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A Comparative Study of Thermal Behaviour and Magnetic Properties of Complexes of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with Poly(vinylpyrrolidone)

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Abstract: The present work explores the thermal and magnetic properties of complexes of the transition metals - Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with polyvinylpyrrolidone (PVP). Differential Scanning Calorimetry (DSC) studies provide insights into glass transition temperatures (Tg), melting temperatures (Tm) and heat capacities (Cp) of these complexes, highlighting significant deviations from pure PVP, indicative of interactions between PVP and metal ions. The absence of crystallization dips in thermograms suggests the amorphous nature of these complexes. Vibrating Sample Magnetometric (VSM) studies reveal the magnetic behaviors of these complexes, including paramagnetic, ferromagnetic and isotropic properties, depending on the metal ion. The hysteresis loops and saturation magnetization values provide a detailed understanding of the magnetic anisotropy and dipole alignment characteristics. The findings establish correlations between the thermal stability, structural changes and magnetic properties induced by metal coordination, offering potential applications in materials science and polymer-metal hybrid development.

Index Terms – Thermal analysis, Glass transition, Magnetic properties, VSM, Hysteresis loop, Amorphous polymers

1. INTRODUCTION

One of the significant experimental methods that help to study the effect of heat on polymers is Differential Scanning Calorimetry (DSC). Glass transitions, polymorphism, purity, degree of crystallinity, melting behaviour, etc. are some of the important aspects of thermal transitions of polymers. DSC technique is used [1-5] to evaluate the purity of the sample and to cure the polymer. The difference in the energies supplied to the complex under study and the reference material is measured as a function of temperature. Insertion of the additives or the changes in the degrees of polymerization results in the change in glass transition temperature (Tg) of the polymer. Physical properties of the polymer change with Tg. A polymer loses its stiffness above its glass transition temperature, [6, 7]. In general the magnetic property and magnetic moment of the complexes are studied by different methods such as Gouy's method [8], Vibrating Sample Magnetometric (VSM) studies [9-14] etc. In this article the thermal and magnetic properties of the complexes of polyvinylpyrrolidone with the transition metals viz. manganese, iron, cobalt, nickel and copper, all in +2 oxidation states, studied by DSC and VSM respectively, are compared.

2. MATERIALS

Complexes of polyvinylpyrrolidone with transition metals Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) are synthesized[15-18] and characterized by elemental analysis, spectroscopic studies such as FTIR, H^1-NMR, C^{13}-NMR. The data obtained by Differential Scanning Calorimetry and Vibrating Sample Magnetometric studies are compared in this article for analyzing the thermal and magnetic properties of the specified complexes.

3. METHODS

The DSC technique is based on the change in heat capacity of a polymer at its glass transition temperature. Glass transition appears as a step in the baseline the DSC thermogram when the temperature of an amorphous solid is increased. The heat capacity of the polymer is more above Tg and less below Tg of the given polymer. Midpoint of the slope is taken as Tg. Above Tg, polymers show high mobility. When heating is continued, above Tg, at some temperature the heat flow decreases drastically showing a dip the thermogram. The corresponding lowest temperature is crystallization temperature, Tc of the polymer. The area of the dip gives the latent energy of crystallization of the polymer. The appearance of dip in the thermogram indicates that the polymer can crystallize. If there is no dip in the thermogram, it indicates that such a polymer does not crystallize. Crystallization is an exothermic transition. If heating is continued beyond the crystallization temperature, Tc, a peak is observed. The flow of extra heat during melting appears as peak in DSC thermogram. The area of the peak is a measure of the latent heat of melting. The temperature at which the peak is observed is melting temperature of the polymer, Tm. Melting is an endothermic transition. Fig. 1. gives the schematic representation of the DSC thermogram.

