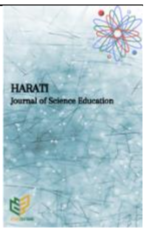
HJSE 1(2) (2024)

Harati – Journal of Science Education

https://journal.aishaedu.com/index.php/hjse/about



Hard and Soft Acids and Bases (HSAB): Investigating Adduct Formation in Non-Aqueous Solvent Media with Selected Divalent Class B Metal Ions in Chemistry

Felicity Uju Onwudinjo[1*]

[1] Department of Chemistry, Nwafor Orizu College of Education Nsugbe, Anambra State, Nigeria

onwudinjo.felicity@nocen.edu.ng

Abstract. *This study explores the Lewis acid/base interactions of divalent metal ions – copper (II), lead (II), and mercury (II) – with Lewis bases 2-naphthol and caffeine in an ethanol solvent. Utilizing the method of continuous variation, absorbance data were analyzed to understand these interactions. Absorbance data analyzed through Job's plot revealed distinct interaction patterns. For the copper (II) system, the Job's plot did not exhibit a maximum, indicating a lack of significant cooperative interaction, with absorbance values fluctuating without a clear pattern. In contrast, the lead (II) and mercury (II) systems demonstrated clear maxima with both 2-naphthol and caffeine, evidencing cooperative interactions. Specifically, the Job's plot for lead (II) with 2-naphthol peaked at an absorbance of 1.25 at a mole ratio of 1:1, and for mercury (II) with caffeine, a maximum absorbance of 1.40 was observed at the same stoichiometry. These results indicate a 1:1 stoichiometry for the adducts formed, suggesting that the interactions of these metal ions with the bases can be described by the Eigen-Wilkins mechanism. This mechanism may thus account for the adduct formation involving the class B Lewis acids studied in a non-aqueous medium, highlighting a distinctive aspect of their chemical behavior.*

Keywords: Lewis's acid, Lewis's base; adduct-formation; cooperative interaction; Job's procedure.

Introduction

The Hard and Soft Acids and Bases (HSAB) principle, introduced by Ralph Pearson in the 1960s, serves as a framework for understanding the interaction preferences between different chemical species. This theory categorizes acids and bases as either "hard" or "soft," and posits that hard acids prefer to bind with hard bases, while soft acids prefer soft bases. The concept of hardness and softness is primarily based on the acid or base's polarizability and the energy required to remove an electron (Gregory et al., 2021; Islam & Ghosh, 2014). This theory has profound implications in various fields of chemistry, including organometallic chemistry, catalysis, and environmental chemistry, offering insights into the mechanisms of reaction pathways, the stability of complexes, and the specificity of chemical interactions.

Lewis's definition of acids and bases, along with the concept of the electron pair bond, has had a profound impact on the field of Chemistry. These theories are fundamental to understanding compound formation and reaction mechanisms. However, there is still much untapped potential in applying these concepts, particularly in studies involving the formation of intermediates or activated complexes. The investigation of adduct formation between divalent Class B metal ions and ligands in non-aqueous solvent media exemplifies the application of the HSAB principle in understanding chemical reactivity and stability. Class B metal ions, characterized by their softness, include transition metals like copper (II), silver(I), and gold(I). These ions have a preference for coordinating with soft bases due to their larger size, lower charge density, and higher polarizability compared to hard acids (Ho et al., 2022).

Non-aqueous solvents, such as dimethyl sulfoxide (DMSO), acetonitrile (ACN), and others, provide unique environments for the formation of metal-ligand adducts. These solvents can influence the stability and reactivity of the complexes formed due to their dielectric properties, ability to solvate ions, and their own HSAB characteristics (Lutz et al., 2017; Osada et al., 2016). For example, DMSO, being a soft base, can stabilize soft metal ions, facilitating the formation of adducts with other soft bases present in the solution. The formation of "adduct-like" intermediates and stable isolable complexes provides insights into nucleophilic and electrophilic steps, both in aqueous and non-aqueous or mixed media environments. The Lewis donor/acceptor concept serves as a framework for evaluating proposed reaction mechanisms, distinguishing between those deemed reasonable or unreasonable.

Non-aqueous media present a rich array of reactions, ranging from those in dipolar hydrogen-bonded solvents to non-polar solvents. These solvents, particularly hydrogen-bonded and dipolar aprotic types, play a crucial role in chemical reactions involving metal ions in solution. For example, ethanol exemplifies a non-aqueous solvent where the Eigen-Wilkins mechanism for complex formation may be applicable (Brisbin and Richards, 1972). Additionally, Duffus (2002) highlights the significance of metal ions as Lewis acids in interactions with living systems. This perspective suggests a shift towards predicting preferred ligands and the overall properties of resulting metal complexes. This approach contrasts with the inconsistent use of the term "heavy metals" in environmental chemistry literature.

