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KINETIC AND THERMODYNAMIC ASPECTS OF METAL-LIGAND COMPLEX FORMATION IN AQUEOUS AND NON-AQUEOUS MEDIA

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Abstract

In the field of coordination chemistry, the creation of metal-ligand complexes is a key process that has wide-ranging ramifications in the fields of biological systems, catalysis, environmental research, and material design. Within the scope of this investigation, the kinetic and thermodynamic features of metal-ligand complexation in both aqueous and non-aqueous environments are investigated. Particular attention is paid to the impact of the solvent environment, the properties of the metal ions, and the characteristics of the ligand. Various thermodynamic parameters, including stability constants (logarithm of K), Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), are subjected to a thorough analysis in order to get a comprehensive understanding of the factors that contribute to the complicated stability and selectivity of a material. In order to get a better understanding of the dynamic behaviour of these systems, kinetic studies concentrate on the formation and dissociation rates of complex systems, as well as activation energies and processes. The results of a comparative investigation show that aqueous media tend to favour quicker kinetics due to high polarity and solvation effects. On the other hand, non-aqueous solvents frequently demonstrate better complex stability due to decreased dielectric constants and distinct solvation structures. The relationship between kinetic accessibility and thermodynamic stability under different solvent conditions is highlighted, which provides a thorough knowledge of the interactions between metals and ligands and guides the rational design of complexes for specific applications in a variety of chemical environments.

Keywords: *Thermodynamic, Kinetic, Metal-Ligand, and Non-Aqueous*

Introduction

Coordination chemistry is built on the foundation of the creation of metal-ligand complexes, which also play an essential part in a broad variety of chemical and biological processes. Catalysis, electroplating, water purification, and drug design are just some of the commercial applications that rely heavily on these complexes. Not only are they essential for understanding processes like enzymatic catalysis, metal ion transport, and detoxification in living organisms, but they are also essential for industrial applications. The stability, reactivity, and functionality of the complex that is produced as a result of the contact between a metal ion and a coordinating ligand are all determined by the nature of the interaction. Thermodynamics and kinetics are the two primary factors that determine the development and behaviour of metal-ligand

complexes. Thermodynamics is concerned with the stability of a complex, which refers to the probability that the complex will form under circumstances of equilibrium as well as the degree to which the ligand attaches to the metal ion more firmly. The quantification of this phenomenon is often accomplished through the use of formation (stability) constants and the accompanying thermodynamic parameters, which include Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These metrics provide insight into the nature of complex creation as well as the attractiveness of complex formation, regardless of whether it is driven by enthalpy or entropy. Kinetics, on the other hand, investigates the pace at which metal-ligand complexes are formed and dissociated, therefore offering insight on the molecular pathways that are involved. When it comes to dynamic systems, where the time-scale of complex creation can have a substantial influence on biological function or industrial performance, this is of utmost importance. Kinetic parameters, which include rate constants and activation energies, are useful in determining whether a system is controlled by kinetic or thermodynamic forces, as well as if intermediary species or transition states play a part in the complexation process as a whole. It is important to note that the solvent medium is a significant factor in both the thermodynamic and kinetic behaviour of interactions between metals and ligands. Due to the fact that aqueous media are extremely polar and capable of significant hydrogen bonding, they make it easier for ligand exchange processes to occur quickly and with high solubility, particularly for metal ions that are easily displaced. On the other hand, the robust hydration shell that surrounds metal ions can occasionally make complexation with ligands that are less hydrophilic more difficult. Non-aqueous solvents, on the other hand, such as ethanol, acetone, dimethyl sulfoxide (DMSO), and acetonitrile, have a wide range of dielectric characteristics and solvation behaviours. They frequently stabilise a variety of species and favour the formation of novel coordination geometries. Although the decreased dielectric constant and changed solvation shell in non-aqueous media might result in stronger binding interactions, it is also possible that reaction kinetics will be slowed down as a result of the decreased mobility of ions and molecules. A fundamental grasp of coordination chemistry is enhanced by gaining an awareness of how kinetic and thermodynamic aspects are modified by the medium. This understanding not only gives practical advice in the construction of complexes with customised properties that can be utilised in a variety of situations, but it also enriches the understanding overall. In order to highlight solvent-dependent trends, mechanistic changes, and implications for real-world applications, the purpose of this work is to examine and compare the kinetic and thermodynamic properties of metal-ligand complexation in both aqueous and non-aqueous systems simultaneously.

