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DEVELOPMENT AND VALIDATION OF NEW ANALYTICAL METHODS FOR THE QUANTIFICATION OF CLOFARABINE IN BULK AND PHARMACEUTICAL DOSAGE FORM

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ABSTRACT

The aim of the method is to develop an analytical procedure for the determination of Clofarabine in Pharmaceutical Formulations. The analytical procedure for determination of Assay in finished product of Clofarabine Injection, 1mg/mL is an In-House procedure. The Chromatographic system consisted of a Shimadzu Class VP Binary pump LC-10ATvp, SIL-10ADvp Auto sampler, CTO-10Avp Column Temperature Oven, SPD-10Avp UV-Visible Detector. All the components of the system are controlled using SCL-10Avp System Controller. Data acquisition was done using LC Solutions software.

KEYWORDS: *Clofarabine, HPLC, Method Development, Validation, ICH Guidelines*

INTRODUCTION

Clofarabine is a purine nucleoside analog indicated for treatment of relapsed or refractory acute lymphoblastic leukaemia (ALL) in children [1].The drug is also increasingly used, outside of its Food and Drug Administration (FDA) approved indication, for treatment of relapsed or refractory acute myeloid leukemia (AML) in adults [2]. It acts by inhibiting DNA synthesis, the enzyme ribonucleotidereductase and repair and activation of mitochondrial repair processes [3]. We recently observed a case of acute kidney injury (AKI) associated with clofarabine treatment. We conducted a review of the literature and utilized the Food and Drug Administration Adverse Event Reporting System (FAERS)[4] to identify spontaneous reporting of renal adverse events with this drug.

Clofarabine administered intraperitoneally had significant activity against a wide variety of human tumour xenografts implanted subcutaneously in athymic nude or severe combined immune deficiency mice [5]. Moderate to excellent sensitivity to tumour growth delays were seen in all eight human colon tumours, three out of four human renal tumours, all four non-small-cell lung tumours, and all three prostate tumours. This spectrum of widespread anticancer activity has been confirmed by other investigators in human tumour xenograft models in mice [6]. The anticancer activity of clofarabine was dose- and schedule-dependent, and greater antitumour activity was associated with more frequent administration [7].Clofarabine is a second generation purine nucleoside analog with antineoplastic activity. Clofarabine is phosphorylated intracellularly to the cytotoxic active 5'-triphosphate metabolite, which inhibits the enzymatic activities of ribonucleotidereductase and DNA polymerase, resulting in inhibition of DNA repair and synthesis of DNA and RNA [8-10].

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Analytical Development Procedure for Determination of Assay in Finished Product of Bendamustine Hydrochloride in Bendamustine Hydrochloride

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Abstract

The present study was conducted to develop and validate an analytical procedure for the determination of Bendamustine Hydrochloride in Pharmaceutical Formulations. The analytical test attribute Bendamustine Hydrochloride was evaluated as per the guidelines of ICH Q2 (R1). The method was validated for the determination of Assay in finished product of Bendamustine Hydrochloride Injection and the method validation parameters were evaluated for the analytical test attribute Bendamustine Hydrochloride meets the acceptance criteria. The results obtained were within the specified limits thus, this method was used for the determination of Assay in finished product of Bendamustine Hydrochloride Injection (6mg/mL) and the samples were analyzed for test item concentration by High Performance Liquid Chromatography.

Keywords Bendamustine Hydrochloride, Validating the Assay, High Performance Liquid Chromatography, ICH Q2 (R1)

Introduction

The validation of analytical procedures is done in order to assure that drug formulations are prepared in a most efficient and cost effective manner. In this context, Assay procedures are intended to measure the analyte present in a given sample. The assay represents a quantitative measurement of the major component(s) in the drug product.

Bendamustine hydrochloride is a nitrogen mustard alkylating agent, structurally related to chlorambucil, which has been elaborated in 1962 in the former German Democratic Republic, and since its very clinical introduction in 1969 has been used exclusively in this country up until the reunion of Germany [1-3]. Bendamustine hydrochloride is among the first rationally designed alkylating drugs, whose structure comprises three pharmacophore moieties: the bis-2-chloroethylamine alkylating group, a benzimidazole ring serving as a purine base mimic (suggesting possible antimetabolite effects), and a butyric acid side chain to increase water solubility [4-6]. The drug has also demonstrated clinical activity in breast cancer [7-8] and small-cell lung cancer.

In this regard and view of the need for a suitable analytical HPLC method for routine analysis of Bendamustine Hydrochloride in formulations. Attempts were made to develop simple, precise and accurate analytical method for estimation of Bendamustine Hydrochloride and extend it for their determination in formulation.

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The accuracy of an analytical procedure expresses the closeness of agreement between the value that is accepted either as a conventional true value or an accepted reference value and the value found.

To demonstrate the accuracy of assay test method, drug substance is spiked quantitatively in to placebo from 50% to 150% of working concentration of test concentration at each level with triplicate preparation and analyzed using the test method. The result for Bendamustine HCl is tabulated in the below table. Typical chromatogram of Accuracy at 100 % level for is exhibited below.

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FORCED DEGRADATION VALIDATION OF BENDAMUSTINE HYDROCHLORIDE IN PHARMACEUTICAL FORMULATIONS BY HPLC

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Abstract

The analytical procedure for determination of Assay in finished product of Bendamustine Hydrochloride in Bendamustine Hydrochloride for injection 25 mg and 100 mg per vial is an In-House procedure. In this regard and view of the need for a suitable analytical HPLC method for routine analysis of Bendamustine Hydrochloride in formulations. Attempts were made to develop simple, precise and accurate analytical method for estimation of Bendamustine Hydrochloride and extend it for their determination in formulation.

Key words: Bendamustine Hydrochloride, HPLC, ICH Q2 (R1), Recovery

Introduction

Bendamustine was carcinogenic in mice. After intraperitoneal injections at 37.5 mg/m^2/day (12.5 mg/kg/day, the lowest dose tested) and 75 mg/m^2/day (25 mg/kg/day) for four days, peritoneal sarcomas in female AB/jena mice were produced. Oral administration at 187.5 mg/m^2/day (62.5 mg/kg/day, the only dose tested) for four days induced mammary carcinomas and pulmonary adenomas. Bendamustine is a mutagen and clastogen. In a reverse bacterial mutation assay (Ames assay), bendamustine was shown to increase revertant frequency in the absence and presence of metabolic activation. Bendamustine was clastogenic in human lymphocytes *in vitro*, and in rat bone marrow cells *in vivo* (increase in micronucleated polychromatic erythrocytes) from 37.5 mg/m^2, the lowest dose tested.

It acts as an alkylating agent causing intra-strand and inter-strand cross-links between DNA bases. After intravenous infusion it is extensively metabolised in the liver by cytochrome p450. More than 95% of the drug is bound to protein – primarily albumin [1-3]. Only free bendamustine is active. Elimination is biphasic with a half-life of 6–10 minutes and a terminal half-life of approximately 30 minutes [4-6]. It is eliminated primarily through the kidneys. Combination therapy with bendamustine and rituximab has demonstrated superior efficacy to a standard rituximabcontaining chemotherapy regimen in patients with previously untreated indolent B-cell non-Hodgkin lymphoma, and it is currently being compared against the standard first-line regimen in CLL: fludarabine, cyclophosphamide, and rituximab. Ongoing and planned studies are evaluating new strategies in which bendamustine is being combined with existing agents and with novel therapies to optimize use in different clinical settings [7-10].

Impaired spermatogenesis, azoospermia, and total germinal aplasia have been reported in male patients treated with alkylating agents, especially in combination with other drugs. In some instances spermatogenesis may return in patients in remission, but this may occur only several years after intensive chemotherapy has been discontinued. Patients should be warned of the potential risk to their reproductive capacities.

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Prediction of Chemical Speciation of Essential Metal ion Complexes of L-Tyrosine in Ethylene glycol and Dimethylformamide media

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ABSTRACT

Chemical speciation of complexes of Co(II), Ni(II) and Cu(II) with L-tyrosine has been studied spectrophotometrically. The complexations were carried out at different pH ranges at the wavelengths of respective complexes. The stoichiometries of the complexes were determined using Job's continuous variation method and the value was found to be 1:2 metals to ligand ratio. Stability constant values were calculated using the continuous variation method. The complexes were found to be stable over the pH range used as there was slight change in the color intensity and absorbance values.

Keywords: Cobalt(II), Nickel(II), Copper(II), Spectrophotometry, Stability constants, Toxicity.

INTRODUCTION

L-Tyrosine is synthesized in the body from phenylalanine and it is a direct precursor of adrenaline and thyroid hormones. Metabolic transformations of tyrosine require the presence of folic acid, niacin, vitamin C and copper. Its metabolic products include melanin, estrogen and encephalin. Tyrosine is used along with tryptophan to aid in the treatment of cocaine abuse and may also be useful in the control of anxiety or depression [1-4].

The supplementation of feed with L-tyrosine is efficacious in cases where high requirements for tyrosine as a melanin precursor occur. This has been demonstrated in cats for intensively coloring the coat. L-Tyrosine may also have the potential to intensify the pigmentation of the coat/plumage of other species, but limited evidence is available [5].

L-Tyrosine is usually absorbed in the proximal small intestine. Any L-tyrosine reaching the large intestine is decarboxylated to tyramine, a biogenic amine, in the human gut. Inadequate degradation (detoxification) of formed tyramine by the gut monoamine oxidases can lead to tyramine entering the systemic circulation. Tyramine acts as a vasopressor [6-7]; it is known to be a cause of migraine headaches in humans [8]. Very recently, for a single oral administration in healthy individuals, a no observed adverse effect level (NOAEL) of 200 mg tyramine/person has

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Development and Validation of an Analytical HPLC Procedure for the Quantification of Busulfan in Pharmaceutical Formulations

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Abstract

The present study was conducted to develop and validate an analytical procedure for the determination of Busulfan in Pharmaceutical Formulations. The analytical test attribute Busulfan was evaluated as per the guidelines of ICH Q2 (R1). The method was validated for the determination of Assay in finished product of Busulfan Injection and the method validation parameters were evaluated for the analytical test attribute Busulfan meets the acceptance criteria. The results obtained were within the specified limits thus, this method was used for the determination of Assay in finished product of Busulfan Injection (6mg/mL) and the samples were analyzed for test item concentration by High Performance Liquid Chromatography.

Keywords *Busulfan, Validating the Assay, High Performance Liquid Chromatography, ICH Q2 (R1)*

INTRODUCTION

Busulfan is an antineoplastic agent with a cell-cycle nonspecific alkylating action (unlike that of the nitrogen mustards) that has a selective depressant action on the bone marrow. In small doses, it depresses granulocytopoiesis and to a lesser extent thrombocytopoiesis, but has little effect on lymphocytes. With larger doses, severe bone-marrow depression eventually ensues [1-4]. Intravenous administration of busulfan to rats for 1 year was reported to induce a variety of tumours in male rats, but the experiments could not be evaluated due to incomplete reporting [5-6].

Busulfan tablets on the market are available only in much smaller doses than those necessary for HCT conditioning [7], as the oral busulfan formulation was originally intended for the CML population [8-10]. Busulfan utilization has undergone dramatic progress in hematopoietic cell transplant (HCT) since its initial approval in 1954 [11]. Busulfan is an alkylating agent originally used in chronic myelogenous leukemia (CML), but it has progressively been recognized as a potent myeloablative agent in preparative regimens for hematopoietic cell transplantation (HCT)

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Quantification of Busulfan in Pharmaceutical Formulations by Analytical HPLC

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Abstract

The present study was conducted to validate an analytical procedure for the Quantification of Busulfan in Pharmaceutical Formulations. The analytical test attribute Busulfan was evaluated as per the guidelines of ICH Q2 (R1). It is a new simple, accurate, precise and reproducible HPLC method has been developed for the estimation of Busulfan (1,4-butanediol dimethanesulfonate) in its inject able dosage. Thus, the proposed HPLC method can be successfully applied for the routine quality control analysis of formulations. A mixture water, acetonitrile and tetrahydrofuran at 30:65:5 (V/V/V) ratios were prepared and used as mobile phase.