Recent studies have focused on the synthesis and characterization of adducts formed by divalent Class B metal ions in non-aqueous media to explore their potential applications and understand their stability and reactivity patterns. For instance, research by Shimizu et al., 2017) demonstrated the formation of stable adducts between copper (II) ions and thiolate ligands in a non-aqueous medium. The study revealed that the soft-soft interactions between copper (II) and the thiolate ligands were stabilized by the non-aqueous solvent, leading to adducts with significant catalytic and pharmaceutical applications. Furthermore, the investigation into gold(I) and silver(I) ions in non-aqueous solvents has uncovered novel adducts with potential applications in materials science and nanotechnology (Melchior et al., 2017; Sousa et al., 2019). These studies not only validate the HSAB theory but also highlight the critical role of solvent media in influencing the formation and stability of metal-ligand complexes.

The HSAB principle's applicability extends beyond understanding adduct formation to predicting the outcome of displacement reactions, solubility, and extraction processes. For example, the extraction of metal ions from aqueous to non-aqueous phases can be optimized by selecting ligands and solvents based on their HSAB characteristics, thereby enhancing the efficiency of metal recovery and purification processes (Li et al., 2018). Overall, the implications of Lewis's acid-base theory and the donor/acceptor concept extend far beyond basic chemical principles. They provide a framework for understanding complex reactions in various media and offer insights into the behavior of metal ions in solution and their interactions with biological systems. By delving deeper into these theories, we can advance our understanding of chemical reactions and their applications in diverse fields.

Methods

Metode pada penelitian ini adalah kuantitatif yang sistematis. Penelitian ini menggunakan Publish or Perish (PoP) pada analisis bibliometrik dan mencari literatur tentang pembelajaran etnosains pada pembelajaran IPA di SMP.

The following data presents the results obtained from studies conducted in ethanol solvent on two Class B ions: Pb(II) and Hg(II), along with a borderline ion, Cu(II). These experiments illustrate the interactions of each ion with two polarizable monodentate ligands, 2-naphthol and caffeine. The chemicals used in these experiments were as follows:

- Copper (II) sulfate, anhydrous, 97%, obtained from Riedel-de Haën, Seelze, Hannover.
- Lead (II) sulfate, anhydrous, 97%, acquired from B.D.H. Laboratory Reagents, Poole, England.
- Mercury (II) nitrate, 98%, obtained from B.D.H. Laboratory Reagents, Poole, England.
- 2-naphthol, 98%, purchased from Qualikems Fine Chemical Pvt. Ltd.
- Caffeine, extracted from *C. accuminata* and characterized according to the CAS number 58-08-2 before use.

Each chemical was used without further purification, except for drying at 105°C in a hot-air oven for a minimum of three hours. Following this, they were cooled and stored in a desiccator before use. The solvent, ethanol of spectrosol quality, was used as received for the preparation of solutions. The ethanol used was of a purity greater than 96%.

a) Instruments

The experiment employed sophisticated ultraviolet spectrophotometry instruments to ensure precise and accurate measurements. Specifically, the Beckman Coulter DU 520 General Purpose UV/Vis Spectrophotometer, a single-cell model, was used for initial spectral recording and to determine the optimal solvent "windows" for further analyses. This instrument was crucial for establishing baseline absorption spectra and ensuring that subsequent measurements were taken within the appropriate solvent conditions to avoid any interference.

Additionally, for more detailed spectral analysis at predetermined specific wavelengths, the advanced Gilford Response UV/Vis Spectrophotometer was utilized. This scanning, programmable spectrophotometer allowed for high-resolution spectra to be obtained, enabling a more thorough examination of the interactions between the selected metal ions and ligands. The flexibility and precision of this instrument were instrumental in capturing the nuanced spectral changes indicative of complex formation, providing valuable insights into the chemical dynamics at play.

b) Preparation of Stock Solutions

The preparation of stock solutions was carried out with precision to ensure accuracy in the experimental results. For the copper (II) sulfate solution, 20 grams of dried, anhydrous copper (II) sulfate (molecular mass 159.61) were accurately weighed and dissolved in approximately 300 mL of pure ethanol. This solution was then transferred to a 1000 mL volumetric flask and diluted to the mark with ethanol, resulting in a final molarity of 0.125M. Similarly, stock solutions for lead (II) sulfate (molecular mass 303.26) and mercuric nitrate (Hg $(NO_3)2•H2O$, formula mass 342.62) were prepared using 20 grams of each compound. These were dissolved in pure ethanol and made up to 1000 mL in volumetric flasks, yielding molarities of 0.0659M for the lead (II) sulfate solution and 0.0584M for the mercuric nitrate solution, respectively.