Furthermore, the kinetics and thermodynamics of complex formation are substantially impacted by the nature of the metal ion and ligand structure that is ultimately selected. A theoretical framework that may be used to anticipate and analyse the intensity and selectivity of these interactions is provided by the hard and soft acid-base (HSAB) principles. In general, hard metal ions, which include alkali and alkaline earth metals, tend to form more robust complexes with hard donor ligands (for example, carboxylates and amines). On the other hand, soft metal ions, which include transition and post-transition metals, prefer soft donor ligands (for example, phosphines and thiols). The activation energy barriers for complex formation and dissociation are modulated by these preferences, which not only have an effect on the stability constants but also on the activation energy barriers. Metal ions are found in a highly hydrated state in aqueous environments, where they are surrounded by water molecules that are strongly linked to one another. There are kinetic barriers that have an effect on the substitution of water ligands by other ligands. These barriers change depending on the charge density, size, and electronic configuration of the metal ion. As an example, transition metals like Fe3+ or Cr3+ have a tendency to have slower ligand exchange rates when compared to labile ions like

Cu3+ or Zn3+. In non-aqueous systems, pH, ionic strength, and temperature are factors that have a reduced but still substantial impact in determining these variances. These variations are further influenced by these external factors. Different coordination behaviours may be shown by metal ions in non-aqueous solvents, which are characterised by the substitution of less polar or aprotic molecules for water particles. It is possible, for instance, for the coordination number and shape of complexes to alter in DMSO or acetonitrile as a result of variations in solvation energy and steric effects. When compared to aquatic systems, these variations frequently result in increased stability constants and changed kinetic profiles. In addition, non-aqueous conditions make it possible to access metal-ligand complexes that are either unstable or insoluble in water, which broadens the scope of coordination chemistry. A comparative knowledge of how solvents impact the stability as well as the formation and dissociation rates of metal-ligand complexes is still lacking, despite the significant work that has been made in this area. The majority of the research that has been done has concentrated either on the thermodynamic stability of isolated systems or on kinetic mechanisms that do not involve a parallel consideration of thermodynamics. In order to close this knowledge gap, it is necessary to use a comprehensive strategy that investigates both the kinetic and thermodynamic characteristics over a wide range of solvent conditions.

THERMODYNAMIC AND KINETIC STABILITY

By distinguishing between the thermodynamic phrases stable and unstable and the kinetic terms labile and inert, it is possible to gain a better understanding of the kinetics and processes of metal complexes. As an illustration, take into consideration the cyano complexes, which are [Ni(CN)4] 2-, [Mn(CN)6] 3-, and [Cr(CN)6] 3-. In terms of kinetics, these complexes are distinct from one another, despite the fact that they are stable from a thermodynamic point of view. When it comes to the cyanide exchange reaction, the rates of exchange of radiocarbon-labeled cyanide are quite variable. Nitrogen(CN)4 The compound [Mn(CN)6] performs a fast exchange of cyanide ions (t1/2≈ 30 s). 3- undergoes transitions at a moderate pace (t1/2 ≈ 1 hour), while [Cr(CN)6] 3- is rather inactive (t1/2 = 24 days). At a temperature of 25 degrees Celsius, complexes that undergo a full reaction within one minute are regarded to be labile, whereas complexes that take longer to react are thought to be inert. Nitrogen(CN)4 An excellent illustration of a complex that is thermodynamically stable yet kinetically unstable is the compound 2-. It is possible to establish a connection between the readiness of Ni2+ to form complexes with five or six coordinates and the tendency of Ni2+ to create complexes with four coordinates. One way in which the loss of ligand field stabilisation energy is somewhat compensated for is by the increased bond energy that is present in the fifth or sixth bond. An example of a complex that is kinetically inert but thermodynamically unstable is the [Co(NH3)6] 3+ cation that is found in acid solution. Although the thermodynamics are favourable, the complex must be allowed to degrade at room temperature for a number of days before it can be considered complete. It has been hypothesised that the inertness of the complex is due to the absence of an appropriate low-energy route for the acidolysis process. There must be either an unstable seven-coordinate species or a five-coordinate species involved in the reaction for [Co(NH3)6] 3+. This reaction must also entail a loss of energy and LFSE simultaneously.

