International Research Journal of Natural and Applied Sciences
ISSN: (2349-4077)
Impact Factor 5.46 Volume 5, Issue 11, November 2018
Website- www.aarf.asia, **Email** : editor@aarf.asia , editoraarf@gmail.com

Correlation between Thermal Stability and Magnetic Properties induced by Metal Coordination to Polymeric Ligand like Poly(vinylpyrrolidone)

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Abstract: In the reported work thermal and magnetic properties of transition metal complexes of 3d-series are studied by Differential Scanning Calorimetry (DSC) and Vibrating Sample Magnetometry (VSM). The metal-complexes studied are manganese, iron, cobalt, nickel and copper with polyvinylpyrrolidone (PVP). Glass transition temperatures (Tg), melting temperatures and heat capacities (Cp)of these complexes obtained by Differential Scanning Calorimetry show significant deviations from pure PVP indicating the interactions between PVP and metal ions. The thermograms obtained do not show any crystallisation dip suggesting the amorphous nature of these complexes. Magnetic behaviours like paramagnetic, ferromagnetic and isotropic properties were studied by Vibrating Sample Magnetometry. The results establish the correlations between the structural changes, thermal stability and magnetic properties induced by metal coordination.

Key Terms: Thermal analysis, DSC, glass transition, magnetic properties, VSM, hysteresis loop.

1. INTRODUCTION

Differential Scanning Calorimetry (DSC) is a crucial technique for studying thermal transitions in polymers, including glass transitions, polymorphism and crystallinity. By measuring energy differences between a sample and reference material as a function of temperature, DSC evaluates sample purity[1-5] and polymer curing. Changes in additives or polymerization degrees affect the glass transition temperature (Tg), altering physical properties like stiffness. Above glass transition temperature, polymers lose stiffness[6,7]. Generally, magnetic properties are studied using methods like Gouy's method[8] and Vibrating Sample Magnetometry (VSM)[9-15]. This article compares thermal and magnetic properties of polyvinylpyrrolidone complexes with second half of 3d-transition metals (Manganesen, Iron, Cobalt, Nickel, Copper), all in +2 oxidation states, using DSC and VSM.

2. MATERIALS

The main reactants and the other chemicals used in the present research work were procured from SD Fine Chemicals, Mumbai. Synthesis of the polymer-metal complexes [16-18] was carried out using the following chemicals: Poly(vinylpyrrolidone)-30K, $MnSO_4{\cdot}H_2O$, $FeSO_4{\cdot}7H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, and $CuSO_4{\cdot}5H_2O$. All the chemicals used are of analar (AR) grade with highest purity. Water used for the entire work was double distilled. Characterization techniques include elemental analysis and spectroscopic methods such as FTIR, ^1H-NMR, and ^{13}C-NMR. The thermal and magnetic properties of these complexes are analyzed and compared using Differential Scanning Calorimetry (DSC) and Vibrating Sample Magnetometry (VSM) data.

3. METHODS

Differential Scanning Calorimetry (DSC) measures changes in heat capacity of polymers at their glass transition temperature (Tg). As an amorphous solid is heated, Tg appears as a step in the DSC thermogram, indicating increased mobility and heat capacity above Tg. The midpoint of this slope defines Tg. Further heating may cause a dip, signifying crystallization at temperature Tc, with the area representing latent energy of crystallization. The absence of this dip indicates that the polymer doesn't 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. A schematic DSC thermogram (Fig.1) illustrates these transitions, providing valuable information on the properties of polymer. Key points in DSC thermogram are Tg, glass transition temperature (step in baseline); Tc, crystallization temperature (dip, exothermic); Tm, melting temperature (peak, endothermic). This technique helps in understanding the behaviour of polymer, its structure and properties.