Keywords- Busulfan, HPLC, ICH Q2 (R1), Validating the Assay

I. Introduction

When Busulfan hydrolyses in aqueous media, the methanesulphonate groups are released. The half-life of the intermediate, 4-methanesulphonyloxybutanol, is extremely short, which makes it unlikely that it is jointly responsible for the biological action of Busulfan [1]. Eventually, as high-dose busulfan emerged as an important component of preparative regimens in the early 2000s, intravenous formulations were marketed to overcome the disadvantages of the original oral compound's bioavailability [2]. Nonetheless, studies comparing intravenous versus oral administration of busulfan used identical dosing frequencies (again, typically q6 h) in their protocols to avoid confounding variables [3].

The second study was done in pediatrics, and found that the rate of veno-occlusive disease (VOD) was higher in the q24 h group compared to the q6 h group [4]. Not only does the reduced dosing frequency yield direct drug cost savings, but it also decreases pharmacy resources required to prepare the IV admixture from four times daily, to just once per day. In particular, busulfan's stability is only 12 hours once admixed, so daily administration is more practical for pharmacy [5].

This drug used in study of platelet-transported serotonin in liver reconstruction [6]. Tonicity which includes interstitial "busulfan lung", hyper pigmentation, seizures, veno-occlusive disease, emesis, and wasting syndrome [7-8]. Recently, intravenous Busulfan formulations were introduced on to the market, in order to minimize variations of inter- and intra-patient systemic exposure, and to provide complete dose assurance [9-11].

ICH- international council for harmonization of technical requirements for pharmaceuticals for human use (ICH) is unique in bringing together the regulatory authorities and pharmaceutical industry to discuss scientific and technical aspects of drug registration.Q2 (R1) Validation of analytical procedures of methodology is document presents a discussion of the characteristics for consideration during the validation of the analytical procedures included as part of registration applications submitted within the EC, Japan and USA. This document does not necessarily seek to cover the testing that may be required for registration in, or export to, other areas of the world. Furthermore, this text presentation serves as a collection of terms, and their definitions, and is not intended to provide direction on how to accomplish validation. These terms and definitions are meant to bridge the differences that often exist between various compendia and regulators of the EC, Japan and USA. The objective of the analytical procedure should be clearly understood since this will govern the validation characteristics which need to be evaluated. Typical validation characteristics which should be considered are Accuracy, Precision, Repeatability, Intermediate Precision, Specificity, Detection Limit, Quantization Limit, Linearity, Range[12-13].

II. Test System

- Instrument Name: High performance liquid chromatography
- Make: Shimadzu

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Analytical Method Development and Validation for Assay Method for Quantification of Busulfan in Pharmaceutical Formulations of by HPLC Method.

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ABSTRACT

A new simple, accurate, precise and reproducible HPLC method has been developed for the estimation of Busulfan (1,4-butanediol dimethanesulfonate) in its injectable dosage. A mixture water, acetonitrile and tetrahydrofuran at 30:65:5 (V/V/V) ratios were prepared and used as mobile phase. The method was validated as per the ICH guidelines. The method was validated for the determination of Assay in finished product of Busulfan Injection and the method validation parameters were evaluated for the analytical test attribute Busulfan meets the acceptance criteria. The results obtained were within the specified limits thus, this method was used for the determination of Assay in finished product of Busulfan Injection (6mg/mL).Thus, the proposed HPLC method can be successfully applied for the routine quality control analysis of formulations.

Keywords: HPLC, Busulfan, validation, mutation, anti-neoplastic.

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Development of analytical procedure for the determination of Bendamustine Hydrochloride in Pharmaceutical Formulations

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Abstract
The aim of the method is to develop analytical procedure for the determination of Bendamustine Hydrochloride in Pharmaceutical Formulations. The analytical procedure for determination of Assay in finished product of Bendamustine Hydrochloride in Bendamustine Hydrochloride for injection 25 mg and 100 mg per vial is an In-House procedure.The method shall be validated for the System precision, Method precision and Intermediate precision. The Chromatographic system consisted of a Shimadzu Class VP Binary pump LC-10ATvp, SIL-10ADvp Auto sampler, CTO-10Avp Column Temperature Oven, SPD-10Avp UV-Visible Detector. All the components of the system are controlled using SCL-10Avp System Controller. Data acquisition was done using LC Solutions software.

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I. Introduction

In order promote a good public health, validation of analytical procedures is done to ensure quality, safety and efficacy of therapeutic drugs used for public health. It's very important to determine the content of Active Pharmaceutical Ingredient or drug content in the presence of excipients, Impurities or various inert substances that originate from raw materials, key starting materials, intermediates, byproducts, manufacturing process steps, impurities that are formed during drug excipient interactions, degradation impurities etc but not limited to. The validation of analytical procedures is done in order to assure that drug formulations are prepared in a most efficient and cost effective manner.

Bendamustine hydrochloride is a nitrogen mustard alkylating agent, structurally related to chlorambucil, which has been elaborated in 1962 in the former German Democratic Republic, and since its very clinical introduction in 1969 has been used exclusively in this country up until the reunion of Germany [1-3]. Bendamustine hydrochloride is among the fi rst rationally designed alkylating drugs, whose structure comprises three pharmacophore moieties: the bis-2-chloroethylamine alkylating group, a benzimidazole ring serving as a purine base mimic (suggesting possible antimetabolite effects), and a butyric acid side chain to increase water solubility [4-6]. The rapid degradation of the drug in serum and the extensive liver metabolism impair its cytotoxic action within a short period of time, necessitating application of relatively high doses [7].

Bendamustine bearing the name Treanda is a chemotherapic medication used in the treatment of chronic lymphocytic leukemia, multiple myeloma, and non-hodgkins lymphoma. Bendamustine is a white, watersoluble microcrystalline powder with amphoteric properties. It acts as an alkylating agent causing intra-strand and inter-strand cross-links between DNA bases. After intravenous infusion it is extensively metabolised in the liver by cytochrome p450 [8-12].

II. Experimental

Materials:
The following material (chemicals and reagents) were used for the preparation of solutions.
Chemicals:

Trifluoroacetic acid	:	AR Grade (Merck Ltd)
Acetonitrile	:	HPLC Grade (Merck Ltd)
Hydrochloric acid	:	AR Grade (Merck Ltd)
Water	:	HPLC grade (Milli Q)

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HPLC method for the development and validation of busulfan in pharmaceutical formulation

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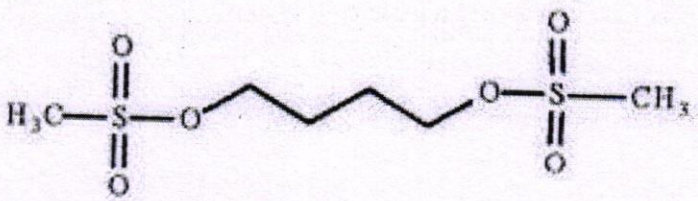
Abstract

A validated HPLC method was developed for the determination of Busulfan (BUS) in pharmaceutical formulation.It is a new simple, accurate, precise and reproducible HPLC method has been developed for the estimation of Busulfan (1,4-butanediol dimethanesulfonate) in its inject able dosage.The method developed in High Performance Liquid Chromatographic method using suitable column (YMC Pack ODS-A (150 x 4.6) mm, 3µm). All the components of the system are controlled using SCL-10Avp System Controller. Data acquisition was done using LC Solutions software.The method was validated as per the ICH guidelines. Thus, the proposed HPLC method can be successfully applied for the routine quality control analysis of formulations. The method developed is simple and is better than the methods reported in the literature and the method is capable to give a good detector response, the recovery calculated was within the range of 98% to 102% of the specification limits.

Keywords: Busulfan (BUS); HPLC, ICH Q2 (R1); Recovery

1 Introduction

Busulfan, a therapeutic alkane ester, is a bifunctional alkylating agent belonging to the antineoplastic therapeutic group of alkane sulfonic acid esters (1,4-butanediol dimethanesulphonate). Two labile sulphonate methane groups are bound to the opposite ends of a butyl chain. The N-7 guanine and Thiol groups of the SN2 form are known to occur in Busulfan [1].



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Novel Method for the Determination of Assay in finished product of Bendamustine Hydrochloride in Pharmaceutical Formulations with High Performance Liquid Chromatography

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ABSTRACT

In this context, Assay procedures are intended to measure the analyte present in a given sample. The assay represents a quantitative measurement of the major component(s) in the drug product. The method was validated as per the ICH guidelines Apart from these Chromatographic parameters like resolution, capacity factor, separation factor, column efficiency and peak asymmetry should also be the ideal for estimation. The analytical procedure for determination of Assay in finished product of Bendamustine Hydrochloride in Bendamustine Hydrochloride for injection 25 mg and 100 mg per vial is an In-House procedure.

Key words: Bendamustine Hydrochloride, HPLC, ICH Q2 (R1), Recovery

1. INTRODUCTION

The cytotoxic agent bendamustine (BM) hydrochloride (Cytosans, Treandas, Ribomustins, IMET-3393; ZIMET-3393) is a multifunctional alkylating agent with a purine-like ring system and a novel mechanism of action.

TREANDA contains bendamustine hydrochloride, an alkylating drug, as the active ingredient. The chemical name of bendamustine hydrochloride is 1Hbenzimidazole-2-butanoic acid, 5-[bis(2-chloroethyl)amino]-1-methyl-, monohydrochloride. Its empirical molecular formula is $C_{16}H_{21}Cl_2N_3O_2 \cdot HCl$, and the molecular weight is 394.7. Bendamustine hydrochloride contains a mechlorethamine group and a benzimidazole heterocyclic ring with a butyric acid substituent, and has the following structural formula:

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AN EFFICIENT SYNTHESIS OF 2, 4, 6 TRI ARYL PYRIDINES USING AMMONIUM CARBONATE IN WATER UNDER SEALED CONDITIONS

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ABSTRACT

Krohnke 2, 4, 6-Triarylpyridines (TAPs) are efficiently synthesized by using various reactants with ammonium carbonate in water under sealed conditions. Using this protocol, Krohnke pyridines (4a-4q) are prepared in higher yields and purities than with other methodologies without the use of a catalyst or an organic solvent.

KEYWORDS

Sealed conditions, Ammonium carbonate, Water and 2, 4, 6-Triarylpyridines.

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INTRODUCTON

Organic transformations in water without using hazardous reagents or solvents are of considerable interest, because of its environmental acceptability, abundance and low cost[1]. Pyridines derivatives represent an important class of six-membered heterocycles widespread in a number of biologically active natural products[2] and pharmaceutical drugs[3]. They have noticeable applications in many fields of chemistry[4]. In particular 2, 4, 6-triarylpyridine is of immense interest because of its unique position in medicinal chemistry[5], such as topoisomerase I and II inhibitory activity, cytotoxicity[6] against several human cancer cell lines[7] antitumor activity[8]. Recent studies providing impetus for further studies in

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Review on History and Evolution of Nanoparticles and Applications in Various Fields

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Abstract: ***One of the most exciting innovations of the 21st century is nanotechnology. Nanoscience is a combination of physics, materials science, and biology that deals with atomic and molecular scale. The top-down approach includes the breakdown into nanosized structures or particles of bulk material. The 'bottom-up' is the alternative approach, which has the opportunity to produce less waste and also more economically. By using natural asbestos nanofibers more than 4,500 years ago, humans have already manipulated ceramic matrix reinforcement. The synthesis of a colloidal Au nanoparticle solution was reported by Michael Faraday in 1857, which was the first scientific explanation to report nanoparticle preparation and initiated the history of nanomaterials in the scientific arena. Carbon-based materials became the foundation of almost every field of science and engineering after the discovery of' graphene. Important advancements in the field of nano-oncology have also been made by enhancing the effectiveness of conventional chemotherapy drugs for a plethora of aggressive human cancers***
Keywords: Nanotechnology, top-bottom approach, drug delivery

I. INTRODUCTION

A Greek prefix meaning 'dwarf' or anything very small is referred to as the prefix 'nano' and represents one thousand millionths of a meter (10-9 m). We should differentiate nanoscience and nanotechnology from each other. Nanoscience is the analysis of structures and molecules on nanometer scales ranging from 1 to 100 nm, and the technology that uses it is called nanotechnology [1] in practical applications such as devices etc. The evolution of nanoscience can be traced back to the time in the 5th century B.C. of the Greeks and Democritus, when scientists considered the question of whether matter is continuous, and thus indefinitely divisible into smaller parts, or made of small, indivisible and indestructible particles, now called atoms by scientists.

