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Molar Conductivities of monomethylammonium double sulphates of Cobalt, Nickel and Copper at 25ºC.

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ABSTRACT: *The double sulphates of copper, nickel and cobalt with monomethylammonium cation were synthesized as reported in literature. The synthesized double sulphates of copper, cobalt and nickel with mono methyl ammonium cation were characterized using FTIR. The characteristic bands for N-H, C-H, SO_4^{2-} for these compounds reported in literature were observed by the synthesized double salts. High conductivities of double salts were indicative of their strong electrolytic nature. These data will be useful when these compounds have to be grafted onto mesoporous materials for catalytic studies.*
Keywords*: conductivity studies, double sulphates, monomethylammonium double sulphates*

I. Introduction

Recently, great interest has been shown in the field of syntheses of double sulphates with non-metallic cations. A lot of data was reported by Jordanovska,V and others [1-5] on double sulphates of divalent, trivalent and rare earths metals with many non-metallic cations. Their group extensively reported the crystal structure, complete analysis vibrational spectra of single crystals, XRD and thermal analysis of the above salts. There was no data concerning the conductivity of these double salts. So it was thought worthwhile to analyze the conductivity of few transition metal double sulphates with powder diffraction data[1] of the double sulphates reported in literature show that cobalt, monomethyl ammonium cation in the present paper. Literature survey reveals the study of thermal decomposition, complete IR interpretation and crystal structure of divalent metal (Co, Ni and Cu) double sulphates with monomethylammonium cation. The X-ray nickel and zinc salts are iso structural whereas copper double sulphates has a different structure. Both the structures belong to triclinic system with $Z = 1$.

II. Experimental

2.1 Synthesis of monomethylammonium sulphate

Aqueous solution of the mono ammonium sulphate was prepared by stepwise neutralization of methyl amine (Laboratory Reagent 40% solution) with dilute sulphuric acid (A.R grade) (≈1N) to pH 4-5. The resultant monomethylammonium sulphate was then diluted to standard volume 100 cm^3.

2.2 Synthesis of double sulphates of Cobalt, Nickel and Copper with MonoMethylAmmonium Sulphates [MMAS]

Aqueous solutions of respective transition metal sulphates (A.R grade) and MMAS were mixed in the molar ratio of 1: 3 as reported in literature [1] .The resultant mixtures were concentrated to a small volume (5-8cm^3) on a steam bath. Dry ethanol was added to this solution after it attained room temperature. The resultant precipitated product was filtered, washed with 95% ethanol and dried over silica gel. The composition of the dried products was then fixed [6]. All the synthesized double sulphates were stored, after powdering, in a dessicator over silica gel.

2.3 IR studies

The spectrum of the sample was recorded on ABBMB 3000 Fourier transform infra red (FTIR) spectrometer in the region 4000 to 500 cm^{-1}. In this technique, the samples surface is contacted with a crystal surface such as germanium. The spectra were performed with the resolution of 16cm^{-1} and recorded at 45° incident angle using Zinc selenide crystal plate.

2.4 Conductivity Studies

Digital conductivity meter, model: RI 503 was used to measure the conductivity. The cell constant was determined using a standard solution of 0.0100mol/cm^3 potassium chloride (KCl). The limiting conductivity of water at 298K was found to be 0.034 mS cm^{-1}.

III. Results And Discussion

The composition of the synthesized double salts was fixed from the results of metal analysis complexometrically and sulphate gravimetrically. Table 1 shows the same.

Table 1: Results for the chemical composition of MMAM^{1}S where M^1= cobalt, nickel and copper

Compound	% M		$\%SO_4$		Empirical formula
	Theor.	Exp.	Theor.	Exp.	
CoMMAS (1:3)	13.95	13.7	40.848	39.5	$(CH_3NH_3)_2Co(SO_4)_2.6H_2O$
NiMMAS (1:3)	13.17	13.0	38.6014	37.3	$(CH_3NH_3)_2Ni(SO_4)_2.6H_2O$
CuMMAS (1:3)	14.85	14.8	39.9521	38.7	$(CH_3NH_3)_2Cu(SO_4)_2.6H_2O$

The infrared spectra of these compounds showed peaks characteristic of coordinated water, N-H, C-H, C-N and O-H stretching and bending bands as reported in literature.
The solutions of different concentrations of double sulphates were prepared in conductivity water and their conductivities were measured. The Tables 2, 3, and 4 show the conductivity data of Copper, Cobalt and Nickel double salts respectively.
From the conductivity of solutions, conductivity of salt was obtained by equation 1:

$\kappa_{Salt} = \kappa_{Soln} - \kappa_{water}$ ……………………………1.