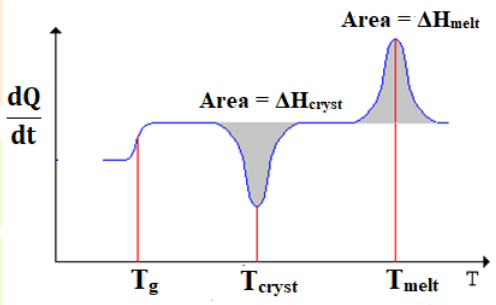

Fig. 1. A schematic representation of DSC thermogram

Crystalline polymers show a dip during crystallization and a peak during melting. Completely amorphous polymers neither show any crystallization point nor show any melting temperature. Both Tc and Tm are observed for the polymers which show both crystalline and amorphous domains. For Tg, there is neither a dip nor a peak as there is heat is neither given out or absorbed by the polymer during the glass transition. At Tg there is only change in heat capacity of the polymer but not in the latent heat of the polymer. The percentage crystallinity of a polymer can be calculated by knowing the latent of melting, ΔHm.

VSM studies measure the magnetic properties of a sample as a function of magnetic field (H), temperature (T) and time. Hysteresis loop describes the characteristics of any type of magnetic material. The hysteresis loop can be determined by Vibrating sSample Magnetometer (VSM).

The primary requisite for a compound to exhibit magnetic behavior is the presence of unpaired electrons. The extent of magnetism is indicated by the number of unpaired electrons present in the compound. Since the electron configuration of the transition metal changes when it forms a coordination compound, both diamagnetism and paramagnetism are affected when a coordination complex is formed. The reason for this change is the repulsive forces that operate between the electrons of the ligands and those of the metal. A coordination compound may be paramagnetic or diamagnetic depending on the strength of the ligand, in spite the metal ion being paramagnetic. The metals iron, cobalt and nickel can become permanent magnets and hence they are ferromagnetic.

When a material is placed in a uniform magnetic field (H), a magnetic moment (M) is induced in it. An object can be magnetized by running current (I) through the coil wrapped around it. This produces external magnetic field. As the current increases, the field increases and magnetization grows. When all the dipoles are aligned, a saturation point is reached. Further increase in current has no effect on magnetization (M) point 'a' in the Fig. 2. Now if the current is reduced, instead of retracing its path back to M = 0, M decreases corresponding to residual magnetization (point 'b'). Now the sample is a permanent magnet. If magnetization should be eliminated then a negative current has to be passed through the coil. As a result, M drops to zero at point 'c'. When a negative current is further increased, a saturation point is reached at 'd'. If current is made zero at this point, the sample becomes a permanent magnet (point 'e'). When the current is again increased in the positive sense, M returns to zero at point 'f'. Further it reached saturation point 'a'. The path traced out is called a hysteresis loop or magnetization curve.

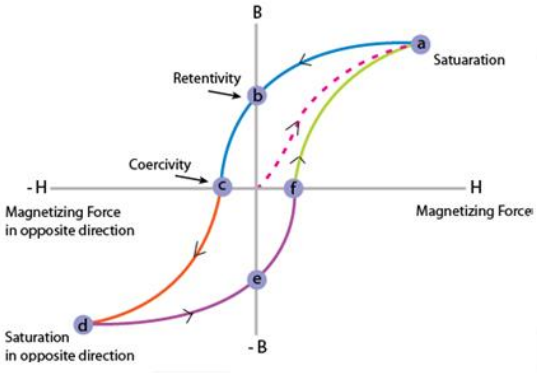

Fig. 2. Hysteresis loop of a magnetic material

The hysteresis loop gives the relation between the magnetization (M) and the applied field (H). The parameters that are extracted from the hysteresis loop such as saturation magnetization (Ms), the remanence (Mr), the coercivity (Hc), the squareness ratio SQR, etc., can be used to characterize the magnetic properties of the sample.

4. RESULTS AND DISCUSSION

COMPARATIVE STUDY OF THERMAL PROPERTIES:

Tg of a polymer changes when different degrees of polymerization are observed or when the additives are inserted. Tg of PVP-30K from literature is 163ºC.

Fig. 3 shows the DSC thermogram of PVP – Mn (II) complex.