One of the most exciting innovations of the 21st century is nanotechnology. It is the ability to transform the theory of nanoscience to useful applications across the nanometer scale of observing, measuring, manipulating, assembling, managing and manufacturing matter. "In the United States, the National Nanotechnology Initiative (NNI) describes nanotechnology as a nanoscale science, engineering and technology (1 to 100 nm) where specific phenomena allow new applications in a broad range of fields, from chemistry, physics and biology to medicine, engineering and electronics"[2].

We should differentiate nanoscience and nanotechnology from each other. Nanoscience is a combination of physics, materials science, and biology that deals with atomic and molecular scale material manipulation, while nanotechnology is the ability to measure, manipulate, assemble, monitor, and generate matter on a nanometer scale. There are several reports available that have given the history of nanoscience and technology, but no study is available that summarizes the revolutionary events of nanoscience and technology from the beginning of that period. It is therefore important to summarize the key events in nanoscience and technology in order to fully understand their progress in this area.

II. THE CREATIVE PIONEERS OF NANOTECHNOLOGY

Richard Feynman, the American physicist and Nobel Prize laureate, presented the idea of nanotechnology in 1959. Feynman gave a lecture entitled "There's Plenty of Room at the Bottom" at the California Institute of Technology during the annual meeting of the American Physical Society (Caltech). "Feynman hypothesized in this lecture, "Why can't we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin? ', and identified the vision of the use of machines for building smaller machines, down to the molecular level [3]. This new idea has shown that the theories of Feynman have been proven correct, and he is considered the father of modern nanotechnology for these reasons. "In 1974, Norio Taniguchi, a Japanese scientist, was the first to use and describe the term "nanotechnology" after fifteen years as: "nanotechnology consists mainly of the processing of material separation, consolidation and deformation by one atom or molecule"[4].

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SECOND ORDER DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF Fe(II) USING 3, 4-DIHYDROXYBENZALDEHYDE TIOSEMICARBAZONE (DHBTSC) IN PRESENCE OF MICELLE MEDIUM

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ABSTRACT

A rapid and sensitive method has been developed for the determination of Fe(II) based on complexation reaction between the metal ion and 3,4,-dihydroxybenzaldehydethiosemicarbazone (DHBTSC) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at λ_{max} 365 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24h. The method obeys Beer's law in the range13.96 to 97.73 ng /ml. The apparent molar absorptivity of 4.21×10^5 L mol^{-1} cm^{-1} and Sandell's sensitivity 0.013ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of ≥ 100 folds in excess of foreign ions. The method was successfully used in the determination of Iron(II) in Leaf sample. Second order derivative spectrophotometric methods were developed at λ_{max} 485nm for the determination of Iron, which was more sensitive than the zero order method.

Keywords: Spectrophotometric Determination, Iron, 3,4-DHBTSC, Surfactant Tween-80, Leaf sample

Chemical Speciation Study of Ternary Complexes of Co(II), Ni(II) and Cu(II) with MSA and L-Dopa in DMF -Water Mixtures

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Abstract:

A computer assisted pH-metric investigation has been carried out on the speciation of complexes of Co(II), Ni(II) and Cu(II) with MSA and L-Dopa. The titrations were performed in the presence of different relative concentrations (M:L:X = 1.0:2.5:2.5; 1.0:2.5:3.75; 1.0:3.75:2.5) of metal (M) to MSA (L) to L-Dopa (X) with sodium hydroxide in varying concentrations (0–60% v/v) of DMF–water mixtures at an ionic strength of 0.16 mol L^{-1} and at a temperature of 303.0 K. Stability constants of the ternary complexes were refined using MINIQUAD75. The species MLX, ML_2X, MLX_2H and $MLXH_2$ for Co(II), Ni(II) and Cu(II) were detected. Influence of the solvent on the speciation was discussed based on the dielectric constant of the medium. The stabilities of the mixed ligand complexes are discussed in terms of the molecular structure of MSA and L-Dopa as well as the nature of the metalion.The species distribution with pH at different compositions of DMF–water mixtures and plausible equilibria for the formation of species were also presented. The bioavailability of the metal ions is explained based on the speciation.

Keywords: Mercaprosuccinic acid, Ternary Complexes, DMF, Speciation

1. Introduction:

The ternary complexes of ligands containing functional groups identical with those present in enzymes find many application in analytical and biological reactions **[1]**. Ternary complexes with nitrogen- and oxygen-donor ligands show remarkably high stability **[2–4]**. Thiomalic acid, $CH_2(COOH)CH(COOH)(SH)$ is a potential tridentate ligand due to its three ionizable groups viz., two carboxylic and one thiol. It has been used as antidote against cadmium, mercury and arsenic poisoning **[5]**. Its magnesium complex has been used in the treatment of rheumatic and bronchial disorders **[6]** and sodium gold (I) thiomalate has been proved to be a potential drug for adjuvant arthritis **[7]**. Chelate formation with Zn(II), Ni(II) and Co(II) was studied potentiometrically **[8]**. Lenz and Martel have made similar studies with Ag(I), Co(II),Hg(II), Zn(II), and Ni(II)**[9]**, Reddy and Bhattacharya with Tl(I), Ni(II) and Mn(II) **[10]** and Mohanty and Patnaik with Mn(II),Ni(II), Zn(II) and Co(II) **[11]**. Roselli studied the reactions of thiomalic acid with several metal ions in different media and concluded that the reactions of Co(II) and uranyl ions are of analytical interest **[12]**. SenSarma has studied the analytical applicability of this acid on the basis of its complexation reactions **[13]**.

Mixed-Ligand Complexes of Co(II), Ni(II) And Cu(II) with Mercaptosuccinic Acid And 1, 10-Phenanthroline in Dimethylformamide Media

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Abstract

The ternary systems of Co(II), Ni(II), and Cu(II) complexes with Mercaptosuccinic acid as Primary Ligand and 1, 10-Phenanthroline as Secondary Ligand are investigated. The stability constants of the complexes were determined pH metrically in Dimethylformamide medium at 303K and I = 0.16 mol/L NaCl. The predominant species detected are MLX, ML_2X, MLXH and MLX_2H. Models containing different numbers of species were refined by using the computer program MINIQUAD75. The best-fit chemical models were arrived at based on statistical parameters. The relative stabilities of the ternary complexes and species distributions of all complexes in solution were evaluated.

Keywords: Mixed-Ligand; MSA, Phen; Ph Metric Studies; Stability Constants.

Introduction

The dicarboxylic reductant, 2-mercaptosuccinic acid (MSA), has three species existing in solution with different charges over the pH range. It may exist as doubly or singly protonated form, or as the dianion having the two carboxylates deprotonated [1]. MSA is an important chiral multi-functional intermediate in organic chemistry and has been widely employed in the synthesis of various biologically active sulfur containing compounds such as antileukemic, spiro[indoline-3,2_-thiazolidine]-2,4-diones [2], and the anti-microbial [3] and antitubercular [4] 4-thiazolidinones. More recently, it has been used in the synthesis of the novel polyanionic inhibitor of HIV and other viruses [5]. The –SH functional group of the latter species remains unionized. 1,10-Phenanthroline (Phen) is a bidentate ligand, and it forms strong complexes with many metal ions. Due to hydrophobicity of aromatic rings in Phen, the solubility of the neutral species is low in water which remarkably increases in organic solvents and also in aqua-organic mixtures. Phen has been reported to be biologically active either alone or in the presence of metal ion.

Small quantities of mineral elements occurring in both plant and animal tissues are called as trace elements. A trace element is considered as essential for both man and animal life if it meets the listed conditions: i) it is present in all healthy tissues, ii) its concentration from one species to the next is fairly constant, iii) depending on the species studied, the amount of each element has to be maintained within its required limit if the functional and structural integrity of the tissues is to be safeguarded and the growth, health and fertility to remain unimpaired, iv) its withdrawal induces reproducibly the same physiological and or structural abnormalities and v) its addition to the diet either prevents or reverses, the abnormalities [6]. Several trace elements are known to fulfill these criteria, of which the most well known are iron, zinc, manganese, selenium, chromium, copper, cobalt, nickel, molybdenum and iodine. Many of them act as catalysts in many enzymatic functions called as metalloenzymes [7].

Cobalt is essential for the production of red blood cells. No metal ion antagonism involving cobalt has been reported, and no ion other than cobalt has been found in nature complexed with the Corrin ring. The effects of cobalt and manganese on some enzymes in the rat liver were studied [8]. Nickel was first suggested to be an essential element in 1936. Nickel is widely distributed in nature, forming about 0.008% of the earth's crust. Water-insoluble nickel compounds may dissolve in biological fluids [9]. Copper is found in certain foods in a greater quantity such as meat, eggs, poultry, nuts, seeds and grains. The human adult requirement is 2 mg/d [10]. The adult human body contains 100-150 mg of copper.

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Chemical Speciation of Mixed-Ligand Complexes of Co(II), Ni(II) and Cu(II) with MSA and L-Dopa in Acetonitrile -Water Mixtures

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***Abstract*: A computer assisted pH-metric investigation has been carried out on the speciation of complexes of Co(II), Ni(II) and Cu(II) with MSA and L-Dopa. The titrations were performed in the presence of different relative concentrations (M:L:X = 1.0:2.5:2.5; 1.0:2.5:3.75; 1.0:3.75:2.5) of metal (M) to MSA (L) to L-Dopa (X) with sodium hydroxide in varying concentrations (0–60% v/v) of acetonitrile–water mixtures at an ionic strength of 0.16 mol L^{-1} and at a temperature of 303.0 K. Stability constants of the ternary complexes were refined using MINIQUAD75. The species MLX, MLX_2, MLX_2H and $MLXH_2$ for Co(II), Ni(II) and Cu(II) were detected. Influence of the solvent on the speciation was discussed based on the dielectric constant of the medium. The stabilities of the mixed ligand complexes are discussed in terms of the molecular structure of MSA and L-Dopa as well as the nature of the metal ion. The species distribution with pH at different compositions of acetonitrile–water mixtures and plausible equilibria for the formation of species were also presented. The bioavailability of the metal ions is explained based on the speciation.**

Index Terms: Mercaprosuccinic acid, Ternary Complexes, Acetonitrile, Speciation.

1. Introduction:

In all living systems, the biochemical functions of both essential and toxic metals are mediated through specific chemical species or complexes and the concentrations of these particular species are important for the biochemical reactions but not just the total concentration of the metal in the system. Hence, extensive attention has been paid in recent years to the study of the chemical speciation of ligands with metal ions [1–4].

Mercaptosuccinic acid (MSA) or thiomalic acid (HOOC-CH(SH)-CH_2- COOH) is a dicarboxylic acid containing a thiol functional group (-SH group) instead of an -OH group in malic acid [5]. It is an important organic compound with multifunctional intermediate in organic synthesis. MSA is a tridentate ligand which has the ability to form strong complexes with many metal ions in natural environment and within cells and it has three replaceable hydrogen ions (two from the carboxylic and one from the sulfhydryl functional groups).

L-3,4-Dihydroxyphenylalanine (dopa) has been clinically used for the treatment of Parkinson's disease since it is a helpful neurotransmitter. L-Dopa is easily converted into dopamine by the enzyme dopa decarboxylase during passage through the intestine and liver, and accordingly only a small percentage of the originally administered amount of dopa becomes available for transport to the brain [6].