Valence Bond Theory

For the purpose of explaining the lability and inertness of complexes, a number of different theories have been proposed. The Valence Bond Theory identifies two distinct forms of octahedral complexes: 1) outer orbital complexes, which employ sp3d 2 hybridisation, and 2) inner orbital complexes, which employ d 2

sp3 hybridisation. Both of these approaches are referred to as hybridisation. It is typically true that outer orbital complexes are unstable. There is a correlation between this weakening and the decreased strength of the bonds of sp3d 2 in comparison to the bonds of d2 sp3. If all three t2g levels in an inner orbital complex are filled, either singly or doubly, then the complex is inert kinetically. This is the situation when the complex is an inner orbital complex. In the event that an inner orbital complex involves the presence of one or two electrons belonging to the t2g set, then at least one level will be unoccupied. As an illustration, in the case of [V(H2O)]3+, two of the three t2g levels are occupied in a single manner. Because of this, the third level can be utilised to receive the electron pair that is handed over by the entering ligand, resulting in the formation of a 7-coordinated intermediate that is less stable. A substitution product is produced as a result of the expulsion of one of the initial six ligands, which causes [V(H2O)]3+ to be unstable. This is done in order to stabilise the compound. This combination, however, is inert because there is no d level that is unoccupied in [Cr(H2O)]3+, which would allow it to take the electron pair that is being provided by the incoming ligand.

Taube's Explanation

It has been suggested by Taube that the degree of lability or inertness of a transition metal complex can be connected with the d electronic configuration of the metal ion. It is reasonable to anticipate that the electrons in a complex that comprises antibonding eg* orbitals will be loosely bonded and quickly shifted; this complex is characterised as being labile. When the metal in question has a t2g orbital that is vacant, the four lobes of that orbital correspond to the directions from which an incoming ligand can approach the complex with a relatively low level of electrostatic repulsion. As a result, it is possible to draw the conclusion that a complex that contains one or more eg* electrons or that contains less than three d electrons ought to be very labile, but a complex that contains any other electronic configuration ought to be generally inert.

Crystal Field Theory

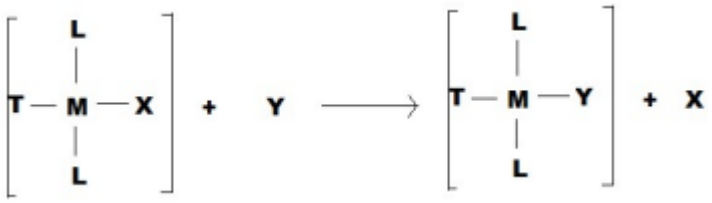
Crystal Field Activation Energy is defined as the change in the Crystal Field Stabilisation Energy that occurs when the reactive complex is changed into the transition state. This definition comes from the theory of crystal fields.

CFAE = CFSE of intermediate – CFSE of reacting complex

The conclusion that can be drawn from this is that octahedral complexes that have CFAEs that are either negative or zero would be unstable, whereas those that have CFAEs that are positive would be sluggish to respond. There is a possibility that octahedral complexes with metal ion topologies of d3 and spin paired d5 and d6 and, to a certain extent, d4 might be sluggish to react via the SN1 and SN2 mechanism. This is because the strong field forces electron spins to couple together. To a similar extent, octahedral complexes that have a metal ion configuration of d8 would have a sluggish reaction rate regardless of the intensity of the ligand field and the mechanism of substitution reaction. Octahedral complexes that have spin-free d4 configurations, d5 configurations, d6 configurations, d7 configurations, d9 configurations, and d10 configurations have CFAEs that are either negative or zero, and as a result, they are potentially unstable.