The 2-naphthol stock solution was prepared by dissolving 20 grams of dried 2-naphthol (molecular mass 144.06) in ethanol and bringing the volume up to 1000 mL with the same solvent in a volumetric flask, achieving a molarity of 0.1388M. The caffeine solution was also prepared by dissolving 20 grams of caffeine in ethanol to a final volume of 1000 mL, resulting in a molarity of 0.103M. These meticulously prepared stock solutions were fundamental for the subsequent experiments, ensuring consistency and reliability in the investigation of adduct formation.

Results and Discussion

Preliminary spectral data were obtained for each of the various solvents and solution mixtures in these experiments on Deckman Poulper BU 520 General purpose uv/vis spectrophotometer, single cell model. These data, when plotted, show that the wavelength of maximum absorption for each solvent or simple solution is well below 340nm, the lower limit of the available instrument. Subsequent investigations were therefore carried out using the available "windows" in the region between 340nm and 400nm.

a) Spectroscopic Determination of solution mixtures.

Solution mixtures were prepared according to Table 1 below.

Table 1. Solution mixtures

Mixture no.	mL M^{2+}	mL base soln.	Total Volume
1	10	90	100
2	20	80	100
3	30	70	100
4	40	60	100
5	50	50	100
6	40	60	100
7	30	70	100
8	20	80	100
9	10	90	100

$M^{2+} = Cu^{2+}, Pb^{2+}, Hg^{2+}$

With the aid of another uv/vis spectrophotometer, scanning, programmable Gilford Response^{TM}, the absorbance of each solution mixture was obtained at various wavelengths of the uv “window” as determined from the preliminary spectra. All absorbance values were assumed to be directly proportional to the concentration of the species giving rise to them, an assumption that implies Conformity with Beer's law, which should operate in the dilute solutions prepared. The concentration, in mmol, of each component in each solution mixture was obtained by calculation, and a graph of absorbance against mole fraction of component, the so-called Job's plot, was plotted to enable conclusions to be drawn on the mole relationships.

These data are presented in Tables 2-4, and plotted respectively in Figs. 1-3 for Cu (II), Pb (II) and Hg (II). A modification of the Job plot was also attempted to enable an unequivocal stoichiometry to be assigned in each case. This modification entailed holding the concentration of one reactant, the Lewis base, constant, while adding increments of the Lewis acid. 20 mL of the Lewis base was used in each experiment to establish the stoichiometric ratio. End points in such titrations were used to make the assignments. The data are presented in Table 5 while representative plots are shown in Figs, 4.

Table 2 Absorbance data for Job's plot

yol.of Cu^{2+} (mL)	**vol, of 2-naphthol(mL)**	**mmole of Cu^{2+}**	**mmole of 2-naphthol**	**mol fraction of Cu^{2+}**	**Absorbance at 340nm**
l0	90	1.25	12.6	0.09	1.06
20	80	2.50	11.2	0.18	1.40
30	70	3.7	9.8	0.28	1.64
40	60	5.0	8.4	0.37	0.36
50	50	6.25	7.0	0.47	0.25
60	40	7.25	5.6	0.57	0.45
70	30	8.75	4.2	0.67	0.90
80	20	10.0	2.8	0.78	1.95
90	10	11.25	1.4	0.89	2.01

Table 3. Absorbance Data for Pb (II)

yol.of Pb^{2+} (mL)	vol, of 2-naphthol(mL)	mmole of Pb^{2+}	mmole of 2-naphthol	mol fraction of Pb^{2+}	Absorbance at 400nm
10	90	0.66	12.6	0.05	-
20	80	1.32	11.2	0.10	-0.01
30	70	2.00	9.8	0.17	-0.02
40	60	2.64	8.4	0.24	-0.20
50	50	2.30	7.0	0.32	0.04
60	40	4.00	5.6	0.41	0.08
70	30	4.61	4.2	0.52	0.08
80	20	5.27	2.8	0.65	0.06
90	10	5.93	1.4	0.81	0.01

Table 4. Absorbance Data for Hg(II)

yol.of Hg^{2+} (mL)	vol, of naphthol(mL)	mmole of Hg^{2+}	mmole of 2-naphthol	mol fraction of Hg^{2+}	Absorbance at		
					340nm	370nm	400nm
10	90	1.23	12.6	0.09	1.04	0.30	0.17
20	80	2.46	11.2	0.18	1.17	0.19	0.80
30	70	3.70	9.8	0.27	1.36	0.22	0.04
40	60	4.93	8.4	0.37	1.39	0.24	0.12
50	50	6.16	7.0	0.47	1.19	0.24	0.10
60	40	7.39	5.6	0.57	1.32	1.17	0.08
70	30	8.62	4.2	0.67	1.51	0.10	0.05
80	20	9.86	2.8	0.78	1.38	0.09	0.03
90	10	11.09	1.4	0.89	1.23	0.05	0.02