Cobalt complexes have gained importance for their applicability in the biological field [7-12]. In the race of synthesizing new drugs, cobalt complexes have attracted a great deal of attention amongst the scientific community due to their therapeutic uses as tumor imaging agent [13], antitumor [14], transport protein transferrin [15], antimycobacterial [16], antiischaemic [17], antiviral [18], antiparasitic [19], antithrombolytic [20], enzymatic therapeutics [21], anti-inflammatory activities [22] and as metabolic modifier [23].

Nickel is used in a wide variety of metallurgical processes such as electroplating and alloy production as well as in nickel cadmium batteries. Besides it plays a well defined role in the biological system and plants [24-26] Nickel is necessary for the biosynthesis of the hydrogenase, carbon monoxide dehydrogenase [27] and found in a number of genera of bacteria. A nickeltetrapyrrole coenzyme, Cofactor F430, is present in the methyl coenzyme M reductase, which powers methanogenic archaea [28]. One of the carbon monoxide dehydrogenase enzymes consists of an Fe-Ni-S cluster [29] .Urease from jack beans and several species of plants is also a nickel protein. The plant enzyme urease : an enzyme that assists in the hydrolysis of urea contains nickel. These plant enzyme systems can affect animals via the microbiological digestion of food in the rumen. Low nickel offers reduce growth, this is particularly true of intra-uterine development. Nickel deficiency is accompanied by histological and biochemical changes and reduced iron resorption and leads to anemia. Its deficiency also results in lower activities of different dehydrogenases and transaminases and, affects carbohydrate metabolism. Nickel can have an impact on human health through infectious diseases arising from nickel dependent bacteria [30].

Copper is distributed widely in the body and occurs in liver, muscle and bone. Copper is transported in the blood stream on a plasma

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Second order Derivative Spectrophotometric determination of Fe(II) using 3,4-DihydroxyBenzaldehydeTiosemicarbazone(DHBTSC) in presence of micelle medium

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ABSTRACT

A rapid and sensitive method has been developed for the determination of Fe(II) based on complexation reaction between the metal ion and 3,4,-dihydroxybenzaldehydethiosemicarbazone (DHBTSC) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at λ_{max} 365 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24h. The method obeys Beer's law in the range13.96 to 97.73 ng /ml. The apparent molar absorptivity of 4.21×10^5 L mol^{-1} cm^{-1} and Sandell's sensitivity 0.013ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of $\geq$ 100 folds in excess of foreign ions. The method was successfully used in the determination of Iron(II) in Leaf sample. Second order derivative spectrophotometric method were developed at λ_{max} 485nm for the determination of Iron, which was more sensitive than the zero order method.

Keywords: Spectrophotometric Determination, Iron, 3,4-DHBTSC, Surfactant Tween-80, Leaf sample.

Introduction

Iron is one of the most important transition element in living systems, being vital to both plants and animals. The stunted growth of the former is well known in soils, which are either themselves deficient in iron or in which high alkalinity renders the iron too insoluble to be accessible to the plants. Iron was the first minor element to be recognized as being essential to human being and was used in the treatment of anaemia. The adult human body contains about 4g of iron (i.e., -0.005% of body weight) of which about 3g are in the form of haemoglobin. Proteins involving iron are also present in the human body and its major function is oxygen *transport* and storage. In water samples, iron may occur in true solution either in ferrous or ferric form. Therefore, the determination of iron in environmental samples is important. There are two main forms of iron salts with numerous formulations such as: amino acid chelates, carbonyl iron, polysaccharide iron, combination products and extended release products available globally[1]

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Chromatographic Method for Quantification of Clofarabine Substances in a Pharmaceutical Formulation

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ABSTRACT

A novel, simple and economic high performance liquid chromatography (HPLC) method has been developed for the estimation of Clofarabine in bulk and tablet dosage form with greater precision and accuracy. The method was validated as per ICH guidelines. Validation studies demonstrated that the proposed HPLC method is simple, specific, rapid, reliable and reproducible. Hence the proposed method can be applied for the routine quality control analysis of Clofarabine in bulk and tablet dosage forms. All the components of the system are controlled using SCL-10Avp System Controller. Data acquisition was done using LC Solutions software.

Key words: Clofarabine, HPLC, Method Development, Validation, ICH guidelines

INTRODUCTION

Clofarabine is a second-generation purine nucleoside analogue designed to overcome the limitations and to incorporate the best qualities of both cladribine and fludarabine. Clofarabine enters cells by passive transport across lipid membranes as well as by active nucleoside transport. Once inside the cell, clofarabine is phosphorylated to its active triphosphate form by cellular kinases, including deoxycytidine kinase. Whereas fludarabine and cladribine inhibit only DNA polymerase and ribonucleotide reductase, respectively, clofarabine inhibits both of these enzymes [1-2]. This results in depletion of the amount of deoxynucleotide triphosphate available for DNA replication, as well as inhibition of DNA strand elongation and RNA transcription [3]. Given its mechanisms of action, clofarabine was predicted to work synergistically with other chemotherapeutic agents such as other purine nucleoside analogues and DNA-damaging or cross-linking agents such as anthracyclines and platinum agents. It initially showed efficacy in treating pediatric acute lymphoblastic leukemias and gained approval from the US Food and Drug Administration in 2004 [4].

Second order Derivative Spectrophotometric determination of Cu(II) using 3,4-Dihydroxy Benzaldehyde Tiosemicarbazone (DHBTSC) in presence of micelle medium.

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ABSTRACT

A rapid and sensitive method has been developed for the determination of Cu(II) based on complexation reaction between the metal ion and 3,4,-dihydroxybenzaldehydethiosemicarbazone (DHBTSC) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted at λ_{max} 370 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24h. The method obeys Beer's law in the range 15.17 to 19.25ng/ml. The apparent molar absorptivity of 6.31×10^5 L mol^{-1} cm^{-1} and Sandell's sensitivity 0.023ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of $\geq$ 100 folds in excess of foreign ions. The method was successfully used in the determination of Copper(II) in Leaf samples and Alloy samples. Second order derivative spectrophotometric methods were developed at λ_{max} 485nm for the determination of Copper, which was more sensitive than the zero order method.

Keywords: Spectrophotometric Determination, Copper, 3,4-DHBTSC, Surfactant Tween-80, Leaf, Alloy samples.

Introduction

Copper is a widely distributed metal in nature, and is an essential metal required by almost all living organisms in some of their biological activities. Deficiency of copper may lead to certain physiological disorders in both plants and animals, but at higher concentrations it works essentially as a pollutant. The 3D-structures of hydrazones and thiosemicarbazones with multidentate chelating properties bind a large number of metal ions exhibiting a wide spectrum of characteristics. The size of chelate ring, thermodynamic/ kinetic stability, quantum effects of the complexes depend upon side chains/spacers/aromatic heterocyclic rings and medium (aqueous, non_aqueous/aqueous-organic mixtures /micelles/vesicles etc.). The applications of these products are spread in diverse disciplines. Some of the typical tasks include analysis, preparation of nonlinear optical materials (NLO'S), processes concerned with smart materials and chemico-bio interactions. The impetus to explore the analytical characteristics of newly synthesized

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Second order Derivative Spectrophotometric determination of Aluminum (III) using 3,4-DihydroxyBenzaldehydeTiosemicarbazone(DHBTSC) in presence of micelle medium

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ABSTRACT

A rapid and sensitive method has been developed for the determination of Aluminum(III) based on complexationreaction between the metal ion and 3,4,-dihydroxybenzaldehydethiosemicarbazone (DHBTSC) in the presence of non-ionic surfactant Tween-80. The important parameters affecting the analytical procedure were optimized. Absorption maximum for a ternary complex was noted atλ_{max} 382 nm. The reaction was found to be rapid at room temperature and absorbance remained constant for more than 24hrs. The method obeys Beer's law in the range of 6.74 to 60.70ng/ml. The apparent molar absorptivity of 6.0×10^5 L mol^{-1} cm^{-1} and Sandell'ssenstivity 0.044ng/ml. The effect of foreign ions was tested by taking a constant concentration of metal ion and determining its concentration in the presence of $\geq$ 100 folds in excess of foreign ions. The method was successfully used in the determination of Aluminum(III) in Water samples and cement samples. Second order derivative spectrophotometric methods were developed at λ_{max} 430nm for the determination of Aluminum, which was more sensitive than the zero order method.

Keywords: Spectrophotometric Determination, Aluminum, 3,4-DHBTSC, Surfactant Tween-80, cement sample, Water sample.

Introduction

Aluminum is recognized as an important toxic substance causing considerable morbidity and mortality , particularly in patients with chronic renal failure. Diseases that have been associated with aluminum include dialysis dementia. Renal osteodystrophyand Alzheimer's disease. Aluminum also has an effect on red blood cels, parathyroid glands and chromosomes. The main clinical manifestations of aluminum toxicity include progressive encephalopathy, osteomalacia, microcytic hypochromic anaemia and cholestasis. Many sources have been shown to be

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Research Article

Method Development of an Analytical Procedure for the Determination of Clofarabine in Pharmaceutical Formulations

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Abstract

A novel, simple and economic high performance liquid chromatography (HPLC) method has been developed for the estimation of Clofarabine in bulk and tablet dosage form with greater precision and accuracy.The method was validated as per ICH guidelines. Validation studies demonstrated that the proposed HPLC method is simple, specific, rapid, reliable and reproducible. Hence the proposed method can be applied for the routine quality control analysis of Clofarabine in bulk and tablet dosage forms. All the components of the system are controlled using SCL-10Avp System Controller. Data acquisition was done using LC Solutions software.

Key words: clofarabine, RP-HPLC, method development, validation, ICH guidelines

Introduction

For many years, the Southern Research Institute has had a programme, supported by the US National Cancer Institute, searching for new nucleoside anticancer drugs. In the early 1980s, two adenine-containing nucleosides, now known as fludarabine (Fludara; Berlex Oncology) and cladribine (Leustatin; Ortho Biotech) were in clinical trials. At the time, it was not clear whether either drug would gain approval by the FDA because some concerns were raised during preclinical and clinical development of these agents. Both drugs were susceptible to glycosidic bond cleavage with fludarabine subject to some phosphorylase cleavage and cladribine subject to both hydrolytic and enzymatic cleavage [1].

Clofarabine administered intraperitoneally had significant activity against a wide variety of human tumourxenografts implanted subcutaneously in athymic nude or severe combined immune deficiency mice [2]. Moderate to excellent sensitivity to tumour growth delays were seen in all eight human colon tumours, three out of four human renal tumours, all four non-small-cell lung tumours, and all three prostate tumours. This spectrum of widespread anticancer activity has been confirmed by other investigators in human tumourxenograft models in mice [3]. The anticancer activity of clofarabine was dose- and schedule-dependent, and greater antitumour activity was associated with more frequent administration [4].Clofarabine is a second generation purine nucleoside analog with antineoplastic activity. Clofarabine is phosphorylated intracellularly to the cytotoxic active 5'-triphosphate metabolite, which inhibits the enzymatic activities of ribonucleotide reductase and DNA polymerase, resulting in inhibition of DNA repair and synthesis of DNA and RNA [5-7].

Acute leukaemia is the most common paediatric cancer, with acute lymphoblastic leukaemia (ALL) and acute myelogenous leukemia (AML) being the two most common types. In the United States alone, ~2,000 children are diagnosed each year with ALL and 500 with AML [8]. Successful treatment of paediatric ALL and AML involves intensive, multi-cyclic therapy with multiple drugs that have various mechanisms of action and dosing regimens [9-10]. Such intense, cyclic treatment regimens with many different agents have reported a projected 5-year disease-free survival of 70% for paediatric patients with ALL and a complete response (CR) rate of 90% in certain forms of childhood acute leukaemia [11].

In this regard and view of the need for a suitable analytical HPLC method for routineanalysis of Clofarabinein formulations.Attempts were made to developsimple, precise and accurate analytical methods for estimation of Clofarabineand extend it for their determination in formulation.

Aim and Objective

The aim of the method is to develop an analytical procedure for the determination of Clofarabine in Pharmaceutical Formulations. The analytical procedure for determination of Assay in finished product of Clofarabine Injection, 1mg/mL is an In-House procedure.