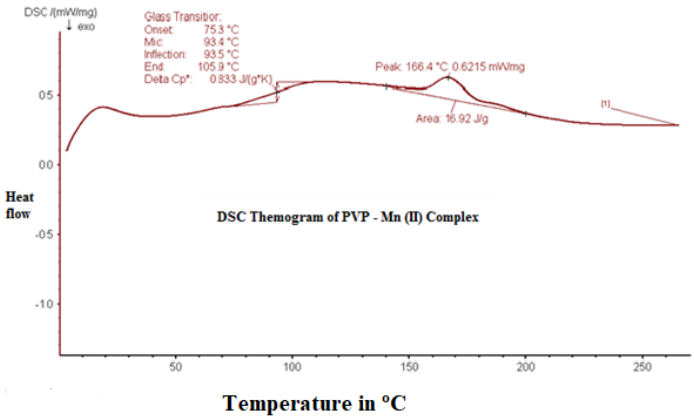

Fig. 3 DSC thermogram of PVP – Mn (II) complex

Thermogram of the complex PVP – Mn (II) shows that its Tg is 93.4ºC. The deviation in the Tg value this complex from that of pure PVP indicates that there is interaction between PVP and manganese ions. The complex melts (Tm) at 166.4ºC. The area under the peak gives the heat capacity of the complex which is equal to 16.92 J/g. Since there is no crystallization dip in the thermogram, the complex is amorphous.

Fig. 4 shows the DSC thermogram of PVP – Fe (II) complex.

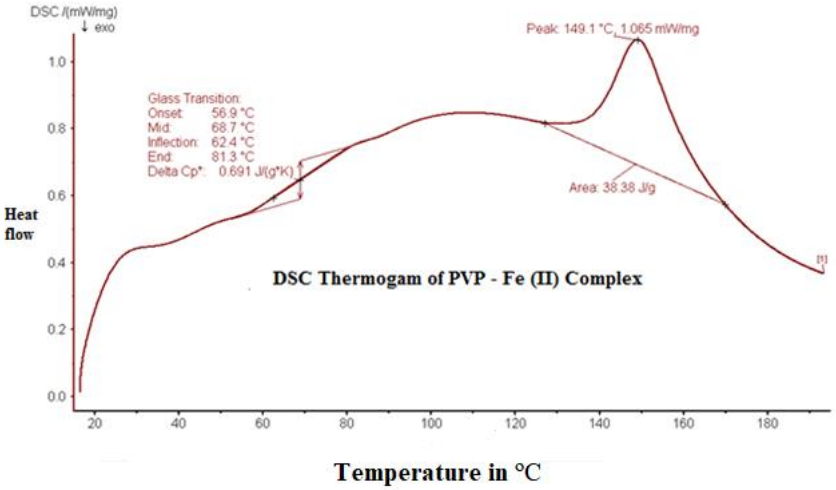

Fig. 4. DSC thermogram of PVP – Fe (II) complex

Thermogram of PVP – Fe (II) complex shows that its Tg is 68.7ºC. The deviation in the Tg value of the PVP – Fe (II) complex indicates that there is interaction between PVP and ferrous ions. The complex melts (Tm) at 149ºC. The area under the peak gives the heat capacity of the complex which is equal to 38.38 J/g for this complex. Since there is no crystallization dip in the thermogram the complex is amorphous.

Fig. 5. shows the DSC thermogram of PVP – Co (II) complex.