Nucleophilic Substitution Reactions In Square Planar Complexes

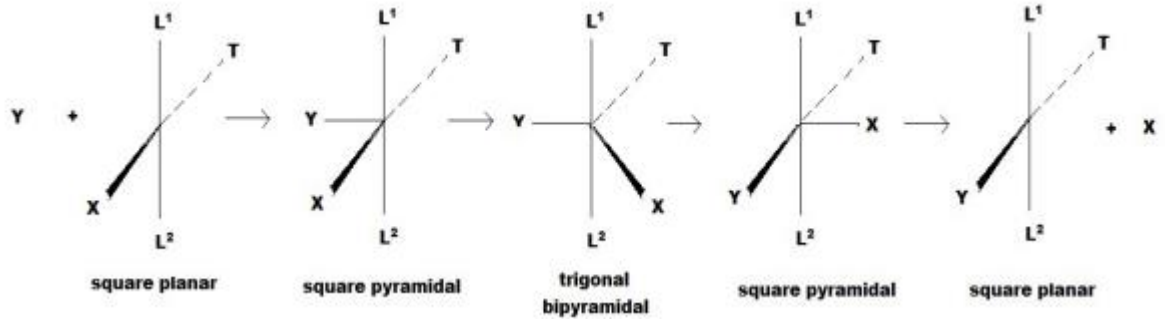
Square planar complexes with d^8 The sort of substitution reactions that configurations go through are as follows:



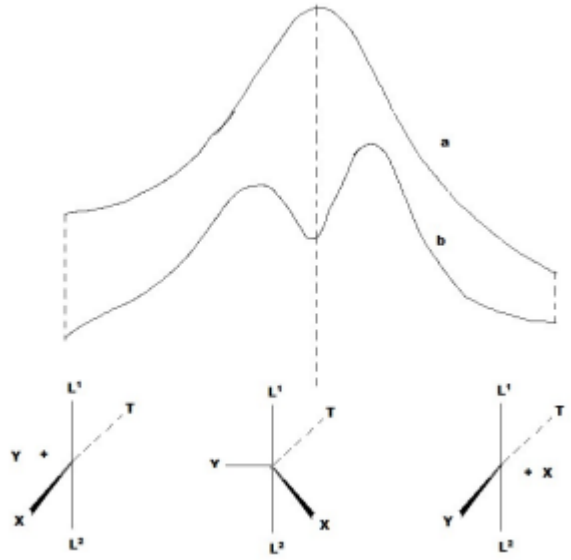
In this scenario, Y represents the nucleophilic ligand that is entering, X represents the ligand that is exiting, and T represents the ligand that is trans to X.

MECHANISM

As a result of the relatively slow replacements, Pt(II) complexes are frequently utilised for the purpose of investigating the mechanism and kinetics. This is because the substitutions are easier to investigate. Scientists have arrived at an associative SN2 mechanism for substitution reactions in square planar complexes through the use of kinetic investigations. Take into consideration a nucleophile Y that is attacking a d8 complex from either side of the equation plane. Repulsion is experienced by the ligand from the filled metal d orbitals as well as from the bonding electrons. This is in addition to the fact that the ligand is drawn to the electron-deficient metal centre. Although electrical repulsions and steric considerations impede the attack, it coordinates to the metal through an empty pz orbital to create a square pyramidal species. This occurs despite the fact that the attack does not proceed immediately. When the square pyramidal species is generated, it will go through a transition that will result in the production of a trigonal bipyramidal structure. It is going to have three ligands in its equatorial plane, which are going to be Y, T, and X. Additionally, two of the groups that were trans to each other in the initial complex are going to occupy the axial positions. As soon as X moves away from the trigonal plane, the T-M-Y angle will become more wide, and the geometry will travel through a square pyramid on its approach to the square planar product.



It is possible for the trigonal bipyramidal species that is produced during the reaction to exist either as an activated complex or as a genuine intermediate. The difference between the two is determined by the length of time that the species has been around. The arrangement of the reactants and products at a peak in the energy curve of the reaction profile, also known as the transition state, is what is meant by the phrase "activated complex." The word "intermediate" suggests that a species has an observable lifespan, even if it is a brief one, and that it is at least slightly more stable than any activated complexes.



