING :

Analytical data lead to the general molecular formula $M1.L'$ for these complexes, where M = alkali metal salt of the O-Hydroxyacetophenone hydrazone, O-Hydroxyacetophenone phenylhydrazone or O-Hydroxyacetophenone – 2, 4 - dinitrophenyl hydrazone and $L' = 1,10$ – phenanthroline. Their IR spectra suggest the coordination of the ligand L' with alkali metals through nitrogen atom of the pyridine fragments. Accordingly, these complexes should have the following structure :

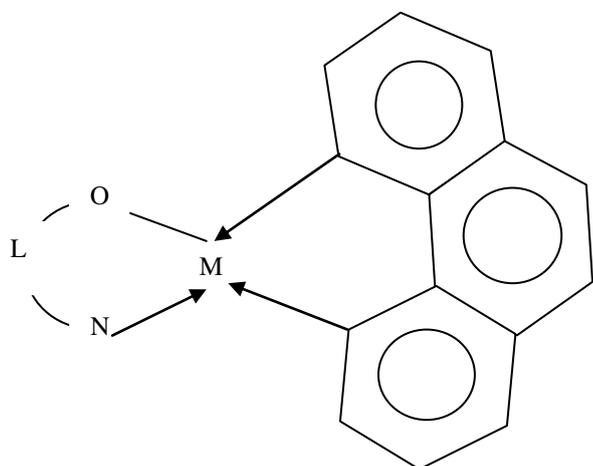


Fig 7.5

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