Table 2: The limiting ionic conductivities value for the CuMMAS at 25^{o}C

C Gram equivalents /dm^3	□ $_{Soln}$ mS cm^{-1}	□ $_{Salt}$ = □ $_{Soln}$ - □ $_{water}$ $mScm^{-1}$	□/($mScm^2mol^{-1}$)	□c	□$_o$'
0.01	5.3727	5.3387	533870	0.1	796821.3119
0.005	3.0427	3.0087	601740	0.07011	784890.7056
0.0025	1.6827	1.6487	659480	0.05	789796.5743
0.00125	0.9027	0.8687	694960	0.035355	786752.5829
0.000625	0.4627	0.4287	685920	0.025	747596.8063

Table 3: The limiting ionic conductivities value for the CoMMAS at 25^{o}C

C Gram equivalents /dm^3	□ $_{Soln}$ mS cm^{-1}	□ $_{Salt}$ = □ $_{Soln}$ - □ $_{water}$ $mScm^{-1}$	□/($mScm^2mol^{-1}$)	□c	□$_o$'
0.01	6.4127	6.3787	637870	0.1	763916.4156
0.005	3.6027	3.5687	713740	0.07011	808013.6434
0.0025	2.0127	1.9787	791480	0.05	862648.6142
0.00125	1.1227	1.0887	870960	0.035355	924915.7257
0.000625	0.6227	0.5887	941920	0.025	982445.9471
0.0003125	0.3527	0.3187	1019840	0.017678	1050481.208

Table 4: The limiting ionic conductivities value for the NiMMAS at 25^{o}C

C Gram equivalents /dm^3	□ $_{Soln}$ mS cm^{-1}	□ $_{Salt}$ = □ $_{Soln}$ - □ $_{water}$ $mScm^{-1}$	□/($mScm^2mol^{-1}$)	□c	□$_o$'
0.01	6.4927	6.487	645870	0.1	768893.1756
0.005	3.5627	3.5287	705740	0.07011	795771.9156
0.0025	1.9127	1.8787	751480	0.05	816826.2337
0.00125	1.0427	1.0087	806960	0.035355	855345.2665
0.000625	0.5527	0.5187	829920	0.025	864500.0703
0.0003125	0.3027	0.2687	859840	0.017678	884868.3727

Three different plots were drawn namely, Concentration C verses molar conductivity Λ_m ,

√C verses molar conductivity Λ and √C verses Λ_o '.
Plots of molar conductivity of different double sulphates verses concentration showed that molar conductivity λ_c increases with decrease in concentration proving that the synthesized compounds are ionic in nature. (strong electrolytes).

The graph obtained for the value of λm versus concentration is shown Figure 1 below:

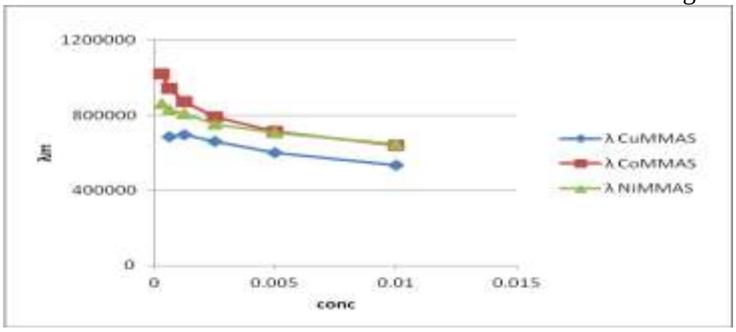

Fig 1: □m versus concentration

Figure 2 shows the of λm versus √C

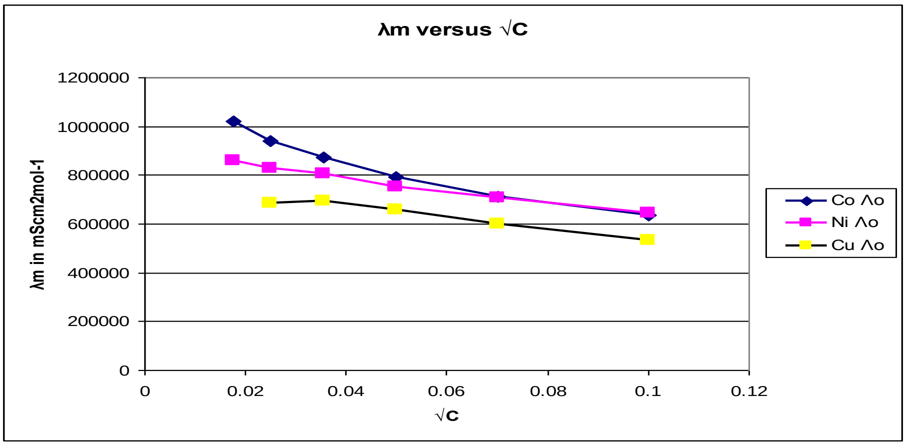

Fig 2: □m versus □C

According to Debye Hŭ ckel Onsager theory the equivalent conductance of a dilute solution of strong electrolyte is a linear function of the square root of the concentration.
The limiting law may be written as:
$\lambda_c = \lambda_o - (A + B\,\lambda_o)\sqrt{C}$ 2
$\lambda = 1000 \times \kappa / C$ 3
C = concentration gram equivalents/ dm^3
A = numerical constant which is a function of the temperature, viscosity and dielectric constant of the solvent
B = numerical constant which is a function of the temperature and dielectric constant of the solvent.
Both A and B also depend on the valence type of the electrolyte and the relative mobilities of anion and cation.
A plot of equivalent conductance of the double salts under study against the square root of the normality is shown in Figures 8-10. It is seen that curves obtained are not linear. This type of deviation from theory has been found to be characteristic of strong electrolytes.
To compute the best value of the limiting conductance, we have used the method of Shedlovsky [7]. The Onsager equation on rearrangement gives,

$$\lambda_o = \frac{\lambda + A\sqrt{C}}{1 - B\sqrt{C}} \quad \text{................................4}$$

Where λ_o' is written in place of λ_o. It is found that λ_o' is not a constant and is a function of the concentration.. Therefore a plot of λ_o' vs C will give a straight line which may be extrapolated to zero concentration to find λ_o.
The plots of of λ_o' vs √C obtained are shown in Figure 2:

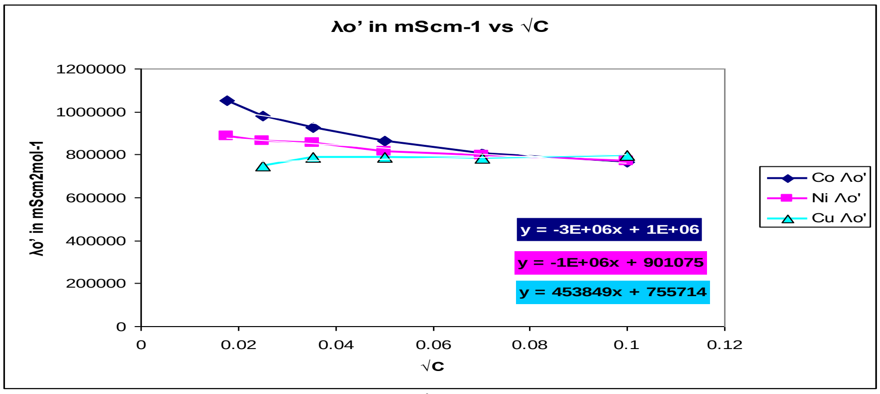

Fig 2: λ_o' versus √C

IV. Conclusion

The synthesized double sulphates of copper, cobalt and nickel with mono methyl ammonium cation were characterized using FTIR. The characteristic bands for N-H, C-H, SO_4^{2-} for these compounds reported in literature were observed by the synthesized double salts. High conductivities of double salts were indicative of their strong electrolytic nature. These data will be useful when these compounds have to be grafted onto mesoporous materials for catalytic studies.

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