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Research Article

Speciation studies of Ternary Complexes of Co (II), Ni (II), and Cu (II) with Mercaptosuccinic acid and 1, 10-Phenanthroline in Acetonitrile-Water mixtures

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Abstract: Interaction of Co (II), Ni(II) and Cu(II) metal ions with Mercaptosuccinic acid and 1,10-Phenanthroline have been studied pH-metrically at an ionic strength of 0.16 mol L^{-1} and at a temperature of 303.0 K in acetonitrile-water mixtures. The stability constants of ternary complexes were calculated using the pH-metric data. Best fit chemical models representing the metal complexes with different compositions were obtained using MINIQUAD75 computer program. Mononuclear complexes of the type MLX, ML_2X, MLXH and MLX_2H, where M=Co (II), Ni (II) or Cu (II), L=MSA and X=Phen were found to exist in acetonitrile-water mixtures. The results show that the stabilities of ternary complexes in acetonitrile-water mixtures are more than in aqueous medium, Further, the trend of the variation in the stability constants with changing dielectric constant of the medium is explained based on the electrostatic and non-electrostatic interactions of the side chains of the ligands, charge neutralization and chelate effect. Species distribution diagrams were generated using HYSS program. Distribution diagrams with pH at different compositions of acetonitrile and structures of plausible ternary complexes are also presented.

Keywords: Mixed-ligand complexes; MSA, Phen; pH metric studies; Stability constants

New Approach To Coupled Fixed Point Theorems in a Metric Spaces endowed with a directed graph via $\theta - \psi$ contraction

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CH. Ramasanyasi Rao, Department of Applied Mathematics, M. V. R. Degree P. G. College, Gajuwaka, Visakhapatnam-530026, Andhra Pradesh, India.

Abstract-In this paper, we present some existence and uniqueness results for coupled fixed point and common fixed point of four mapping in a complete metric space endowed with directed graph via a new $\theta - \psi$ contraction.

Keywords- Metric spaces with a graph, edge preserving, coupled fixed point, $\theta - \psi$ contraction.

Introduction

In 2006, the concepts of fixed point theory and graph theory were combined by Espinola and Kirk ([3]). Jachymski([4]) and Chifu ([2]) came up with an interesting idea of using the language of graph theory in the study of fixed point results.

A graph is an ordered pair $G = (V, E)$, where V is a non empty set and the elements in V are called vertices or nodes and E is a binary relation on V. i.e., $E \subseteq (V \times T)$. The elements of E are called edges.

In this paper we concentrate on directed graphs.

Let G^{-1} be the conversion of the graph G. i.e., the graph obtained from G by reversing the direction of edges. Simply, $E(G^{-1}) = \{(y, x): (x, y) \in E(G)\}$. A directed graph G is called a oriented graph if $(x, y) \in E(G)$, then $(y, x) \notin E(G)$.

Definition 1.1 [2] A function $S: X \times X \to X$ is said to be G – continuous if $\{x_{n_i}\} \to p$, $\{y_{n_i}\} \to q$ and $(x_{n_i}, x_{n_{i+1}}) \in E(G)$, $(y_{n_i}, y_{n_{i+1}}) \in E(G^{-1})$ implies $S(x_{n_i}, x_{n_{i+1}}) \to S(p, q)$ and $S(y_{n_i}, y_{n_{i+1}}) \to S(q, p)$ as $i \to \infty$, where $(x, y), (p, q) \in X \times X$ and $(n_i)_{i \in N}$ be a sequence of positive integers.

Definition 1.2 [2]) Let (X, d) be a complete metric space endowed with a directed graph G. Then the triplet (X, d, G) has property (A) if

(i) for any sequence $\{x_n\}_{n \in N}$ in X such that $\{x_n\} \to p$ and $(x_n, x_{n+1}) \in E(G)$ implies $(x_n, p) \in E(G)$

(ii) for any sequence $\{y_n\}_{n \in N}$ in X such that $\{y_n\} \to q$ and $(y_n, y_{n+1}) \in E(G^{-1})$ implies $(y_n, q) \in E(G^{-1})$.

Many authors studied about the coupled fixed points and coupled coincident points and common coupled fixed points and the G- continuous properties (see [2], [19], [15], [7]).

By taking the inspiration from the above authors G. Adilakshmi and G.N.V. Kishore([1]) introduced a G – fg contraction on metric space endowed with a graph for four mappings.

Definition 1.3 ([1]) Suppose (X, d) be a metric space endowed with a directed graph G. Let us consider the mappings $S, T: X \times X \to X$ and $f, g: X \to X$ with defining the following sets

(I) $(X \times X)_{Sf} = \{(x, y) \in X \times X: (fx, S(x, y)) \in E(G), (fy, S(y, x)) \in E(G^{-1})\}$
and (i) f is edge preserving. i.e., $(fx, fu) \in E(G), (fy, fv) \in E(G^{-1})$
implies $(f(fx), f(fu)) \in E(G)$ and $(f(fy), f(fv)) \in E(G^{-1})$.
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implies $(S(x, y), S(u, v)) \in E(G)$ and $(S(y, x), S(v, u)) \in E(G^{-1})$.

(II) $(X \times X)_{Tg} = \{(u, v) \in X \times X: (gu, T(u, v)) \in E(G), (gv, T(v, u)) \in E(G^{-1})\}$
and (i) g is edge preserving. i.e., $(gx, gu) \in E(G), (gy, gv) \in E(G^{-1})$
implies $(g(gx), g(gu)) \in E(G)$ and $(g(gy), g(gv)) \in E(G^{-1})$.

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Common Coupled Fixed Point Results In A Metric Space Via Graph Theory

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Abstract-In this paper, we present some existence and uniqueness results for coupled fixed point and common fixed point of four mapping in a complete metric space endowed with directed graph via a new $G-(fg)_2-$ contraction.

Keywords-Metric spaces with a graph, edge preserving, coupled fixed point.

Introduction

In 2006, the concepts of fixed point theory and graph theory were combined by Espinola and Kirk ([3]). Jachymski([4]) and Chifu ([2]) came up with an interesting idea of using the language of graph theory in the study of fixed point results.

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Let G^{-1} be the conversion of the graph G. i.e., the graph obtained from G by reversing the direction of edges. Simply, $E(G^{-1})=\{(y,x):(x,y)\in E(G)\}$.

A directed graph G is called a oriented graph if $(x,y)\in E(G)$, then $(y,x)\notin E(G)$.

Preliminaries

Definition 1.1 [2] A function $S:X\times X\to X$ is said to be $G-$ continuous if $\{x_{n_i}\}\to p$, $\{y_{n_i}\}\to q$ and $(x_{n_i},x_{n_{i+1}})\in E(G)$, $(y_{n_i},y_{n_{i+1}})\in E(G^{-1})$ implies $S(x_{n_i},x_{n_{i+1}})\to S(p,q)$ and $S(y_{n_i},y_{n_{i+1}})\to S(q,p)$ as $i\to\infty$, where $(x,y),(p,q)\in X\times X$ and $(n_i)_{i\in N}$ be a sequence of positive integers.

Definition 1.2 [2] Let (X, d) be a complete metric space endowed with a directed graph G. Then the triplet (X, d, G) has property (A) if

(i) for any sequence $\{x_n\}_{n\in N}$ in X such that $\{x_n\}\to p$ and $(x_n,x_{n+1})\in E(G)$ implies $(x_n,p)\in E(G)$
(ii) for any sequence $\{y_n\}_{n\in N}$ in X such that $\{y_n\}\to q$ and $(y_n,y_{n+1})\in E(G^{-1})$ implies $(y_n,q)\in E(G^{-1})$.

Many authors studied about the coupled fixed points and coupled coincident points and common coupled fixed points and the G- continuous properties (see [2], [21], [16], [7]) By taking the inspiration from the above authors G. Adilakshmi and G.N.V. Kishore([1]) introduced a $G-fg$ contraction on metric space endowed with a graph for four mappings.

Definition 1.3 ([1]) Suppose (X, d) be a metric space endowed with a directed graph G. Let us consider the mappings $S,T:X\times X\to X$ and $f,g:X\to X$ with defining the following sets

(I) $(X\times X)_{Sf}=\{(x,y)\in X\times X:(fx,S(x,y))\in E(G),(fy,S(y,x))\in E(G^{-1})\}$
and (i) f is edge preserving. i.e., $(fx,fu)\in E(G),(fy,fv)\in E(G^{-1})$
implies $(f(fx),f(fu))\in E(G)$ and $(f(fy),f(fv))\in E(G^{-1})$.
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implies $(S(x,y),S(u,v))\in E(G)$ and $(S(y,x),S(v,u))\in E(G^{-1})$.
(II) $(X\times X)_{Tg}=\{(u,v)\in X\times X:(gu,T(u,v))\in E(G),(gv,T(v,u))\in E(G^{-1})\}$
and (i) g is edge preserving. i.e., $(gx,gu)\in E(G),(gy,gv)\in E(G^{-1})$
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Fixed Point Theorems On Complex Valued Dislocated Quasi b-Metric Spaces

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Abstract-The objective of this paper is to introduce a new metric space i.e., complex valued dislocated quasi *b*-metric space. Proved that Banach fixed point theorem verified on this space. We also proved that there exists a unique common fixed point for the four self maps defined on the above space. We verified our results with an example.

Keywords-Fixed Point, dislocated, quasi complex valued b-metric space.

Introduction

Fixed points theory plays an important role in various fields of mathematics such as mathematical analysis, general topology and functional analysis. There are important applications of fixed point theory in mathematics, computer science, Engineering and image processing.

In 2011, A. Azam ([7]) introduced the notation of complex valued metric space and gave common fixed point results for mappings. Sintunavarat and Kuman ([10]) in 2012 extended and improved a result of Azam and applied this to the unique common solution of system of Uryshone integral equation. Further, in 2013 K.P.R.Rao and Swamy P.R ([11]) introduced the complex valued b-metric space. In 2000, Hitzler, P.Seda ([12])([14]) introduced dislocated metric spaces and also verified Banach contraction principle. Dislocated metric space has a significant role in topology, logical programming and electronics engineering. Thereafter, in 2005, Zeyada F.M, Hassan G.H and Ahmad M.A ([15]) presented the complete dislocated quasi-metric spaces and generalized the results of Hitzler ([12])in dislocated quasi-metric spaces. In 2018, Ozgur Ege ([1]) introduced the concept of complex valued dislocated metric space and verified Banach contraction principle.

Preliminaries

The definitions of dislocated quasi *b*- metric space and their convergence and completeness properties are discussed in [5].

Definition 2.1 ([1]) Let X be a non empty set. Assume that a function $d: X \times X \to C$ satisfies the following conditions.

(Cd_1) $d(l, m) = d(m, l)$;

(Cd_2) $d(l, m) = d(m, l) = 0$ implies $l = m$;

(Cd_3) $d(l, m) \lesssim d(l, r) + d(r, m)$ for all $l, m, r \in X$

If d is said to be complex valued dislocated metric on X and (X, d) is called a complex valued dislocated metric space.

Definition 2.2 ([1]) Let (X, d) be a complex valued dislocated metric space. A mapping $T: X \to X$ is called contraction if there exists $0 \leq k < 1$ such that

(1) $d(Tl, Tm) \leq kd(l, m)$ for all $a, b \in X$.

Since the following two lemmas are the analogues of the lemmas in ([7]), we state these for complex valued d-metric spaces without their proofs.

Lemma 2.3 Let (X, d) be a complex valued dislocated metric space and let $\{l_n\}$ be a sequence in X. Then $\{l_n\}$ converges to x if an only if $|d(l_n, l)| \to 0$ as $n \to \infty$.

Lemma 2.4 Let (X, d) be a complex valued dislocated metric space and let $\{x_n\}$ be a sequence in X. Then $\{l_n\}$ is a Cauchy sequence if and only if $|d(l_n, l_{n+m})| \to 0$ as $n \to \infty$.

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$(\phi - \psi)$ Contractive Type Fixed Point Results In Metric Spaces Via Graph Theory

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CH. Ramasanyasi Rao, Department of Mathematics, M. V. R. Degree P. G. College, Gajuwaka, Visakhapatnam- 530026, Andhra Pradesh, India.