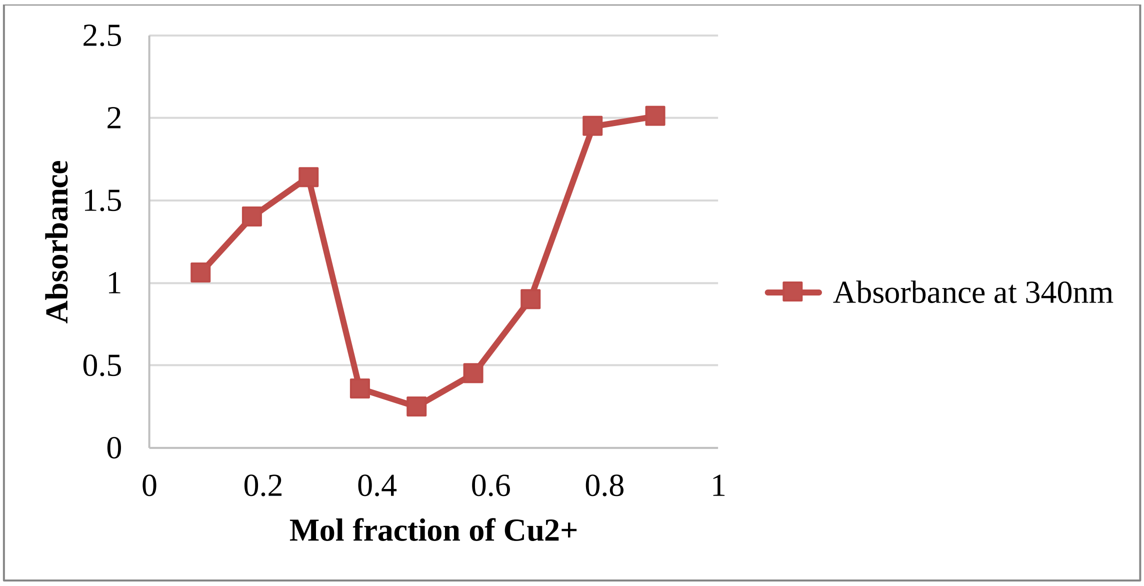


Figure 1. Graph of absorbance versus mol fraction of Cu^{2+}

Figure 1 shows the graph of absorbance versus mol fraction of Cu^{2+}. The data suggests a non-linear relationship between the mole fraction of Cu2+ and its absorbance at 340 nm. Initially, as the mole fraction increases from 0.09 to 0.28, there's a steady increase in absorbance, indicating a direct correlation. However, the trend reverses dramatically as the mole fraction increases further to 0.47, where absorbance decreases significantly, suggesting potential saturation or complex formation that alters the expected absorbance. Surprisingly, from a mole fraction of 0.57 onwards, absorbance again increases, peaking at 0.89. This pattern could imply multiple phases or interactions affecting the Cu2+ ions' optical properties at different concentrations.