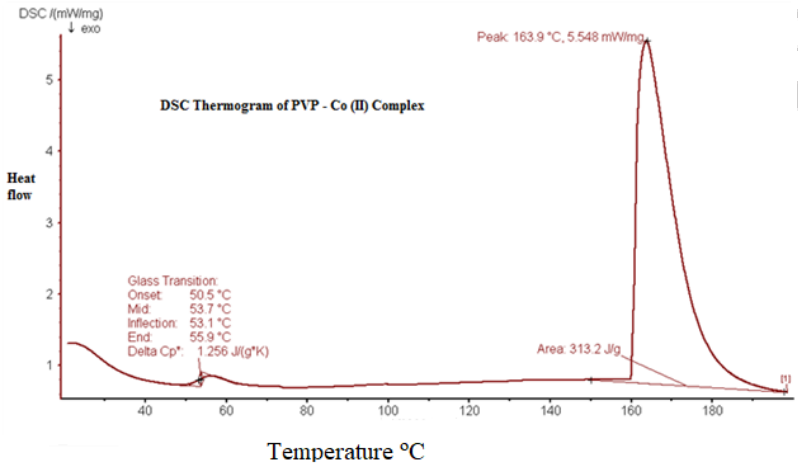

Fig. 5. DSC thermogram of PVP – Co (II) complex

Thermogram of PVP – Co (II) complex shows that its Tg is 53.7ºC. The deviation in the Tg value of the PVP – Co (II) complex indicates that there is interaction between PVP and cobalt ions. The complex melts (Tm) at 163.9ºC. The area under the peak gives the heat capacity of the complex which is equal to 313.2 J/g for this complex. Since there is no crystallization dip in the thermogram the complex is amorphous.

Fig. 6. shows the DSC thermogram of PVP – Ni (II) complex.

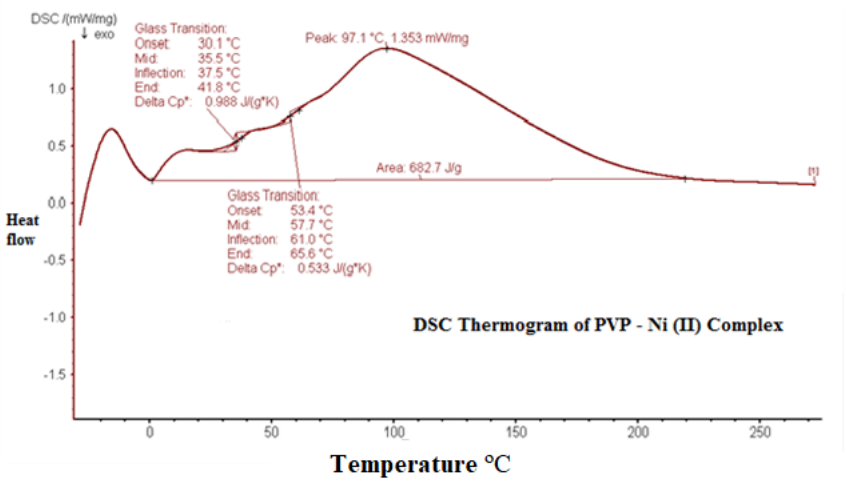

Fig. 6. DSC thermogram of PVP – Ni (II) complex

Thermogram of PVP- Ni (II) complex shows two glass transition temperatures one at 35.5ºC and another at 57.7 ºC. The deviation in the Tg value of the PVP – Ni complex from that of pure PVP indicates that there is interaction between PVP and nickel ions. The complex melts (Tm) at 97.1ºC. The area under the peak gives the heat capacity of the complex which is equal to 682.7 J/g for this complex. Since there is no crystallization dip in the thermogram the complex is amorphous.

Fig. 7. shows the DSC thermogram of PVP – Cu (II) complex.

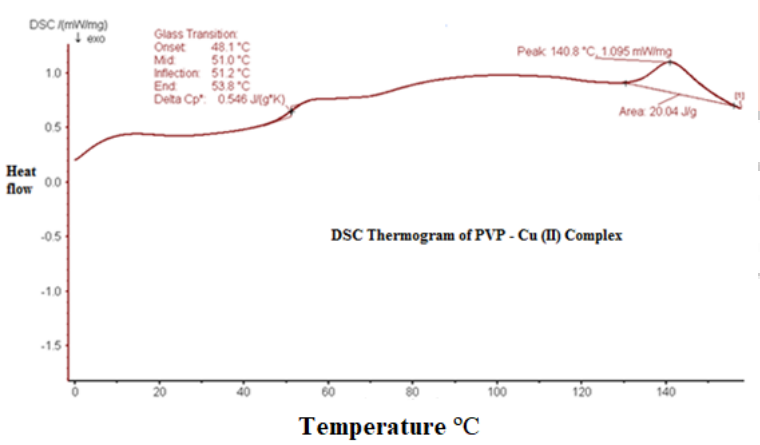

Fig. 7. DSC thermogram of PVP – Cu (II) complex

Thermogram of the complex PVP – Cu (II) shows that its Tg is 51.0ºC. The deviation in the Tg value of the PVP – Cu (II) complex indicates that there is interaction between PVP and copper ions. The complex melts (Tm) at 140.8ºC. The area under the peak gives the heat capacity of the complex which is equal to 120.04 J/g for this complex. Since there is no crystallization dip in the thermogram the complex is amorphous.