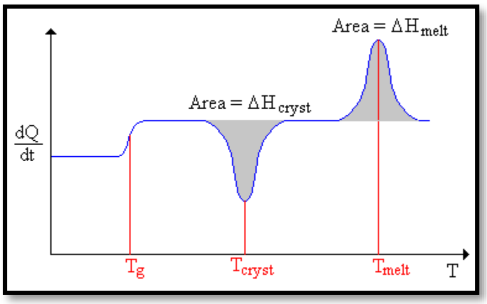

Fig. 1. A schematic representation of DSC thermogram

Crystalline polymers exhibit a dip during crystallization and a peak during melting [1-3]. In contrast, completely amorphous polymers lack crystallization and melting temperatures. Polymers with both crystalline and amorphous domains display both Tc (crystallization temperature) and Tm (melting temperature). The glass transition temperature (Tg) is characterized by a change in heat capacity without a dip or peak, as no heat is absorbed or released [4,5]. Tg only involves a change in heat capacity, not latent heat. The percentage crystallinity can be calculated using the latent heat of melting (ΔHm) [6-8].

Vibrating Sample Magnetometry (VSM) measures magnetic properties as a function of magnetic field (H), temperature (T), and time, determining the hysteresis loop that describes magnetic material characteristics [9-15]. The presence of unpaired electrons is a primary requirement for a compound to exhibit magnetic behaviour. The extent of magnetism is directly related to the number of unpaired electrons. When transition metals form coordination compounds, their electron configuration changes affecting both diamagnetism and paramagnetism due to repulsive forces between electrons of ligand and those of metal. The magnetic properties of coordination compounds depend on ligand strength, with paramagnetic or diamagnetic behaviour possible despite a paramagnetic metal ion. Certain metals like 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. Magnetization occurs when current (I) is passed through a coil wrapped around the material, generating an external magnetic field. As current increases, magnetization grows until all dipoles are aligned, reaching a saturation point (point 'a' in Fig. 2) [3]. Reducing current doesn't retrace the path to M = 0; instead, residual magnetization remains (point 'b'), making the sample a permanent magnet [4]. To eliminate magnetization, a negative current is required, bringing M to zero at point 'c' [5]. Further increasing negative current reaches another saturation point (point 'd'). The path traced out, from 'a' to 'f' and back to 'a', forms a hysteresis loop or magnetization curve, characterizing the material's magnetic properties [6].

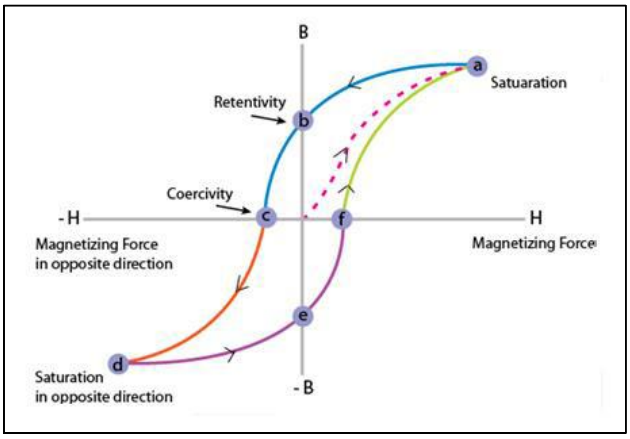

Fig. 2. Hysteresis loop of a magnetic material

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

4. RESULTS AND DISCUSSION

COMPARASION OF THERMAL PROPERTIES:

The glass transition temperature (Tg) of a polymer varies with changes in degree of polymerization or with insertion of additives. According to literature, PVP-30K has a Tg of 163 °C.

The DSC thermogram of the PVP-Mn(II) complex is presented in Fig. 3, illustrating its thermal properties.