Abstract--This paper deals with metric spaces via graph theory and obtained unique common coupled fixed point results for four maps. In this connection a new $(\phi - \psi)$ contraction has been introduced.

Keywords--Metric spaces with a graph, edge preserving, coupled fixed point, $(\phi - \psi)$ contraction.

Introduction

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Jachymski([4]) and chifu ([2]) came up with an interesting idea of using the language of graph theory in the study of fixed point results.

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In this paper we concentrate on directed graphs.
Let G^{-1} be the conversion of the graph G. i.e., the graph obtained from G by reversing the direction of edges. Simply, $E(G^{-1}) = \{(y, x): (x, y) \in E(G)\}$.
A directed graph G is called a oriented graph if $(x, y) \in E(G)$, then $(y, x) \notin E(G)$.

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Many authors studied about the coupled fixed points and coupled coincident points and common coupled fixed points and the G- continuous properties (see [2], [21], [16], [7]) By taking the inspiration from the above authors G. Adilakshmi and G.N.V. Kishore([1]) introduced a G – fg contraction on metric space endowed with a graph for four mappings.

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(ii) S is f edge preserving. i.e., $(fx, fu) \in E(G), (fy, fv) \in E(G^{-1})$
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(II) $(X \times X)_{Tg} = \{(u, v) \in X \times X: (gu, T(u, v)) \in E(G), (gv, T(v, u)) \in E(G^{-1})\}$
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implies $(g(gx), g(gu)) \in E(G)$ and $(g(gy), g(gv)) \in E(G^{-1})$.
(ii) T is g edge preserving. i.e., $(gx, gu) \in E(G), (gy, gv) \in E(G^{-1})$

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Review Article

A TRIPLE FIXED POINT THEOREM OF CARISTI TYPE CONTRACTION FOR MULTI VALUED MAPS IN A HAUSSDORFF METRIC SPACE

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Abstract

The main aim of this paper is to obtain a unique common tripled fixed point of caristi type caristi type ontraction for multi valued mappings in a Haussdorff metric space

Keywords: Metric space , compatible maps, tripled fixed point, Haussdorff metric.

DOI: http://dx.doi.org/10.31838/jcr.07.02.112

INTRODUCTION

The concept of standard metric space is a fundamental tool in topology,functional analysis and nonlinear analysis. This structure has attracted a considerable attention from mathematicians because of the development of the fixed point theory in standard metric space. Since Banach Introduced this theory in 1922([10]), it has been extended and generalized by several authors. Caristi type fixed point theorem is one of these generalizations. It is a modified ϵ -variation principle of Ekeland([9]). In 1976, Caristi proved the following famous fixed point theorem.

Theorem 1.1 *[6] Let (X,d) be complete metric space and $f: X \to R$ be lower semi continuous function and bounded below function. A mapping $T: X \to X$ is said to be Caristi type map on X dominated by f if T satisfies $d(x,Tx) \le f(x) - f(Tx)$ for each $x \in X$. Then T has a fixed point.*

S.B.Nadler introduced the concept of multivalued contraction mappings in the year 1969([11]).

Definition 1.2 *([11]) Let (X,d) be a metric space. We define the Hausdorff metric on $CB(X)$ induced by d. That is $H(A,B) = max[\sup_{l \in A} d(l,B), \sup_{m \in B} d(m,A)]$ for all $A, B \in CB(X)$, where $CB(X)$ denotes the family of all nonempty closed and bounded subsets of X and $d(l,B) = inf\{d(l,b): b \in B\}$, for all $l \in X$.*

Definition 1.3 *([11]) Let (X,d) be a metric space. A map $T: X \to CB(X)$ is said to be multivalued contraction if there exists $0 \le \alpha < 1$ such that $H(Tl,Tm) \le \alpha d(l,m)$, for all $l, m \in X$.*

Lemma 1.4 *([8]) Let X be a nonempty set and $g: X \to X$ be a mapping. then there exists a subset $E \subseteq X$ such that $g(E) = g(X)$ and $g: E \to E$ is one one.*

Now we give the following definitions for hybrid pair of mappings.

Definition 1.5 *([7])Let X be a non empty set, $T: X \times X \times X \to 2^X$ (collection of non empty subsets of X) and $f: X \to X$.*

(i) The point $(l,m,n) \in X \times X \times X$ is called a tripled fixed point of T if

$$l \in T(l,m,n)$$
$$m \in T(m,l,m)$$
$$n \in T(n,m,l)$$

(ii) The point $(l,m,n) \in X \times X \times X$ is called a tripled coincident point of T and f if

$$fl \in T(l,m,n)$$
$$fm \in T(m,l,m)$$
$$fn \in T(n,m,l)$$

(iii) The point $(l,m,n) \in X \times X \times X$ is called a tripled common fixed point of T and f if

$$l = fl \in T(l,m,n)$$
$$m = fm \in T(m,l,m)$$
$$n = fn \in T(n,m,l)$$

Definition 1.6 *[7] Let $T: X \times X \times X \to X$ be a multi valued map and f be self map on X. The hybrid pair $\{T,f\}$ is called $w-$compatible if $f(T(l,m,n)) \subseteq T(fl,fm,fn)$ whenever (l,m,n) is tripled coincidence point of T and f.*

Lemma 1.7 *[See [5]] Let $\lhd$ be a reflexive relation on a nonempty set M and $\phi: M \to R$ a function bounded from below, then $\chi \lhd \gamma$ and $\chi \ne \gamma$; then $\phi(\chi) > \phi(\gamma)$.*

Throughout this paper, we assume that $\zeta: [0,\infty) \to [0,\infty)$ is an upper semi continuous function.

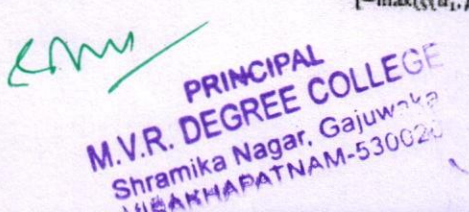
Now we prove our main results.

RESULTS AND DISCUSSIONS

Theorem 2.1 *Let (X,d) be a complete metric space and let $S: X \times X \times X \to CB(X)$ be a set valued mapping satisfies*

$$H(S(l,m,n),S(a_1,b_1,c_1)) \le \max\left\{\begin{matrix}\zeta\left(\max\{\varsigma(l,a_1),\varsigma(m,b_1),\varsigma(n,c_1)\}\right),\\ \zeta\left(\max\{\varsigma(a_1,\beta_1),\varsigma(a_2,\beta_2),\varsigma(a_3,\beta_3)\}\right)\end{matrix}\right\}$$

$$\left[\begin{matrix}\max\{\varsigma(l,a_1),\varsigma(m,b_1),\varsigma(n,c_1)\})\\ -\max\{\varsigma(a_1,\beta_1),\varsigma(a_2,\beta_2),\varsigma(a_3,\beta_3)\})\end{matrix}\right]$$



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Review Article

COUPLED FIXED POINT THEOREM FOR FOUR MAPS ON A METRIC SPACES ENDOWED WITH A GRAPH

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Abstract

The main aim of this paper to introduce a new notation $G-fg-$ contraction and a new edge preserving property. With help of this proved a coupled coincidence fixed point theorem for four maps with a graph in a metric space.

Keywords: Metric spaces with a graph, edge preserving, coupled fixed point.

DOI: http://dx.doi.org/10.31838/jcr.07.02.113

INTRODUCTION

In 2006, the concepts of fixed point theory and graph theory were combined by Espinola and Kirk ([3]). Jachymski[[4]] and Chifu ([2]) came up with an interesting idea of using the language of graph theory in the study of fixed point results.

A graph is an ordered pair $G=(V,E)$, where V is a non empty set and the elements in V are called vertices or nodes and E is a binary relation on V. i.e., $E\subseteq(V\times T)$. The elements of E are called edges.

In this paper we concentrate on directed graphs.

Let G^{-1} be the conversion of the graph G. i.e., the graph obtained from G by reversing the direction of edges. Simply, $E(G^{-1})=\{(y,x):(x,y)\in E(G)\}$.

A directed graph G is called a oriented graph if $(x,y)\in E(G)$, then $(y,x)\notin E(G)$.

Definition 1.1 *[2] A function $S:X\times X\to X$ is said to be $G-$ continuous if $\{x_{n_i}\}\to p$, $\{y_{n_i}\}\to q$ and $(x_{n_i},x_{n_{i+1}})\in E(G)$, $(y_{n_i},y_{n_{i+1}})\in E(G^{-1})$ implies $S(x_{n_i},x_{n_{i+1}})\to S(p,q)$ and $S(y_{n_i},y_{n_{i+1}})\to S(q,p)$ as $i\to\infty$, where $(x,y),(p,q)\in X\times X$ and $(n_i)_{i\in N}$ be a sequence of positive integers.*

Definition 1.2 *[2]) Let (X,d) be a complete metric space endowed with a directed graph G. Then the triplet (X,d,G) has property (A) if*

(i) for any sequence $\{x_n\}_{n\in N}$ in X such that $\{x_n\}\to p$ and $(x_n,x_{n+1})\in E(G)$ implies $(x_n,p)\in E(G)$

(ii) for any sequence $\{y_n\}_{n\in N}$ in X such that $\{y_n\}\to q$ and $(y_n,y_{n+1})\in E(G^{-1})$ implies $(y_n,q)\in E(G^{-1})$.

Many authors studied about the coupled fixed points and coupled coincident points and common coupled fixed points and the G- continuous properties (see [2], [19], [15], [7]) By taking the inspiration from the above authors G. Adilakshmi and G.N.V. Kishore[[1]] introduced a $G-fg$ contraction on metric space endowed with a graph for four mappings.

Definition 1.3 *([1]) Suppose (X,d) be a metric space endowed with a directed graph G. Let us consider the mappings $S,T:X\times X\to X$ and $f,g:X\to X$ with defining the following sets*

(I) $(X\times X)_{Sf}=\{(x,y)\in X\times X:(fx,S(x,y))\in E(G),(fy,S(y,x))\in E(G^{-1})\}$

and *(i) f is edge preserving. i.e., $(fx,fu)\in E(G),(fy,fv)\in E(G^{-1})$*

implies $(f(fx),f(fu))\in E(G)$ and $(f(fy),f(fv))\in E(G^{-1})$.

(ii) S is f edge preserving. i.e., $(fx,fu)\in E(G),(fy,fv)\in E(G^{-1})$

implies $(S(x,y),S(u,v))\in E(G)$ and $(S(y,x),S(v,u))\in E(G^{-1})$.

(II) $(X\times X)_{Tg}=\{(u,v)\in X\times X:(gu,T(u,v))\in E(G),(gv,T(v,u))\in E(G^{-1})\}$

and *(i) g is edge preserving. i.e., $(gx,gu)\in E(G),(gy,gv)\in E(G^{-1})$*

implies $(g(gx),g(gu))\in E(G)$ and $(g(gy),g(gv))\in E(G^{-1})$.

(ii) T is g edge preserving. i.e., $(gx,gu)\in E(G),(gy,gv)\in E(G^{-1})$

implies $(T(x,y),T(u,v))\in E(G)$ and $(T(y,x),T(v,u))\in E(G^{-1})$.

(III) $(X\times X)_{ST}^{fg}=(X\times X)_{Sf}\cap(X\times X)_{Tg}$

ST are said to be $G-fg$ contraction if

(i) f,g are edge preserving respectively. i.e., $(fx,gu)\in E(G),(fy,gv)\in E(G^{-1})$

implies $(f(fx),g(gu))\in E(G)$ and $(f(fy),g(gv))\in E(G^{-1})$.

(ii) S,T are $fg-$edge preserving. i.e., $(fx,gu)\in E(G),(fy,gv)\in E(G^{-1})$

implies $(S(x,y),T(u,v))\in E(G)$ and $(S(y,x),T(v,u))\in E(G^{-1})$

FS-COMPLEMENT OPERATOR- FS-FUNCTIONS – COMPLEMENTED IMAGES AND INVERSE IMAGES –SOME PROPERTIES-A REVIEW

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Abstract: In this paper we review complement of an image and inverse image of an Fs-subset under an Fs-function and study the corresponding Fs-subset properties.