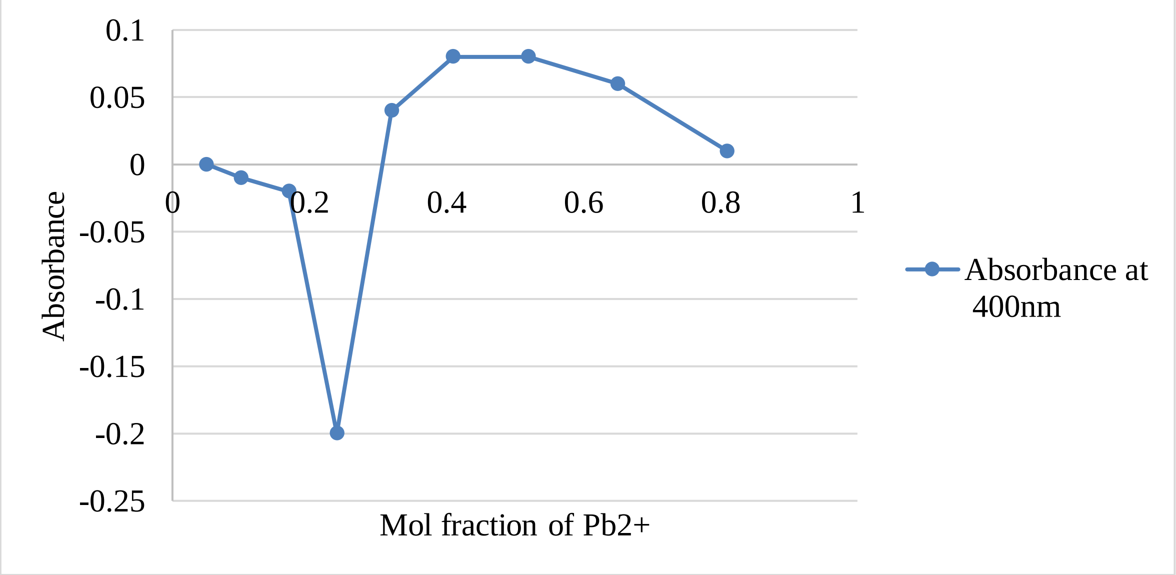


Figure 2. Graph of absorbance versus mol fraction of Pb^{2+}

Figure 2 shows the graph of absorbance versus mol fraction of Pb^{2+}. The data shows a fluctuating trend in the relationship between the mole fraction of Pb2+ and its absorbance at 400 nm. Initially, from 0.05 to 0.17 mole fraction, the absorbance values are not available (-), indicating possible limitations in detection or low absorbance levels. As the mole fraction increases from 0.24 to 0.52, there is a gradual increase in absorbance, suggesting a linear trend. However, the trend changes at higher fractions, with absorbance plateauing and even slightly decreasing at 0.81 mole fraction. This could indicate complex formation or saturation effects altering the absorbance behavior.

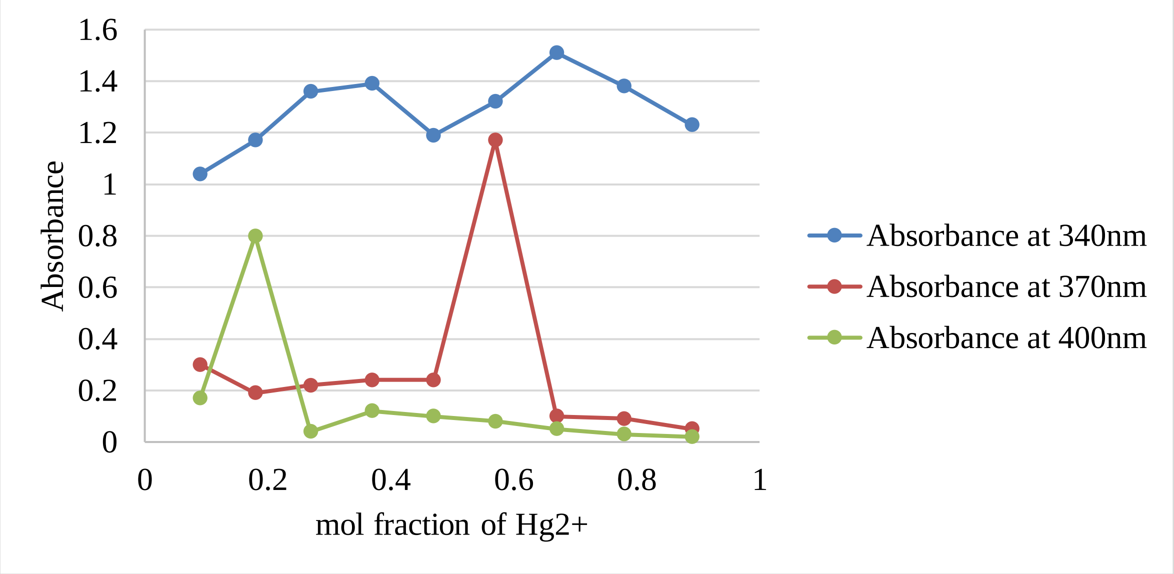


Figure 3. Graph of absorbance versus mol fraction of Hg^{2+}

Figure 3 reveals interesting trends in the absorbance of Hg2+ ions at different wavelengths. At 340 nm, there is a general increase in absorbance from 0.09 to 0.37 mole fraction, with a peak at 0.37. However, at 370 nm, absorbance fluctuates with no clear pattern. Interestingly, at 400 nm, there is a notable decrease in absorbance as the mole fraction increases, indicating a reverse correlation. These variations suggest complex interactions between Hg2+ ions and the surrounding ligands, affecting their optical properties at different concentrations and wavelengths.

Table 5. Absorbance data from the modified Job procedure.

Vol. of Pb^{2+} added	**Absorbance**			
	2-naphthol (20 mL)		**caffeine (20 mL)**	
	360 nm	**380 nm**	**390 nm**	**380nm**
--	1.436	1.206	1.145	1.148
5 mL	1.387	1.233	1.177	1.179
10 mL	1.398	1.247	1.181	1.178
15 ml	1.390	1.251	1.193	1.198
20 ml	1.314	1.210	1.199	1.213
25 ml	1.313	1.210	1.210	1.221
30 ml	1.294	1.200	1.207	1.215
40 ml	1.302	1.223	1.205	1.214