COMPARATIVE STUDY OF MAGNETIC PROPERTIES:

Fig. 8 shows the magnetization curve of PVP – Mn (II) complex obtained by VSM studies.

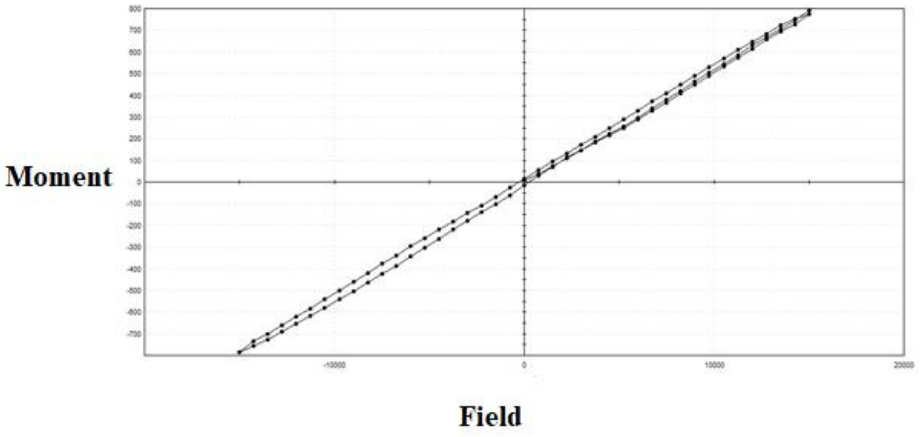

Fig. 8. Magnetization curve of PVP – Mn (II) complex

Linear magnetization of the PVP – Manganese (II) complex sample is shown in the VSM curve. As the applied field (H) varies between positive and negative values, the dipole moment realign without randomness, showing that the complex is isotropic. The sample reaches saturation around 15000 G. But at H = 0, magnetization, M is also zero. Hence there is no residual magnetization. Consequently, it may not turn into a permanent magnet for the given domain. It is only paramagnetic.

Fig. 9 shows the magnetization curve of PVP – Fe (II) complex obtained by VSM studies.

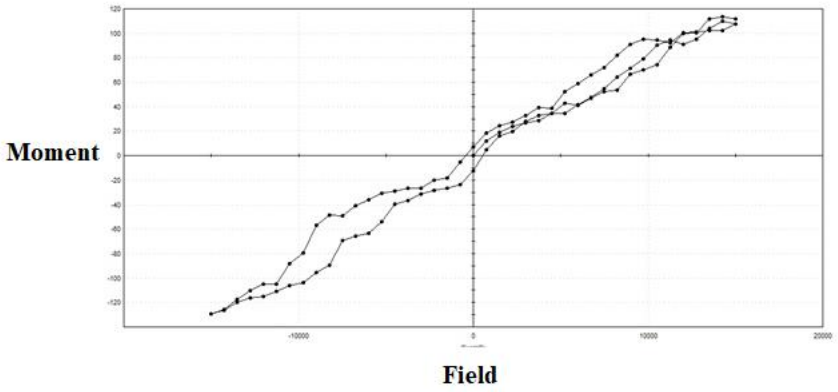

Fig. 9. Magnetization Curve of PVP – Fe (II) complex

VSM curve of the PVP – Fe (II) complex shows curvilinear magnetization of the sample. As the applied field (H) varies between -20000G and +20000G, the dipole moments align randomly, showing the complex to be anisotropic. For a zero external field, there is small trace of residual magnetization. Hence the complex is ferromagnetic for low dipole moments. For all higher fields the sample exhibits paramagnetic behaviour.

Fig. 10. Shows the magnetization curve of PVP – Co (II) complex obtained by VSM studies.