Keywords: Fs-set, Fs-subset, Fs-empty set, Fs-Complement, Fs-function, Image of an Fs-subset, Inverse image of an Fs-set.

Introduction: Several mathematicians studied numerous aspects of fuzzy sets. Recently many researchers put their efforts in order to prove collection of all fuzzy subsets of a given fuzzy set is Boolean algebra under suitable operations [21].Vaddiparthi Yogeswara, G.Srinivas and Biswajit Rath [11] introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions. Also Vaddiparthi Yogeswara, Biswajit Rath introduced the concept of the Fs-function between Fs-sets and image of an Fs-subset under an Fs-function and studied some properties [17]. The concept of inverse image of an Fs-subset under an Fs-function was introduced by Vaddiparthi Yogeswara, Biswajit Rath, Ch.Ramasanyasi Rao etc [23,24, 25].In this paper, we review the research material about images of Fs-functions under a Complement Operator published by Vaddiparthi Yogeswara, etc.... We extracted all the results in those publications and presented in an order adopting a new convenient notation. Throughout this paper starting from section-IV, we fix Fs-function $f:\mathcal{B} \to \mathcal{C}$ such that $\mu_{1B_1} = M_B$, $\mu_{2B} = 0$, $L_B = [0, M_B]$, $\mu_{1C_1} = M_C$, $\mu_{2C} = 0$, $L_C = [0, M_C]$.For all lattice theoretic properties and Boolean algebraic properties one can refer Szasz [3], Garret Birkshoff[4],Steven Givant • Paul Halmos[2] and Thomas Jech[5].For results in topology one can refer[10]

F-SETS-FS-SETS AND CHOICE AXIOM – A REVIEW

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Abstract: A limitation of L-fuzzy sets and generalization of L-fuzzy sets to f-sets by N V E S Murthy be discussed. Further, generalization of f-sets by V.yogeswara etc.....,which are called Fs-sets be also discussed. How the axiom of choice is absent in L-fuzzy sets and exist in f-sets and Fs-sets can be known in this review.

Key words: L-fuzzy sets,F-sets,Fs-sets,Axiom of choice.

Introduction: After the study of numerous aspects of fuzzy sets by several mathematicians including Zadeh[1],Murthy [2] introduced f-sets in order to prove Axiom of choice for fuzzy sets which is not present in L-fuzzy set theory in [3]. The collection of all f-subsets of given f-set with his definition f-complement [4] could not form a compete Boolean algebra. Also for any f-subset $\mathscr{B} = (B,\overline{B},L_B)$ and for any $b \in B$ the complement of $\overline{B}b$ – denoted by $(\overline{B}b)^c$ is not discussed in the f-set theory introduced by Murthy[2]. Recently many researchers put their efforts in order to prove collection of all fuzzy subsets of given fuzzy set is Boolean algebra under suitable operations and it seems among them the efforts of Neog and Sut [5,6] and Mamoni [7] are most successful. Particularly in the definition of membership function of Neog and Sut [5] namely, $\mu_1(x)-\mu_2(x)$, $-\mu_2(x)$ will not be in the real interval [0,1]. To eliminate those lacunae Vaddiparthi Yogeswara, G. Srinivas and Biswajit Rath introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions. They are successful in their efforts in proving that result with some conditions. In papers [9] and [10] Vaddiparthi Yogeswara, Biswajit Rath and S. V. G. Reddy introduced the concept of Fs-Function between two Fs-subsets of given Fs-set and defined an image of an Fs-subset under a given Fs-function. Also they studied the properties of images under various kinds of Fs-functions.

F-MAPS-FS-FUNCTIONS – A REVIEW

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Abstract: In this section the notions of an f-map, increasing f-map, decreasing f-map and preserving f-map, and the various categories which can be formed out of these maps are introduced, Further, generalization of f-maps by V.Yogeswara etc.....,which are called Fs-functions are discussed in this review.

Keywords: F-Map, Fs-Functions, Increasing ,Decreasing.

Introduction: The theory of f-maps were introduced by Murthy[2]. The generalisation of f-maps which are called Fs-functions is done by V.Yogeswara etc... [9,10]. We discussed in his review, elaborately f-maps, Fs-functions and corresponding images. \Vaddiparthi Yogeswara, Biswajit Rath and S. V. G. Reddy introduced the concept of Fs-Function between two Fs-subsets of given Fs-set and defined an image of an Fs-subset under a given Fs-function. Also they studied the properties of images under various kinds of Fs-functions.

Section-1:

F-Maps :

1.1 Definition: Let $W = (W, \overline{W}, L_W)$ and $U = (U, \overline{U}, L_U)$ be a pair of f-sets.
For any map f: $W \longrightarrow U$ and complete homomorphism$\emptyset$: $L_W \longrightarrow L_U$, the ordered pair $(f, \emptyset)$ is said to be an f-map from $(W, \overline{W}, L_W)$ to $(U, \overline{U}, L_U)$ and in this case we write $(f, \emptyset): (W, \overline{W}, L_W) \longrightarrow (U, \overline{U}, L_U)$.
Let $(f, \emptyset): (W, \overline{W}, L_W) \longrightarrow (U, \overline{U}, L_U)$ be an f-map.
We say $(f, \emptyset)$ is an increasing f-map whenever $Uf \geq \emptyset W$ and in this case we write
$(f, \emptyset)_i: (W, \overline{W}, L_W) \longrightarrow (U, \overline{U}, L_U)$.
We say $(f, \emptyset)$ is a decreasing f-map whenever $Uf \leq \emptyset W$ and in this case we write
$(f, \emptyset)_d: (W, \overline{W}, L_W) \longrightarrow (U, \overline{U}, L_U)$.
We say $(f, \emptyset)$ is a preserving f-map whenever $Uf = \emptyset W$ and in this case we write
$(f, \emptyset)_d: (W, \overline{W}, L_W) \longrightarrow (U, \overline{U}, L_U)$.
The class of all f-sets together with morphism sets hom
$((W, \overline{W}, L_W), (U, \overline{U}, L_U)) = \{(f, \emptyset) | (f, \emptyset): (W, \overline{W}, L_W) \longrightarrow (U, \overline{U}, L_U)\}$
for any pair of f-sets $(W, \overline{W}, L_W)$ and $(U, \overline{U}, L_U)$ define a category when the partial operation

F-COMPLEMENT OF F-SUBSETS- FS- DE MORGAN LAWS- A REVIEW

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Abstract: In this paper we review the complementation f-subsets, Fs-subsets and DeMorgan laws of Fs-subsets.

Keywords: Fs-set, Fs-subset, Fs-empty set, Fs-union, Fs-intersection, Fs-complement and Fs-De Morgan laws.

Introduction: Murthy[1] introduced F-set in order to prove Axiom of choice for fuzzy sets which is not present in

L -fuzzy sets introduced by Goguen[3],Also Murthy[2],in his generalisation of L-fuzzy sets which are called f-sets, he introduced the complement of f-subset [2] .With this definition the DE Morgan laws are not satisfied .To answer this incomphrensiveness, V.Yogeswara etc introduced Fs-set theory. In this review we discuss elaborately the limitation of f-sets and advantage of Fs-sets in defining complementation and proving Fs-De Morganlaws.We denote the largest element of a complete Boolean algebra L_A[1.1] by M_A, the complement of b in L_A in by b^c. For any crisp subset U, the usual set complement o f U , i s denoted by $\mathbb{U}^c$ and $\mathbb{U}^c$UA is denoted by C_AU. Complete Boolean algebras in this paper are generally represented by suitable diagrams. For all lattice theoretic properties and Boolean algebraic properties we refer S zasz [6], Garret Birkhoff[7],Steven Givant • Paul Halmos[5] and Thomas Jech[8]

Section-1:

F-Complement of An F-Subset:

1.1 Definition: For any f-set $\mathcal{X}$ and for any f-subset $\mathcal{W} = (W, \bar{W}, L_W)$ of $\mathcal{X}$, the f-subset $\mathcal{U} = (U, \bar{U}, L_U)$ of $\mathcal{X}$, where $U = X - W$, $\bar{U} = \bar{X}|U$, $L_U = (\bar{U}U)L_X$ is said to be the f-compliment of $\mathcal{W}$ and is denoted by $\mathcal{W}^C$.

1.2Theorem: The following are true for any f-set $\mathcal{X} = (X, \bar{X}, L_X)$:

1. Always $[\cup_{i\in I} \mathcal{W}_i]^C \subseteq \cap_{i\in I} \mathcal{W}_i^C$, for any family of f-subsets $(\mathcal{W}_i)_{i\in I}$ of $\mathcal{X}$

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The Operations Fs-Union, Fs-Intersection and Fs-Complement Operator in Fs-Set Theory- Some Results

Vaddiparthi Yogeswara, K.V.Umakameswari, D.Raghu Ram, Ch. Ramasanyasi Rao, Biswajit Rath

Abstract: ***In this Paper, we prove the collection of all FS - subsets of a given FS-set with the symmetric operation satisfies a distributive law namely FS –intersection operation distributes over the symmetric difference operation with some conditions.***

Keywords: ***Fs-set, Fs-subset, Fs-union, Fs-intersection, Fs-Complement, symmetric difference Operation.***

I. INTRODUCTION

Ever since Zadeh [8] introduced the notion of fuzzy sets in his pioneering work, several mathematicians studied numerous aspects of fuzzy sets.

Recently many researchers put their efforts in order to prove collection of all fuzzy subsets of a given fuzzy set is Boolean algebra under suitable operations [21].VaddiparthiYogeswara,G.Srinivas and BiswajitRath[11] introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions.In this Paper, we prove the collection of all FS -subsets of a given FS-set with the symmetric operation satisfies a distributive law namely FS – intersection operation distributes over the symmetric difference operation with some conditions. . All other relevant results are proved in the next section. We denote the largest element of a complete Boolean algebra L_A[1.1] by $M_A$or 1_A. Throughout this paper starting from section-1, For all lattice theoretic properties and Boolean algebraic properties one can refer Szasz [3], Garret Birkhoff[4],Steven Givant• Paul Halmos[2] and Thomas Jech[5].

A. Fs-Set

Let U be a universal set, $A_1 \subseteq U$ and let $A \subseteq U$ be non-empty. A four tuple $\mathcal{A}(A_1, A, \bar{A}(\mu_{1A_1}, \mu_{2A}), L_A)$ is said be an Fs-set if, and only if

(1) $A \subseteq A_1$

(2) L_A is a complete Boolean Algebra

(3) $\mu_{1A_1}: A_1 \to L_A$,$\mu_{2A}: A \to L_A$,are functions such that $\mu_{1A_1}|A \geq \mu_{2A}$

(4) $\bar{A}: A \to L_A$ is defined by $\bar{A}x = \mu_{1A_1}x \wedge (\mu_{2A}x)^c$,for each $x \in A$

(5)

B. Fs-subset

Let $\mathcal{A}=(A_1, A, \bar{A}(\mu_{1A_1}, \mu_{2A}), L_A)$ and $\mathcal{B}=(B_1, B, \bar{B}(\mu_{1B_1}, \mu_{2B}), L_B)$ be a pair of Fs-sets. $\mathcal{B}$is said to be an Fs-subset of $\mathcal{A}$, denoted by $\mathcal{B} \subseteq \mathcal{A}$, if, and only if

(1) $B_1 \subseteq A_1$, $A \subseteq B$

(2) L_B is a complete subalgebra of L_A or $L_B \leq L_A$

(3) $\mu_{1B_1} \leq \mu_{1A_1}|B_1$, and $\mu_{2B}|A \geq \mu_{2A}$

C. Definition of Fs-complement of an Fs-subset:

Consider a particular Fs-set$\mathcal{A} = (A_1, A, \bar{A}(\mu_{1A_1}, \mu_{2A}), L_A)$,$A \neq \Phi$,where

[1] $A \subseteq A_1$

[2] $L_A = [0, M_A]$, $M_A = \vee \bar{A}A = \vee_{a \in A} \bar{A}a$

[3] $\mu_{1A_1} = M_A, \mu_{2A} = 0$,

$\bar{A}x = \mu_{1A_1}x \wedge (\mu_{2A}x)^c = M_A$, for each $x \in A$

Given $\mathcal{B}=(B_1, B, \bar{B}(\mu_{1B_1}, \mu_{2B}), L_B)$. We define Fs-complement of $\mathcal{B}$, denoted by $\mathcal{B}^{C_{\mathcal{A}}}$ for B=A and $L_B = L_A$ as follows:

$\mathcal{B}^{C_{\mathcal{A}}} = \mathcal{D}=(D_1, D, \bar{D}(\mu_{1D_1}, \mu_{2D}), L_D)$, where

(a') $D_1 = C_A B_1 = B_1^c \cup A, D = B = A$

(b') $L_D = L_A$

(c') $\mu_{1D_1}: D_1 \to L_A$, is defined by $\mu_{1D_1}x = M_A$

$\mu_{2D}: A \to L_A$, is defined by $\mu_{2D}x = \bar{B}x = \mu_{1B_1}x \wedge (\mu_{2B}x)^c$

$\bar{D}: A \to L_A$,is defined by$\bar{D}x = \mu_{1D_1}x \wedge (\mu_{2D}x)^c = M_A \wedge (\bar{B}x)^c = (\bar{B}x)^c$.