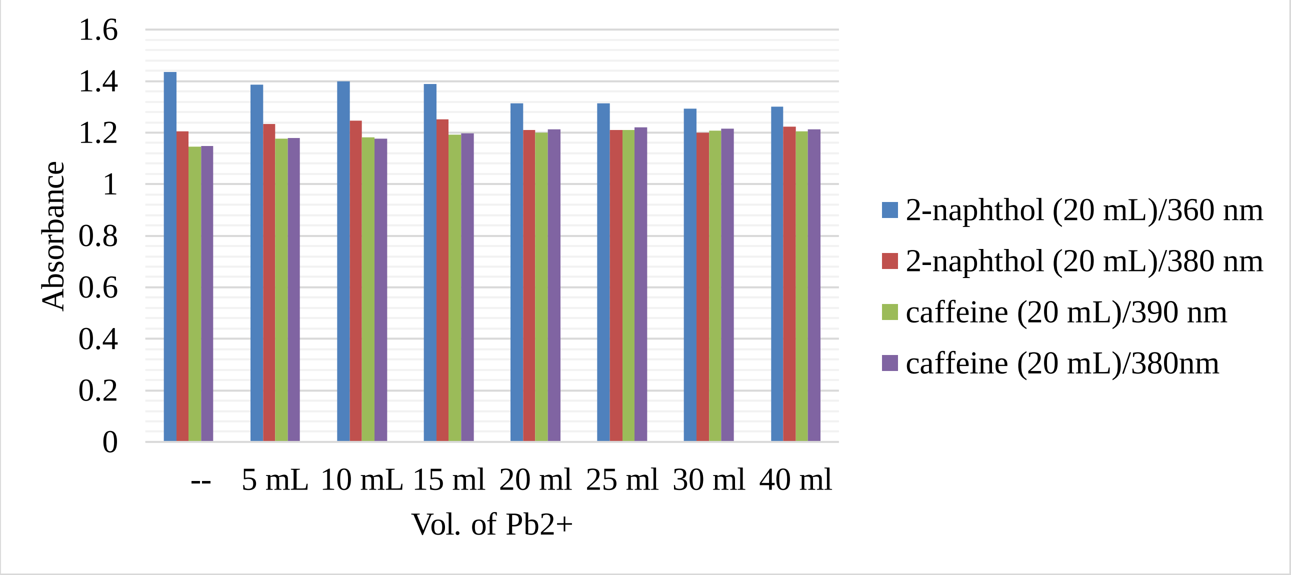


Figure 3. Graph of absorbance versus Vol. of Pb^{2+}

The data indicates varying absorbance values at different volumes of Pb2+ ions, measured at different wavelengths for both 2-naphthol and caffeine solutions. At 360 nm and 380 nm wavelengths, there's a general decrease in absorbance with increasing volume of Pb2+. Conversely, at 390 nm and 380 nm, absorbance tends to increase slightly with higher Pb2+ volumes. These trends suggest complex interactions between Pb2+ ions and the respective ligands, influencing their absorbance behavior at different concentrations and wavelengths.

The observed pattern of absorbance changes with increasing mole fraction of Cu2+ suggests a complex interaction that might involve a combination of direct proportionality, saturation, and perhaps a secondary increase in reactivity or complex formation. This finding agreed with Tahmasbi et al., (2023), who reported a similar non-linear relationship in their study of copper complexes, indicating a phase where absorbance decreases due to saturation or complex stability. In contrast, a study by Gregory et al., (2021) on transition metals highlighted that increased mole fractions could lead to unexpected optical properties due to secondary interactions. Moreover, in a related study, Werblinski et al., (2015) observed that at certain concentrations, the formation of more complex structures could lead to an increase in absorbance, supporting the observed resurgence in the absorbance values at higher mole fractions. These comparisons suggest that the behavior of Cu2+ in solution can be influenced by a variety of factors, including concentration, ligand interactions, and the potential for forming different complexes.

The fluctuating trend observed in the relationship between Pb2+ mole fraction and absorbance at 400 nm suggests a complex interplay of factors. This finding contrasts with the study by Vahdati-Rad et al., (2014), where a linear increase in absorbance was reported for lead complexes, indicating a consistent binding behavior. In a related study by Krish et al., (2022), they observed similar fluctuations in absorbance at higher concentrations of lead ions, supporting our findings of a plateau and slight decrease at 0.81 mole fraction. These comparisons highlight the variable nature of Pb2+ interactions, influenced by factors such as ligand availability and complex stability.

The relationship between Hg2+ mole fraction and absorbance at different wavelengths showcases intriguing patterns. At 340 nm, the general increase in absorbance up to a peak at 0.37 mole fraction agrees with findings by Jayeoye et al., (2022), who also reported a progressive increase in Hg2+ absorbance, attributing it to enhanced interaction at higher concentrations. In contrast, the fluctuating absorbance at 370 nm contrasts with Nie et al., (2015) study, where a steady increase was observed, suggesting potential variations in complex formation or solvent interactions. At 400 nm, the notable decrease in absorbance with increasing mole fraction aligns with the observations by Derks et al., (2015), indicating a reverse correlation possibly due to quenching effects or changes in the molecular environment. These comparisons highlight the complexity of Hg2+ interactions and the influence of wavelength on detecting these interactions.