The coordinates and energy profile of a square planar substitution reaction that include a trigonal bipyramidal activated complex and a trigonal bipyramidal intermediate are presented here.

KINETICS

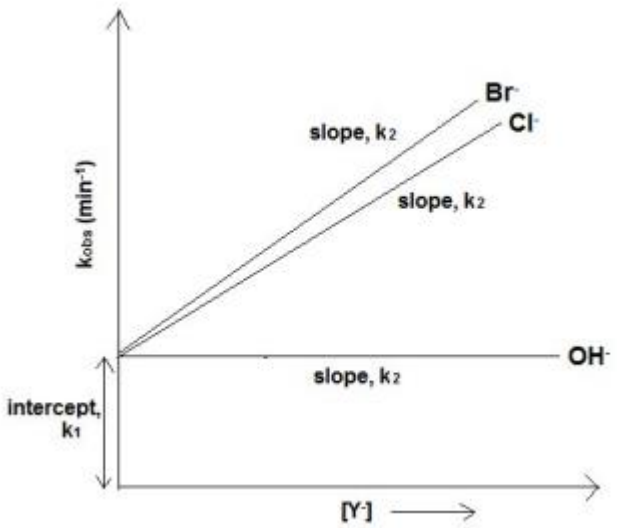
It is possible to show the kinetics of the reaction by using the reaction itself,

$[PtA3X]^{n+} + Y^- \rightarrow [PtA3Y]^{n+} + X^-$ in the presence of water.

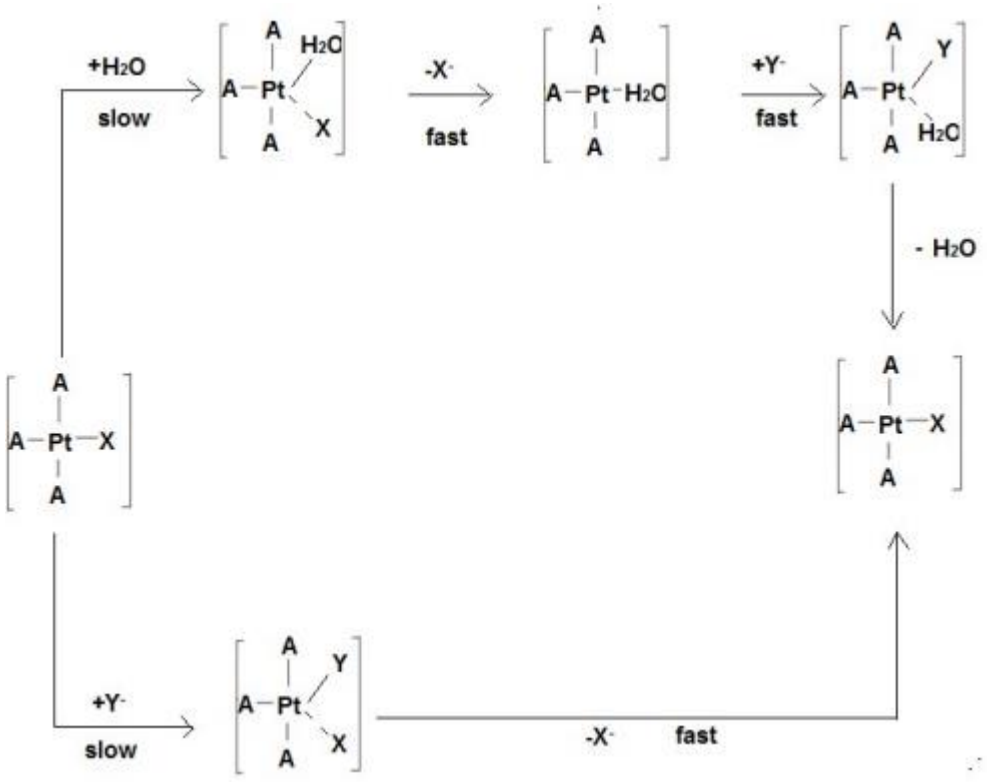
For this reaction, a two term rate law was found out.