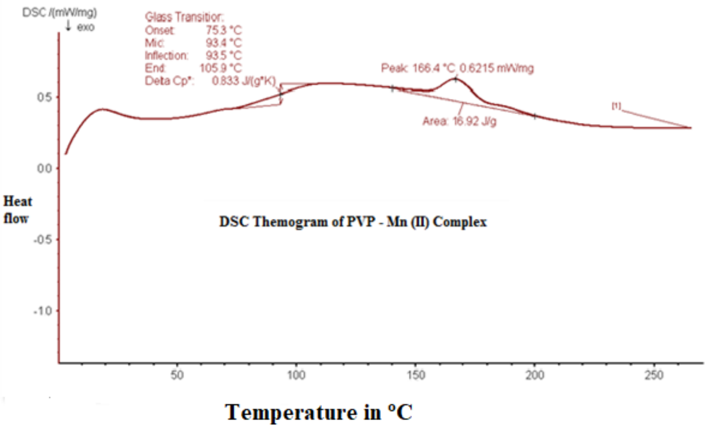

Fig. 3 DSC thermogram of PVP – Mn (II) complex

Thermal Properties of PVP-Mn(II) Complex: The DSC thermogram of the PVP-Mn(II) complex shows a glass transition temperature (Tg) of 93.4°C. This value deviates significantly from the Tg of pure PVP, which is 163°C. This deviation indicates a strong interaction between the PVP polymer and manganese ions, likely due to coordination bonding.

Melting Behaviour: The complex exhibits a melting temperature (Tm) of 166.4°C. The area under the melting peak corresponds to a heat capacity of 16.92 J/g.

Amorphous Nature: The absence of a crystallization dip in the thermogram suggests that the PVP-Mn(II) complex is amorphous in nature.

The DSC thermogram of the PVP-Fe(II) complex is presented in Fig. 4.

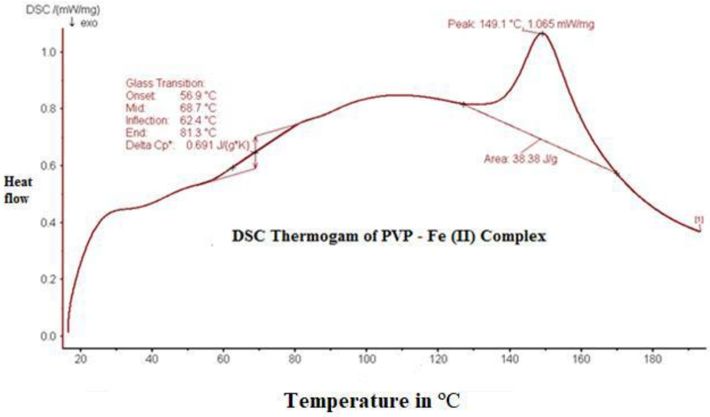

Fig. 4. DSC thermogram of PVP – Fe (II) complex

Thermal Properties of PVP-Fe(II) Complex: The DSC thermogram of the PVP-Fe(II) complex shows a glass transition temperature (Tg) of 68.7°C. This deviation from the Tg of pure PVP indicates a significant interaction between the PVP polymer and ferrous ions, likely due to coordination bonding or complexation.

Melting Behaviour: The complex exhibits a melting temperature (Tm) of 149°C. The area under the melting peak corresponds to a heat capacity of 38.38 J/g, indicating the energy required for melting.

Amorphous Nature: The absence of a crystallization dip in the thermogram suggests that the PVP-Fe(II) complex is amorphous in nature, lacking a crystalline structure.

DSC thermogram of the PVP-Co(II) complex is presented in Fig. 5.

