

## **An Spectroscopic Investigation of Complex Formation in Manganese (II) Sulphate Aliphatic Amine System**

By PADMAJA SHUKLA

### **Abstract**

Visible absorption spectra of Manganese sulphate and various aliphatic amine solutions were analysed in order to extract information regarding different amine. Manganese (II) complexes. The presence of only 2 different complexes has been indicated by the shift of absorption maxima. The energy changes of these complexes due to the replacement of water molecules with amines have been calculated and an explanation is provided for this shift in the observed position of absorption maxima.

### **Introduction**

A survey of the literature shows that a number of complexes of Manganese (II) sulphate with different amines have been studied<sup>1) 2)</sup>. In the present paper the results of an systematic spectroscopic investigation of manganese sulphate solutions with different molar quantities of various amines are reported. Methyl, ethyl, propyl, butyl, dimethyl and diethyl amines were used for the purpose of study.

### **Experimental**

The spectra were obtained with a Unicam SP 500 recording spectrophotometer on  $2 \cdot 10^{-2}$  manganese sulphate solution, in presence of different molar quantities of aliphatic amines. The pH of the solution was buffered at low value with approximately 2 M ammonium sulphate solution.

### **Results and Discussion**

It is a known fact that complex formation in solution is a step-wise process and many of the complexes so formed are quite stable so that they can be studied to a certain extent<sup>3)</sup>. It has therefore been found that gradual addition of ammonia or amines to copper or nickel sulphate and cobalt

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chloride solutions results in the formation of 4 or 6 different complexes respectively, each of which shows a definite absorption maxima and are named as mono, di, tri, tetra, penta and hexa amines on the basis of number of amine molecules that they contain<sup>4) 5) 6)</sup>.

If ammonia or other aliphatic amines are added to the manganese solution, the colour of the solution changes till it becomes pale and pink when amine has been added in excess. For the spectroscopic study, various amine solutions are added to manganese (II) sulphate solution in water. Because at each integral ratio, more than one complex is expected to exist in appreciable quantity, the value of the actual absorption maximum is found by plotting the true absorptivity against wavelength, latter being obtained by solving the equation,

$$AS = b_k a_k C_{ki}$$

where  $AS_i$  is the absorption at wavelength  $\lambda$  for the  $i$ th (Amine)<sup>o</sup>/(manganese)<sup>o</sup> ratio,  $b$  is cell thickness,  $a_k$  is the absorptivity index for the  $K^{\text{th}}$  species at  $\lambda$  and  $C$  is the concentration of the  $K^{\text{th}}$  compound at  $i^{\text{th}}$  ratio. Addition of amine in different moles ratios, does not cause any appreciable change in the position of absorption bands. When any amine solution has been added in excess then only the position of absorption maxima change. Considerably, so that they can now be recorded accurately. It thus appears that unlike copper and nickel sulphate solutions, in this case by the addition of amine only one stable complex is formed and that is the hexamine.

Each complex exhibits 6 sharp absorption bands which show a considerable shift if compared to manganese sulphate solution. The energy in K. calories absorbed per mole of these complexes for each absorption band, has been calculated by the equation  $E = NKC/\lambda$  where  $N = \text{AVOGADRO's number}$ ,  $h$  is PLANCK's constant  $C$ , velocity of light and  $\lambda$  wavelength under consideration.

It is observed that as the water ligands are replaced by various amines resulting in the formation of hexamine the energy values change significantly. It is further noted that the energy values in compounds of different amine are constant and are unaffected by the increasing mol. wt. of the amines.

Manganese sulphate exists in solution as  $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$  ion containing octahedrally co-ordinated Manganese (II). The ground state of the free ion in an octahedral field will be  $d^5$ , that is each 'd' orbital has 1 electron and their spins are parallel. This same state is the 'S' ground state of the free ion and it is not split by the ligand. Since, for every conceivable alteration of

4) PADMAJA SHUKLA, J. prakt. Chem., in press.

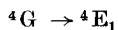
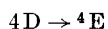
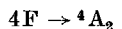
5) PADMAJA SHUKLA and GOPAL NARAIN, J. prakt. Chem. (submitted).

6) PADMAJA SHUKLA and GOPAL NARAIN, Z. phys. Chem. (submitted).

Table 1  
Shift- in wavelengths with addition of amines

Amine used	$\lambda_{\max}$ in m $\mu$	Molar absorbance	Energy ( $E \cdot 10^6$ )
1. Ammonia	350, 375, 395, 400, 425, 550	.02, .022, .019, .04, .022, .0198	3.499, 3.192, 3.03, 2.992, 2.819, 2.176
2. Methyl amine	352, 375, 395, 402, 425, 560	.02, .021, .0198, .0399, .022, .0198	3.493, 3.192, 3.03, 2.984, 2.819, 2.137
3. Ethyl amine	352, 370, 392, 401, 423, 560	.019, .020, .0199, .041, .021, .020	3.493, 3.235, 3.07, 2.992, 2.812, 2.131
4. Propyl amine	355, 370, 392, 400, 423, 562	.0195, .020, .020, .042, .020, .021	3.372, 3.235, 3.062, 2.989, 2.880, 2.137
5. Butyl amine	345, 365, 389, 405, 425, 550	.020, .022, .0199, .040, .0198, .02	3.470, 3.28, 3.084, 2.956, 2.819, 2.176
6. Dimethyl amine	348, 366, 390, 400, 425, 558	.021, .021, .02, .045, .02, .022	3.510, 3.275, 3.07, 2.992, 2.819, 2.146
7. Diethyl amine	340, 360, 395, 402, 420, 552	.02, .022, .0198, .045, .021, .021	3.521, 3.325, 3.03, 2.985, 2.850, 2.169

electron distribution  $t_{2g}^3 e_g^2$  with all spins parallel, results in the pairing of 2 or 4 spins thus making quartet or doublet states. Hence all excited states of  $d^5$  system have different spin multiplicity from the ground state and transitions to them are spin forbidden. Because of weak spin-orbit interactions, such transitions are not totally absent, but give rise to very weak absorption bands as indicated by the molar absorbance values. Further there are 4 RUSSEL SAUNDER'S state of the free ion which are quartets and the possible states of transition are



All these observed bands can be fitted by taking  $\Delta$  equal to  $8600 \text{ cm}^{-1}$ . The sharpest band is observed at  $400 \text{ m}\mu$  and there is a slight shoulder at about  $395 \text{ cm}^{-1}$ , which is because of the fact that  ${}^4E$  and  ${}^4A_1$  states arising from  ${}^4G$  are degenerate. The narrowness of the bands arise due to the transitions to upper states with zero slope.

In case of hexaquo manganese (II) ion, the solution is pale pink in colour and the bands are observed at  $350 \text{ m}\mu$  (0.02),  $375 \text{ m}\mu$  (0.022),  $395 \text{ m}\mu$  (0.019),  $400 \text{ m}\mu$  (0.04),  $425 \text{ m}\mu$  (0.022),  $550 \text{ m}\mu$  (0.0198). When amines are added, which lie toward the stronger end of spectrochemical series, the position of the various absorption bands begins to shift to lower wavelength or higher frequency region (Tab. 1). Due to a subsequent increase in ligand field, an hypsochromic effect is produced which is the cause of the band shift. In different hexamines complexes of various amines, the position and the intensity of the absorption bands remain nearly constant, but they show considerable change if compared to hexaquo complex. As the ligand field increases electron has more energy available to jump from 1 level to another, but due to theoretical regions, there can not be any apparent change in the magnitude of the transition, as these are only a few transitions possible.

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