$$\text{Rate} = k_1[PtA_3X^{n+}] + k_2[PtA_3X^{n+}]\,[Y^-]$$

k1 represents the first order rate constant for a reaction that is controlled by a solvent, and k2 represents the second order rate constant for a reaction that involves Y-. In order to execute the reactions with a significant amount of nucleophile, Y-, the study of the rate constants is carried out successfully. The observed rate constant, denoted by kobs, conforms to the pseudo first order and is connected to both k1 and k2 by the equation kobs = k1+ k2[Y-]. Therefore, linear graphs of kobs against distinct nucleophile concentrations, denoted by [Y-], should be constructed for the same complex. These plots should have the same intercepts, k1, but different slopes, k2.



The plots representing the kobs for the reaction [Pt(dien)Cl]+ + Y- → [Pt(dien)Y]+ + Cl- are plotted versus the concentration of the nucleophile, [Y-]. With the rate law that was obtained, it can be deduced that the reaction between [PtA3X]n+ and Y-, which results in the formation of [PtA3Y]n+, takes place by a two-path mechanism. However, only one of these mechanisms requires Yin as the rate-determining step.



Whereas the bottom path is the direct way (also known as the reagent path), the top path is the solvent path, which is also referred to as the Y- independent path. Over the course of the solvent route, the X- ion is gradually replaced by the solvent H2O. Shortly after that, Y- takes its position in a swift and decisive manner. According to the results of the experiments, the Yin-independent path is not an SN1 process; rather, it is a direct SN2 displacement of the leaving group by the nucleophile in a path that is presumably of the second order, whereas the solvent path yields pseudo first order kinetics. In contrast to the rate constant k2,

which is caused by the direct displacement of the leaving group by the nucleophile, the rate constant k1 is caused via the solvent route. It is therefore possible to name the solvent path k1 as ks and the direct displacement path k2 as kY in order to ensure that

$$k_{obs} = k_s + k_Y[Y^-]$$

Thermodynamic Considerations

Irving and Williams (1953) were among the first researchers to construct the well-known Irving-Williams series, which rates the stability constants of divalent first-row transition metal complexes. This series was established from the results of early experiments. The results of their research laid the groundwork for the knowledge that the stability of metal-ligand complexes is affected by the ionic radius as well as the electronic configuration of the metal ions. Since then, the thermodynamic parameters, particularly the formation constant (K), Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°), have been extensively utilised for the purpose of describing and forecasting the behaviour of complexes. A detailed analysis of metal-ligand stability in aqueous solution was presented by Martell and Hancock (1996). They placed particular emphasis on the role that the solvent dielectric constant and hydration energy play in this process. The researchers found that high dielectric solvents, such as water, enhance ion dissociation and promote complexation through favourable electrostatic interactions. However, it is possible that these solvents may also compete with ligands due to the intense solvation of metal ions. On the other hand, Rabenstein and Isab (1982) conducted research that investigated thermodynamic stability in non-aqueous systems. They found that lower dielectric media, such as methanol and DMSO, have a tendency to produce higher apparent stability constants. This is because there is less competition from solvent molecules and there is limited solvation of free ions in these media.

Kinetic Aspects of Complex Formation

In addition, the kinetics of interactions between metals and ligands has been a significant area of research. Both Taube (1952) and Basolo and Pearson (1967) were pioneers in the field of ligand substitution kinetics. They classified metal complexes as either labile or inert depending on the exchange rates of their ligands. The results of their study lay the framework for understanding the processes that drive ligand exchange, including associative, dissociative, and interchange pathways. In more recent studies, such as the ones conducted by Lincoln and Wilkins (1991), the stopped-flow spectrophotometer was utilised to investigate the fast kinetics of metal-ligand synthesis in both aqueous and mixed solvent systems. The results of their investigation indicate that the reaction route and activation energy can undergo considerable modifications in response to variations in the composition of the solvent, the pH, and the ionic strength.