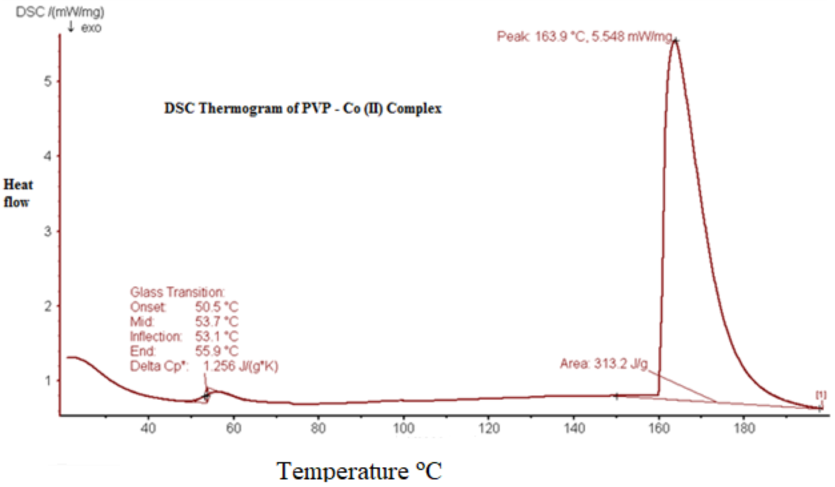

Fig. 5. DSC thermogram of PVP – Co (II) complex

Thermal Properties of PVP-Co(II) Complex: The DSC thermogram of the PVP-Co(II) complex shows a glass transition temperature (Tg) of 53.7°C. This significant deviation from the Tg of pure PVP indicates a strong interaction between the PVP polymer and cobalt ions, likely due to coordination bonding or complexation.

Melting Behaviour: The complex exhibits a melting temperature (Tm) of 163.9°C. The area under the melting peak corresponds to a heat capacity of 313.2 J/g, indicating the energy required for melting.

Amorphous Nature: The absence of a crystallization dip in the thermogram suggests that the PVP-Co(II) complex is amorphous in nature, lacking a crystalline structure.

DSC thermogram of the PVP-Ni(II) complex is presented in Fig. 6.

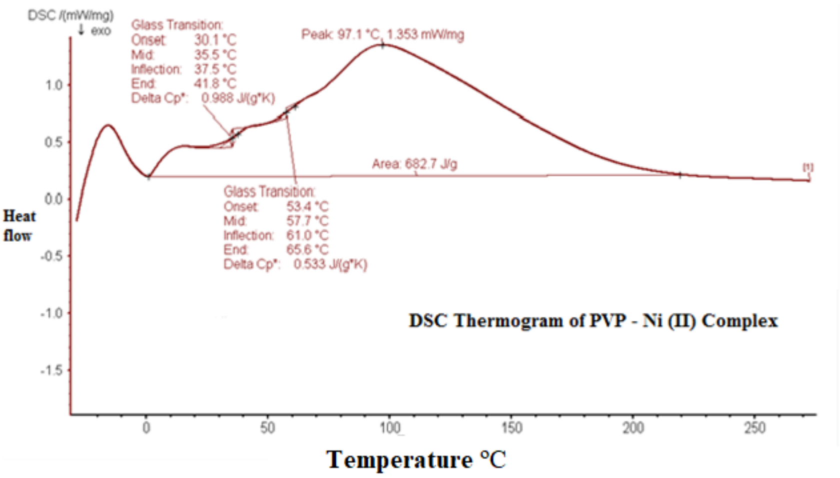

Fig. 6. DSC thermogram of PVP – Ni (II) complex

Thermal Properties of PVP-Ni(II) Complex: The DSC thermogram of the PVP-Ni(II) complex reveals two glass transition temperatures (Tg), 35.5°C and 57.7°C, suggesting phase separation or heterogeneous interactions between PVP and nickel ions.

Melting Behaviour: The complex exhibits a melting temperature (Tm) of 97.1°C, with a heat capacity of 682.7 J/g, indicating the energy required for melting.

Amorphous Nature: The absence of a crystallization dip in the thermogram confirms the amorphous nature of the PVP-Ni(II) complex.