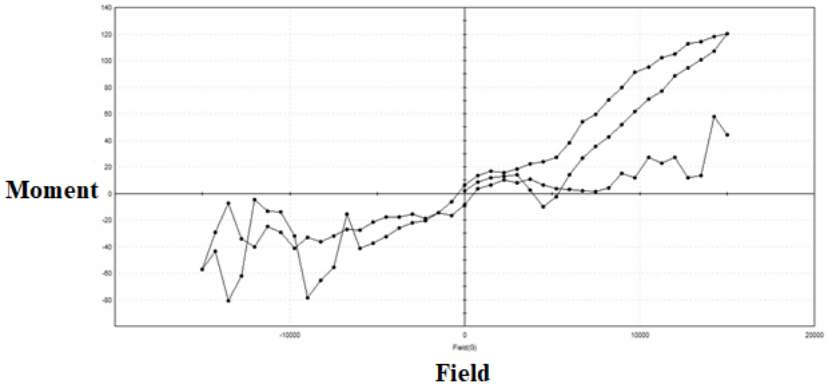

Fig. 10. Magnetization Curve of PVP – Co (II) complex

The magnetization curve (Field, H versus dipole moment, μ) shows abrupt local maxima and minima. Non linearity in dipole moment shows maximum anisotropic nature. The dipole moments are non-linear and extremely random when field is switched between positive and negative values. However, small traces of ferromagnetic nature are exhibited at zero external field and at H ≈ 5000 G. The complex is mainly paramagnetic in nature.

Fig. 11. Shows the magnetization curve of PVP – Ni (II) complex obtained by VSM studies is shown in the

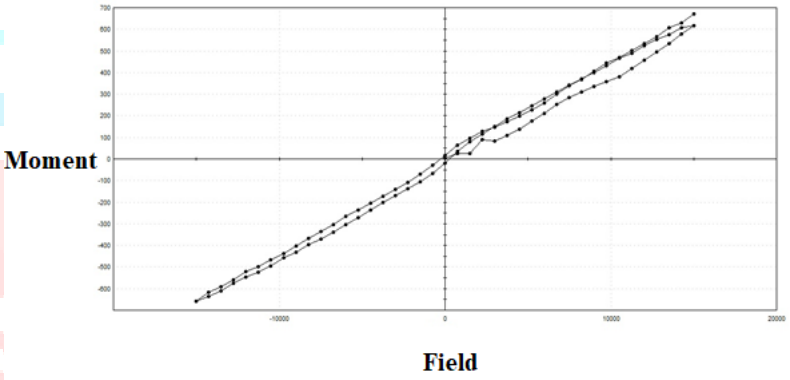

Fig. 11. Magnetization Curve of PVP – Nickel (II) complex

VSM curve of the PVP – Ni (II) complex shows similar behaviour as that of PVP – Mn (II) complex. VSM curve of the PVP – Ni (II) complex shows linear magnetization of the sample. As the applied field (H) varies between positive and negative values, the dipole moment realign without randomness, showing that the complex is isotropic. The sample reaches saturation around 15000 G. But at H = 0, magnetization, M is also zero. Hence there is no residual magnetization. Consequently, it may not turn into a permanent magnet for the given domain. It is only paramagnetic.

Fig. 12. Shows the magnetization curve of PVP – Cu (II) complex obtained by VSM studies.

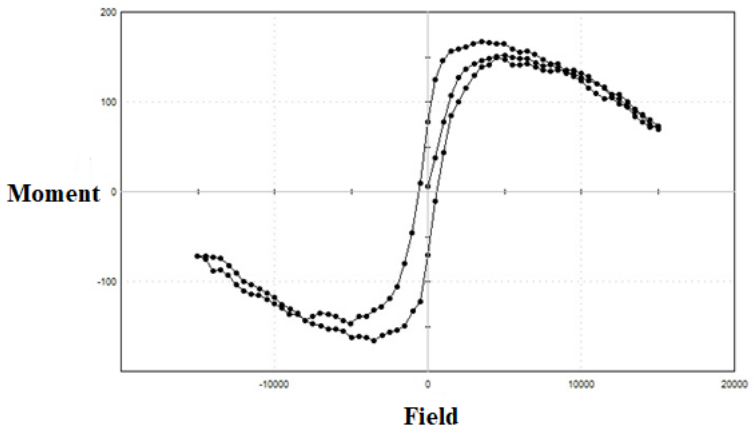

Fig. 12. Magnetization Curve of PVP – Cu (II) complex

The complex exhibits permanent magnetism as it shows non-zero residual dipole moment even at null fields. As the applied field increases, magnetization also increases but for higher values of H, there is a decrease in μ. Similarly, as –H increases –μ becomes small and attains saturation. Hence PVP – Cu (II) complex shows permanent magnetism at lower fields and paramagnetism at higher fields.