Role of Solvent Medium

Not only does the solvent medium modify the thermodynamic favorability of complex formation, but it also changes the rate at which ligands are exchanged. This is a twofold contribution that the solvent media makes. The importance of solvation dynamics and solvent coordination in the regulation of metal-ligand interactions was brought to light by research conducted by Bjerrum (1957) and Burgess (1978) in subsequent experiments. It is possible for strong hydrogen bonding and solvation shells surrounding metal ions to slow down the replacement of ligands in aqueous environments, unless the substitution is driven by enthalpic or entropic forces.

In contrast, research conducted by Cummings and Rosenberg (1980) in non-aqueous solvents demonstrated that the reduced coordinating capacity of such media might minimise the amount of competition amongst solvents and favour quicker coordination with incoming ligands. This was particularly true in polar aprotic solvents such as acetonitrile or DMSO.

Comparative Studies in Mixed and Non-Aqueous Media

Gritzner and Kuta (1984) After conducting comparative investigations on complex formation in water, methanol, ethanol, and acetone, researchers came to the conclusion that the change in the dielectric constant of the solvent has a direct correlation with the observed variance in equilibrium and rate constants across the different solvents. In addition to this, they observed substantial variations in coordination geometry and oxidation states, which were determined by the polarity of the solvent.

Khalil et al. (2005) a number of different solvents were used to explore the complexation of transition metals with Schiff bases. The results showed that there were significant differences in both the stability constants and the reaction processes. When it comes to comprehending complexation behaviour, their findings emphasise the significance of taking into account solute-solvent interactions, particularly hydrogen bonding, solvation shells, and the viscosity of the solvent.

Application-Driven Studies

In addition, recent research has placed an emphasis on the practical significance of solvent effects on the interactions between metals and ligands. Koeppe et al. (2012), for instance, investigated the ways in which the design of metal-based catalysts is affected by the kinetic and thermodynamic characteristics present in various solvents during the experiment. Similarly, research in the pharmaceutical industry has been centred on optimising the stability of metallodrugs (such as cisplatin analogues) in biological fluids (Patel et al., 2018). Particular emphasis has been paid to the mimicking of solvents and the kinetics of complexation.

Conclusion

Exploring the process of metal-ligand complex formation is crucial for delving into the core concepts of coordination chemistry and their various practical uses in domains including environmental chemistry, biology, materials science, and catalysis. The study of metal-ligand interactions in aqueous and non-aqueous environments, including their kinetic and thermodynamic properties, shows that the solvent environment significantly affects complex behaviour. Thermodynamically speaking, aqueous solvents aid in the dissociation of ionic species and frequently promote the quick creation of complexes due to their strong solvation capabilities and high dielectric constant. The apparent stability constants can be reduced and ligand access can be hindered when firmly bound hydration shells surround metal ions. On the other hand, complexes are stabilised more efficiently in non-aqueous solvents, especially polar aprotic media such as DMSO and acetonitrile, since free metal ions are weakly solvated. This results in greater formation constants and different coordination geometries. Because water is a transition-state medium and reactants are very mobile in it, ligand exchange reactions in water tend to be quicker, especially for labile metal ions. Although complexes formed in non-aqueous media tend to be more stable, their kinetic behaviour may be slower than in water-based media owing to factors including decreased ion mobility, viscosity effects, and the specifics of solvent-ligand competition. The individual ligand and metal, as well as the solvent, pH, and temperature, can alter the process of complex formation, which can be associative, dissociative, or exchange. Based on

the results of the comparison, it is clear that there is no one best solvent system; rather, the selection of a medium should be in accordance with the desired chemical result, whether it improved complex stability, faster reaction kinetics, or exact control over geometry and oxidation states. Thermodynamic and kinetic studies of metal-ligand systems in relation to solvents help chemists design reactions for specific uses, such as reliable medication delivery systems or effective catalysis. Finally, the significance of a dual kinetic-thermodynamic method in assessing the development of metal-ligand complexes is emphasised by this work. The importance of the solvent environment as a dynamic and equilibrium-determining agent in coordination processes is highlighted. Further study in this area, especially with new ligands and mixed solvent systems, will improve our capacity to create and manage complicated chemical systems in both watery and dry settings.

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