DSC thermogram of the PVP-Cu(II) complex is presented in Fig. 7

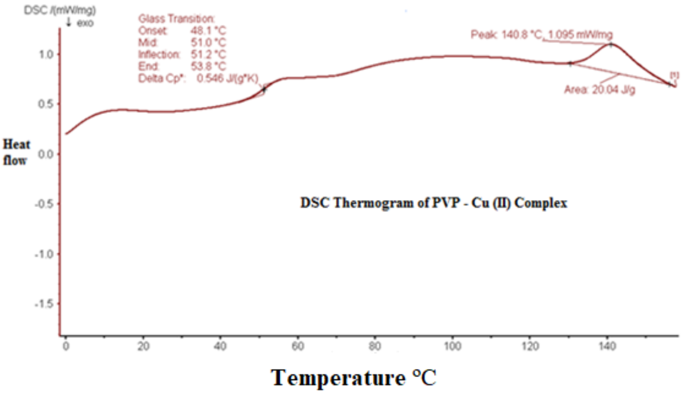

Fig. 7. DSC thermogram of PVP – Cu (II) complex

Thermal Properties of PVP-Cu(II) Complex: The DSC thermogram of the PVP-Cu(II) complex shows a glass transition temperature (Tg) of 51.0°C. This deviation from pure PVP's Tg indicates a significant interaction between the PVP polymer and copper ions, likely due to coordination bonding or complexation.

Melting Behaviour: The complex exhibits a melting temperature (Tm) of 140.8°C. The area under the melting peak corresponds to a heat capacity of 120.04 J/g, indicating the energy required for melting.

Amorphous Nature: The absence of a crystallization dip in the thermogram confirms that the PVP-Cu(II) complex is amorphous in nature, lacking a crystalline structure.

By analyzing these thermograms, researchers can better understand the relationships between polymer structure, metal ion interactions, and thermal behaviour. Comparison of thermal properties and interactions between PVP and different metal ions provide valuable insights into:

- How different metal ions influence the thermal behaviour and structure of PVP complexes.
- The strength and nature of interactions between PVP and metal ions.
- Potential applications of these complexes based on their thermal properties.

COMPARASION OF MAGNETIC PROPERTIES:

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

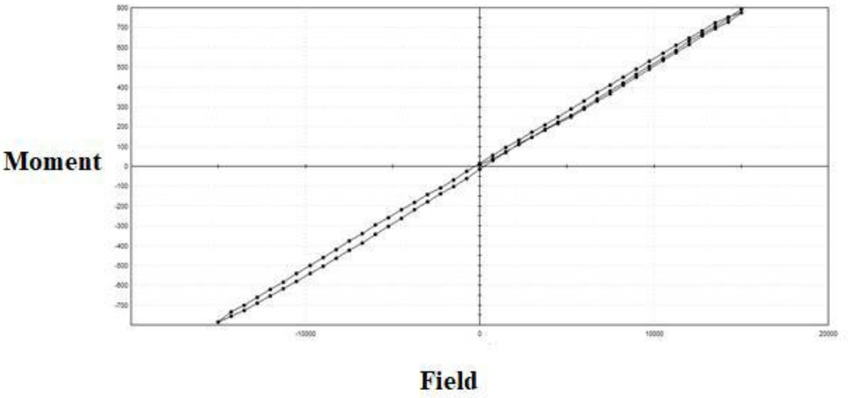

Fig. 8. Magnetization curve of PVP – Mn (II) complex

Magnetic Properties of PVP-Mn(II) Complex: The VSM (Vibrating Sample Magnetometer) curve of the PVP-Mn(II) complex reveals linear magnetization behaviour, indicating that the complex is isotropic. This means that the dipole moments realign without randomness as the applied magnetic field (H) varies.

Saturation Magnetization: The sample reaches saturation magnetization at approximately 15,000 G (Gauss), indicating the maximum alignment of dipole moments.

Paramagnetic Nature: The absence of residual magnetization (M = 0) at zero applied field (H = 0) confirms that the PVP-Mn(II) complex is paramagnetic. This means that the complex does not retain any magnetization when the external magnetic field is removed, and it does not behave as a permanent magnet.

Implications: The paramagnetic nature of the PVP-Mn(II) complex suggests potential applications in areas such as magnetic resonance imaging (MRI), magnetic sensing, biomedical applications.

Fig. 9 shows the magnetization curve of PVP – Fe (II) complex.