5. Conclusion

DSC studies show that the PVP – metal complexes studied are amorphous as there is no crystallization dip in the DSC thermogram of any of the complexes.

Magnetization curve (hysteresis curve) obtained by VSM studies reveal that all the complexes are paramagnetic whereas PVP – Fe (II) complex is ferromagnetic.

6. REFERENCES:

1. Mohod R B, Aswar A S. "Thermal and structural studies of Mn (II), Co (II), Ni (II), Cu (II), Zn (II) and Cd (II) chelate polymers of bis(mercaptoacetamido)-diaminodiphenylmethane." *Journal of the Indian Council of Chemists* Vol. 17, no. 1, (2000): pp 38-40.

2. "www.pslc.ws/macrog/dsc.html."

3. Thomas, Leonard C. *Thermal Analysis and Rheology.*

4. Wikipedia, the free encyclopedia. *Differential Scanning Calorimeter.*

5. Turner D T, Schwartz A. "The glass transition temperature of poly(vinylpyrrolidone) by differential scanning calorimetry." *Polymer,* Vol. 26, (1985): pp 757-762.

6. Perkin Elmer's DSC Family. *Differential Scanning Calorimetry.*

7. Mettler Toledo Thermal Analysis Systems. *Usercom.*

8. Thananjayan Kaliyappan, Palaninathan Kannan. "Polymer- metal complexes, synthesis and characterization of poly(2-hydroxy-4-acryloyloxyacetophenone-formaldehyde)-metal complexes." *Iranian Journal of Polymer Science and Technology,* Vol. 4 (1), (1995): pp 18-25.

9. Dodrill B C. *Magnetic Media Measurements with VSM.* Westerville, Ohio.

10. Vavruska Jan. *Comparison of Traditional VSM and VSM Analysis.* 2010.

11. Schmidgall E R, Moskowitz B m, Dahlberg E D, Kuhlman K R. *Magnetic Analysis Techniques Applied to Desert Varnish.* 2003.

12. Gupta S K, Gartley M G. *XRD and VSM Analysis of Nanostructured Cu-Co Aloys.* Rochester, New York: JCPDS-International Centre for Diffraction Data, 1999.

13. David J Griffiths. *Hyisteresis - Introduction to Electrodynamics.* Pearson Prentice Hall Publication, 3rd Edition.

14. Wesley Burgei. *Anisotropic and Isotropic Nature.*

15. Anasuya K V, M K Veeraiah, Hemalatha P, Manju M "Synthesis and Characterisation of poly(vinylpyrrolidone) – Nickel(II) Complexes" *IOSR Journal of Applied Chemistry* Vol. 3 Issue 8, Aug 2014, PP 61-66.

16. Anasuya K V, M K Veeraiah, Hemalatha P, "Synthesis and Characterisation of poly(vinylpyrrolidone) – Copper(II) Complexes" *Research Journal of Chemical Sciences* Vol. 5(2), Feb 2015, PP 64-69.

17. Anasuya K V, Aisha Siddekha, "Studies on Formation of Complexes between Poly(vinylpyrrolidone) and Iron(II) Salts and its Antimicrobial Properties" *IOSR Journal of Emerging Technologies and Innovative Research (JETIR).* Vol 8, Issue 11, Nov 2021, PP 126-131.

18. Manhong Liu, Xiaoping Yan, Hanfan Liu, Weiyong Yu. "An investigation of the interaction between polyvinylpyrrolidone and metal cations." *Reactive and Functional Polymers,* Vol. 44 (1), (2000): pp 55-64.