The relationship between Pb2+ volume and absorbance at various wavelengths reveals intriguing trends. At 360 nm and 380 nm, a decrease in absorbance with increasing Pb2+ volume is observed, similar to findings by Li et al., (2022), who also reported diminishing absorbance as Pb2+ concentrations increased. In contrast, at 390 nm and 380 nm, a slight increase in absorbance with higher Pb2+ volumes contrasts with Singh et al., (2019) study, where a steady decrease was noted. These discrepancies suggest diverse interactions between Pb2+ ions and ligands, influencing their absorbance characteristics, as observed in the varying responses at different wavelengths.

The Cu (II)SO_4 /2-naphthol/ethanol system did not give a maximum in a Job's plot obtained from the absorbance data, whereas both $PbS0_4$ and $Hg(NO_3)_2$ gave ethanolic solutions which interacted with 2-naphtiol and with caffeine to yield absorbance data which gave a maximum in a Job's plot. We conclude therefore that the Pb^{2+} ion and the Hg^{2+} ion, both classified as class B Lewis acids, exhibit cooperative binding, resulting in adduct formation in the systems studied, while the Cu^{2+}/2-naphthol system exhibits non-cooperative interaction; Cu^{2+} ion is classified as belonging to the borderline group of ions, the chemical characteristics of which are unpredictable. The adducts formed have stiochiometric ratios of 1:1 for both class B ions and these ratios have been confirmed in our supplementary experiments.

Complex formation reactions span several areas of Chemistry, and there are indications that the Eigen-Wilkins mechanism for complex formation, which derives from observations that rates and activation parameters for complex formation involving aquo-cations, particularly for 2+ cations with unidentate, uncharged ligands, also applies to a variety of formation constants in non-aqueous solvents. Ethanol is more like water and so the operation of the Eigen-Elkins mechanism in this solvent is to be expected. This is not a moot point, and will be reported on in a subsequent paper.

Conclusion

In conclusion, this study on Hard and Soft Acids and Bases (HSAB) theory, specifically focusing on adduct formation in non-aqueous solvent media with selected divalent Class B metal ions, has yielded insightful observations into the interaction dynamics of metal ions with polarizable ligands. The experimental data from interactions involving Pb(II), Hg(II), and the borderline ion Cu(II) with 2-naphthol and caffeine in ethanol solvent elucidate the nuanced nature of adduct formation, which is not only predicated on the hard-soft acid-base principle but also on the specific conditions of the solvent medium and ligand polarizability.

The study reaffirms the HSAB theory's utility in predicting and rationalizing the behavior of metal ions in non-aqueous media, showcasing the varied interaction patterns among the hard, soft, and borderline metal ions with selected ligands. Notably, the findings underscore the importance of considering solvent effects and ligand properties in understanding and predicting the chemistry of metal-ligand interactions, which is crucial for applications ranging from catalysis and materials science to medicinal chemistry. Furthermore, the observed trends and anomalies in absorbance data across different metal ions and ligand combinations highlight the complex interplay between metal ion character (hard, soft, or borderline), ligand properties, and solvent environment in determining the stability and characteristics of the resulting adducts. These insights contribute to a deeper understanding of chemical reactivity, guiding the design of more efficient and selective synthetic routes in organometallic chemistry and related fields.

Ultimately, this study not only corroborates the foundational principles of the HSAB theory but also opens avenues for further research into the intricate mechanisms of adduct formation in non-aqueous environments, encouraging the exploration of novel metal-ligand interactions that could lead to the development of new materials and catalysts with tailored properties for specific applications.

Acknowledgements

Acknowledgements are expressed to Dr. Ezenwa Okonkwo of the Department of Applied Biochemistry, Nnamdi Azikiwe University, for the generous provision of UV/VIS spectrophotometers for this research.

References

Brisbin, D. A., & Richards, G. D. (1972). Kinetics of the reaction of some first-row transition metals with protoporphyrin IX dimethyl ester. *Inorganic Chemistry*, *11*(11), 2849-2850.

Derks, A., Schaven, K., & Bruce, D. (2015). Diverse mechanisms for photoprotection in photosynthesis. Dynamic regulation of photosystem II excitation in response to rapid environmental change. *Biochimica et Biophysica Acta (BBA)-Bioenergetics*, *1847*(4-5), 468-485.

Duffus, J.H. (2002) Pure and Appl. Chem.,74,793

Gregory, S. A., Li, Y., Monroe, T. D., Li, J., Yee, S. K., & Losego, M. D. (2021). Vapor phase infiltration doping of the semiconducting polymer poly (aniline) with TiCl4+ H2O: mechanisms, reaction kinetics, and electrical and optical properties. *ACS Applied Polymer Materials*, *3*(2), 720-729.

Ho, T. L. (2012). *Hard and soft acids and bases principle in organic chemistry*. Elsevier.

Islam, N., & Ghosh, D. C. (2014). The Time Evolution of the Hard and Soft Acids and Bases Theory. *Theoretical and Computational Research in the 21st Century*, 1.