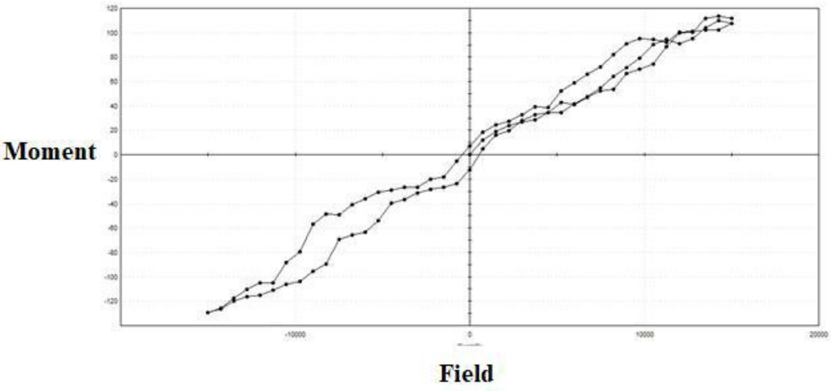

Fig. 9. Magnetization Curve of PVP – Fe (II) complex

Magnetic Properties of PVP-Fe(II) Complex: The VSM curve of the PVP-Fe(II) complex shows curvilinear magnetization, indicating anisotropic behaviour. This suggests that the dipole moments align randomly in response to varying applied magnetic fields.

Ferromagnetic Behaviour: At low dipole moments and zero external field, a small residual magnetization is observed, indicating ferromagnetic behaviour. This means that the complex retains some magnetization even in the absence of an external magnetic field.

Paramagnetic Behaviour: At higher applied fields, the complex exhibits paramagnetic behaviour, where the magnetization is directly proportional to the applied field.

Implications: The dual magnetic behaviour of the PVP-Fe(II) complex, exhibiting both ferromagnetic and paramagnetic properties, makes it an interesting material for further research and potential applications.

Fig. 10. Shows the magnetization curve of PVP – Co (II) complex.

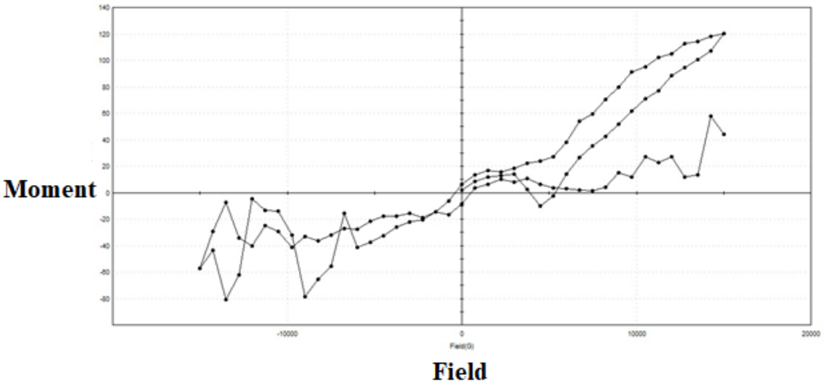

Fig. 10. Magnetization Curve of PVP – Co (II) complex

Magnetic Properties of the Complex: The magnetization curve (Field, H vs. dipole moment, μ) exhibits abrupt local maxima and minima, indicating complex magnetic behaviour and non-linearity in dipole moment, suggesting high anisotropy. The dipole moments are extremely random when the field is switched between positive and negative values.

Ferromagnetic and Paramagnetic Behaviour: The complex is predominantly paramagnetic suggesting that it is mostly influenced by the external magnetic field. Small traces of ferromagnetic nature are observed at zero external field and around 5,000 G.

Implications: The complex magnetic behaviour of the PVP-Co(II) complex, as shown in Fig. 11, makes it an interesting material for further research and potential applications in magnetic sensing, biomedical applications.

Fig. 11. Shows the magnetization curve of PVP – Ni (II) complex.

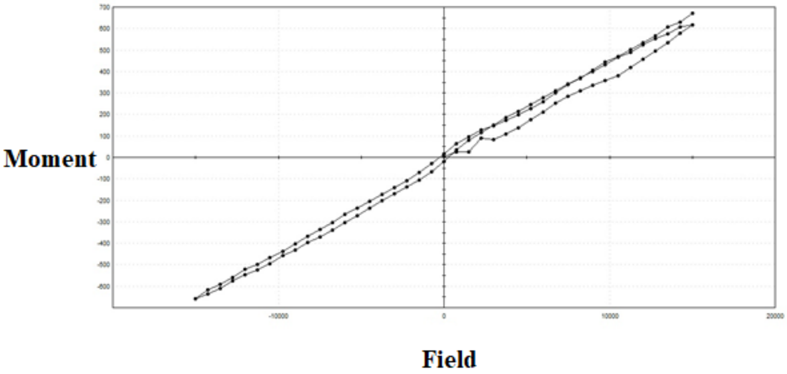

Fig. 11. Magnetization Curve of PVP – Nickel (II) complex

Magnetic Properties of PVP-Ni(II) Complex: The VSM curve of the PVP-Ni(II) complex exhibits linear magnetization: indicating isotropic behaviour. As the applied field (H) varies between positive and negative values, the dipole moment realign without randomness, showing that the complex is isotropic. Saturation is observed at approximately 15,000 G.

Paramagnetic Nature: The complex exhibits no residual magnetization at zero applied field (H = 0). Consequently, it may not turn into a permanent magnet for the given domain. It is only paramagnetic. The similarity in behaviour with the PVP-Mn(II) complex suggests potential similarities in their magnetic properties.

Fig. 12. Shows the magnetization curve of PVP – Cu (II) complex.

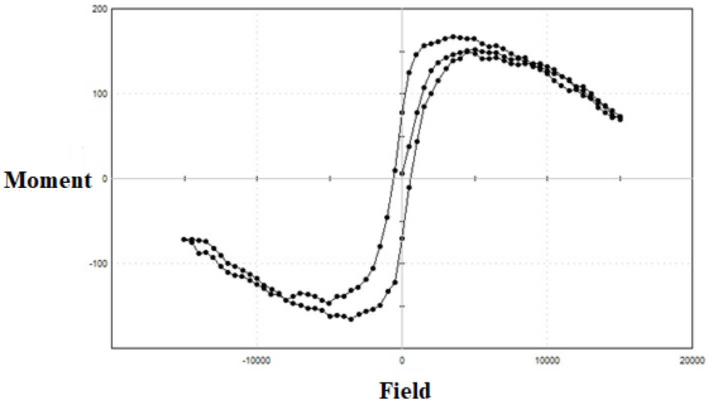

Fig. 12. Magnetization Curve of PVP – Cu (II) complex

This suggests a dual magnetic behaviour, with permanent magnetism at lower fields and paramagnetism at higher fields.

Magnetic Properties of PVP-Cu(II) Complex: The PVP-Cu(II) complex exhibits permanent magnetism, retaining a non-zero residual dipole moment even at zero applied field. As the applied field increases, magnetization initially increases, but at higher fields, the dipole moment decreases, and the complex exhibits paramagnetic behaviour, eventually saturating.

Dual Magnetic Behaviour: The complex exhibits permanent magnetism: at lower fields and paramagnetism at higher fields, with saturation.

Implications: This dual behaviour suggests potential applications in magnetic storage, magnetic sensing and biomedical applications.

5. CONCLUSION

DSC studies confirm that the PVP-metal complexes are amorphous, characterized by the absence of a crystallization dip in the thermogram. This suggests a disordered structure. VSM studies reveal that all complexes exhibit paramagnetic behaviour, while the PVP-Fe(II) complex shows ferromagnetic properties.

Implications: The combination of amorphous structure and varying magnetic properties makes these complexes interesting for further research and potential applications in magnetic materials, biomedical field and advanced technologies. Further analysis can provide insights into the properties and potential uses of these complexes.

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