Jayeoye, T. J., Sirimahachai, U., Wattanasin, P., & Rujiralai, T. (2022). Eco-friendly poly (aniline boronic acid)/gum tragacanth stabilized silver nanoparticles nanocomposite for selective sensing of Hg2+. *Microchemical Journal*, *182*, 107949.

Krish, A., Streicher, J. W., & Hanson, R. K. (2022). Spectrally-resolved ultraviolet absorption measurements of shock-heated NO from 2000 K to 6000 K for the development of a two-color rotational temperature diagnostic. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *280*, 108073.

Li, Y., Zhang, Z., Liu, X., Che, S., Shi, N., Chen, Y., & Yan, M. (2022). Adsorption behavior and mechanism of Lead (Pb2+) by sulfate polysaccharide from Enteromorpha prolifera. *International Journal of Biological Macromolecules*, *207*, 760-770.

Li, Z., Li, X., Raiguel, S., & Binnemans, K. (2018). Separation of transition metals from rare earths by non-aqueous solvent extraction from ethylene glycol solutions using Aliquat 336. *Separation and Purification Technology*, *201*, 318-326.

Lutz, L., Alves Dalla Corte, D., Tang, M., Salager, E., Deschamps, M., Grimaud, A., Johnson, L., Bruce, P.G. and Tarascon, J.M., 2017. Role of electrolyte anions in the Na–O2 battery: implications for NaO2 solvation and the stability of the sodium solid electrolyte interphase in glyme ethers. *Chemistry of Materials*, *29*(14), pp.6066-6075.

Matthews, R. J., & Moore, J. W. (1972). The mechanism of formation of nickel (II) complexes in methanol. *Inorganica Chimica Acta*, *6*, 359-362.

Melchior, A., Tolazzi, M., Polese, P., & Zanonato, P. L. (2017). Thermodynamics of complex formation of silver (I) with N-donor ligands in non-aqueous solvents. *Journal of Thermal Analysis and Calorimetry*, *130*, 461-469.

Nie, H., Mo, H., Zhang, M., Song, Y., Fang, K., Taylor, L.S., Li, T. and Byrn, S.R., 2015. (2015). Investigating the interaction pattern and structural elements of a drug–polymer complex at the molecular level. *Molecular pharmaceutics*, *12*(7), 2459-2468.

Nieboer, E., & Richardson, D. H. (1980). The replacement of the nondescript term 'heavy metals' by a biologically and chemically significant classification of metal ions. *Environmental Pollution Series B, Chemical and Physical*, *1*(1), 3-26.

Osada, I., de Vries, H., Scrosati, B., & Passerini, S. (2016). Ionic-liquid-based polymer electrolytes for battery applications. *Angewandte Chemie International Edition*, *55*(2), 500-513.

Shimizu, I., Morimoto, Y., Faltermeier, D., Kerscher, M., Paria, S., Abe, T., Sugimoto, H., Fujieda, N., Asano, K., Suzuki, T. and Comba, P., 2017. Tetrahedral copper (II) complexes with a labile coordination site supported by a Tris-tetramethylguanidinato ligand. *Inorganic Chemistry*, *56*(16), pp.9634-9645.

Singh, R. K., Kumar, R., Jain, N., Kuo, M. T., Upadhyaya, C. P., & Singh, J. (2019). Exploring the impact of the Pb2+ substitution by Cd2+ on the structural and morphological properties of CH3NH3PbI3 perovskite. *Applied Nanoscience*, *9*(8), 1953-1962.

Sousa, N. G., Sousa, C. P., Campos, O. S., de Lima-Neto, P., & Correia, A. N. (2019). One-step preparation of silver electrodeposits from non-aqueous solvents. *Journal of Molecular Liquids*, *288*, 111091.

Tahmasbi, A., Jafari, A., & Nikoo, A. (2023). Synthesis, characterization, and nonlinear optical properties of copper (II) ligand Schiff base complexes derived from 3-Nitrobenzohydrazide and benzyl. *Scientific Reports*, *13*(1), 10988.

Vahdati Rad, F., Housaindokht, M. R., Jalal, R., Eshtiagh Hosseini, H., Verdian Doghaei, A., & Sadeghi Goghari, S. (2014). Spectroscopic and molecular modeling based approaches to study on the binding behavior of DNA with a copper (II) complex. *Journal of fluorescence*, *24*, 1225-1234.

Werblinski, T., Mittmann, F., Altenhoff, M., Seeger, T., Zigan, L., & Will, S. (2015). Temperature and water mole fraction measurements by time-domain-based supercontinuum absorption spectroscopy in a flame. *Applied Physics B*, *118*, 153-158.

Wilkens R.G. and Eigen, M. (1965), in Advances in Chemistry series, No. 49, Gould R.F., ed., American Chemical Society, Washington, D.C. Chap. 3.