D. Definition

Let $\mathcal{B}=(B_1, B, \bar{B}(\mu_{1B_1}, \mu_{2B}), L_B)$ and $\mathcal{C}=(C_1, C, \bar{C}(\mu_{1C_1}, \mu_{2C}), L_C)$ be a pair of Fs-subsets of$\mathcal{A}$. Then, the Fs-union of $\mathcal{B}$ and $\mathcal{C}$, denoted by $\mathcal{B} \cup \mathcal{C}$ is defined as $\mathcal{B} \cup \mathcal{C}=\mathcal{D}=(D_1, D, \bar{D}(\mu_{1D_1}, \mu_{2D}), L_D)$,where

(1) $D_1 = B_1 \cup C_1$, $D = B \cap C$

(2) $L_D = L_B \vee L_C =$ The complete subalgebra generated by $L_B \cup L_C$

(3) $\mu_{1D_1}: D_1 \to L_D$ is

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FS-Cartesian Product Topological Space and its Compactness

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Abstract: ***For any nonempty family*** $\{(\mathcal{B}_i, \mathfrak{T}_i)\}$ ***of compact FsB-Toplogical Spaces, the corresponding Fs-product space is also compact.***

Index Terms: ***Fs-Set, Fs-Subset, (b,β) object, Fs-Point, FsB-Toplogical Space.***

I. INTRODUCTION

Axiom choice is not true in the theory of L-Fuzzy sets .Nistla V.E.S Murthy [10] proved Axiom Choice of fuzzy sets in his theory of F-sets. VaddiparthiYogeswara[2] etc ... developed the theory of Fs-sets with the goal of introducing the complement of a fuzzy set which was not satisfactorily explained by previous relevant theories .Also VaddiparthiYogeswara, BiswajitRath ,Ch.RamaSanyaasiRao ,K.V.UmaKameswari,D.Raghu Ram introduced the concept of FsB-topological Space on a given Fs –subset of an Fs-set and also they introduced FsB-subspace in the same paper .Fs-points and Fs-point set FSP($\mathcal{W}$) are introduced by VaddiparthiYogeswara etc...[2] and based on Fs-set theory they defined a pair of relations between P(FSP($\mathcal{W}$))and $\mathcal{L}(\mathcal{W})$. Here FSP($\mathcal{W}$) stands for Fs-Point set of $\mathcal{W}$, $\mathcal{L}(\mathcal{W})$ stands for collection of allFs-subsets of $\mathcal{W}$ and P(FSP($\mathcal{W}$)) is power set of FSP($\mathcal{W}$) and proved one of them is a '$\wedge$'- complete homomorphism and other is '$\vee$'- complete homomorphism and searched some properties of these relations between complemented constructed crisp sets and Fs-complemented sets through thesehomomorphismand ultimately they proved a representation theorem connecting Fs-subsets of $\mathcal{W}$ to crisp subsets of FSP($\mathcal{W}$) via homomorphisms.For a given non-empty family of compact Fs-toplogicalspaces , we prove in this paper their Fs-Cartesian Product space is also compact. Fs-Sets, Fs- Set functions etc... in brief are explained in first four sections of this paper. '$\cup$' and '$\cap$' sands for natural set union and Fs-union and Similarly '$\cap$'. M_A or 1_A sands for largest element of a given complete Boolean Algebra L_A. For all lattice theoretic and relevant Properties one can refer [5],[8],[15],[16],[17].$ET, the category of sets with usual maps between crisp sets.CBOO, the category of complete Boolean algebras with complete homomorphism between complete Boolean algebras.$(\prod_{i\in I} A_i, (P_i)_{i\in I})$is the product of $(A_i)_{i\in I}$ in $ET. Meanings of all the following things can known from [2]. (i) $ET (ii) CBOO (iii) Fs-Cartesian Product (iv) Axiom choice.

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SECTION-1

1.1 Fs-set: : A four tuple of the form $\mathcal{W} = (W_1, W, \bar{W}(\mu_{1W_1}, \mu_{2W}), L_W)$ is an Fs-set iff, $W \sqsubset W_1 \sqsubset U$

(1) L_W is a complete Boolean Algebra

(2) $\mu_{1W_1}: W_1 \to L_W$,$\mu_{2W}: W \to L_W$ are mappings such that

$$\mu_{1W_1}|W \geq \mu_{2W}$$

(3) $\bar{W}$: $W \to L_W$ is defined by

$$\bar{W}x = \mu_{1W_1}x \wedge (\mu_{2W}x)^c \text{ for each } x \in W$$

Where W is a non-void subset of some universal set U

1.2 Fs-subset: Suppose $\mathcal{W} = (W_1, W, \bar{W}(\mu_{1W_1}, \mu_{2W}), L_W)$ and $\mathcal{U} = (U_1, U, \bar{U}(\mu_{1U_1}, \mu_{2U}), L_U)$ are two Fs-sets. We say $\mathcal{U}$ is anFs-subset of $\mathcal{W}$, in symbol, we write $\mathcal{U} \sqsubset \mathcal{W}$, iff

(1) $U_1 \sqsubset W_1$, $W \sqsubset U$

(2) L_U is a complete subalgebra of L_W or $L_U \leq L_W$

(3) $\mu_{1U_1} \leq \mu_{1W_1}|U_1$, and $\mu_{2U}|W \geq \mu_{2W}$

1.3 ArbitraryFs-unions and arbitrary Fs-intersections

For any $(\mathcal{U}_i)_{i\in I}, \mathcal{U}_i = (U_{1i}, U_i, \bar{U}_i(\mu_{1U_{1i}}, \mu_{2U_i}), L_{U_i}) \sqsubset \mathcal{W}=(W_1, W, \bar{W}(\mu_{1W_1}, \mu_{2W}), L_W)$, $i \in I$

(1): $\bigsqcup_{i\in I} \mathcal{U}_i = \varphi_W$, for $I = \varphi$

(2): If $I \neq \varphi$, $\bigsqcup_{i\in I} \mathcal{U}_i = \mathcal{U} = (U_1, U, \bar{U}(\mu_{1U_1}, \mu_{2U}), L_U)$, where

(a) $U_1 = \bigsqcup_{i\in I} U_{1i}$,$U = \bigsqcap_{i\in I} U_i$

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Images of FS-set Functions and Hausdroff Property on FSB-Toplogical Spaces

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Chemical Speciation of Binary Complexes of Co(II), Ni(II) and Cu(II) with 1,10 Phenanthroline in Acetonitrile-Water and DMF Water Mixtures

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***Abstract*: A computer assisted pH-metric investigation has been carried out on the speciation of complexes of Co(II), Ni(II) and Cu(II) with 1,10-Phenanthroline. The titrations were performed in the presence of different relative concentrations with sodium hydroxide in varying concentrations (0–60% v/v) of acetonitrile–water mixtures and DMF-water mixtures at an ionic strength of 0.16 mol L-1 and at a temperature of 303.0 K. Stability constants of the binary complexes were refined using MINIQUAD75. The best-fit chemical models were selected based on various statistical parameters. The models for binary complex systems contain the chemical species ML2, ML3 and ML2H for Co(II), Ni(II) and Cu(II) in acetonitrile-water and DMF-water mixtures. The trend in the variation of stability constants with change in the mole fraction of the medium was explained based on electrostatic and non-electrostatic forces. Distribution of the species with pH at different compositions of acetonitrile-water and DMF-water mixtures was also presented.**

***Keywords*: 1, 10-Phenanthroline, Acetonitrile, Distribution diagrams, Dielectric constant, MINIQUAD75**

1. Introduction

One of the major applications of the transition metal complexes is their medical testing as antibacterial and antitumor agents aiming toward the discovery of an effective and safe therapeutic procedure for the treatment of several bacterial infections and cancers. Research in medicinal inorganic chemistry has prolonged in current years by exploiting a variety of chelating ligands to modify and control the properties of metal ions in biological systems [1–3]. In chemotherapy, the extensive applications have been found to be transition metal ions coordinated to a nitrogen containing ligands, such as 1,10–Phenanthroline. There are several biologically active molecules which contain various hetero atoms such as nitrogen, sulphur and oxygen, for perpetuity drawn the attention of chemist over the years mainly because of their biological consequence.

The ligand 1,10–Phenanthroline is sturdy field bidentate ligand that form very stable chelates with many first-row transition metals [4]. 1,10 Phenonthroline (Phen) or 4,5-diazaPhenanthrene is a tricyclic compound. Phen is a metal chelator. As a bidentate ligand in coordination chemistry, it forms strong Complexes with many metal ions through N-atoms [5-11]. Due to hydrophobicity of aromatic rings of Phen, the solubility of the neutral species is low in water which remarkably increases in organic solvents and also in aqua-organic mixtures.

Due to its superb ability to coordinate many metal ions, Phen and its derivatives are frequently used in many processes involving metal complexes, in which they can be featured in many roles; for example, as ligand for catalysis [12] or as stabilizing agents for nano particle synthesis [13].Phen has been used as important heterocyclic ligand for a large number of metal complexes that play an important role in a variety of important technological and medicinal applications; for example, promising applications in the field of electroluminescent materials [14-17], organic light-emitting devices (OLED) [18], organic semiconductors [19] or as chemical nucleases and therapeutic agents, due to their ability to bind or interact with the DNA bio macromolecule [20-23].

Metals by themselves and in proper balance to one another have important biochemical and nutritional functions [24-25]. The bioavailability of these minerals is also a very important factor, depending on the food source and also upon the pH of intestine [26-27]. Co(II), Cu(II) and Ni(II) are associated with several enzymes [28-29] and any variation in their concentration leads to metabolic disorders [30]. Hence speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ions. In biological fluids, metal ions exist in non-exchangeable form as in metallo-proteins or loosely bound to some bioligands as in metal-activated proteins.

The loosely bound metal ions are in equilibrium with simple metal ions present in the bio-fluids. These simultaneous equilibria involving a variety of metal ions and ligands are important in bio-fluids [31].

Chemical Speciation Of Binary Complexes Of Co(II), Cu(II) And Ni(II) With Mercaptosuccinic Acid In Acetonitrile-Water And DMF-Water Mixtures

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ABSTRACT:

A computer assisted pH-metric investigation has been carried out on the speciation of complexes of Co(II), Ni(II) and Cu(II) with MSA. The titrations were performed in the presence of different relative concentrations with sodium hydroxide in varying concentrations (0–60% v/v) of acetonitrile–water mixtures and DMF-water mixtures at an ionic strength of 0.16 mol L^{-1} and at a temperature of 303.0 K. Stability constants of the binary complexes were refined using MINIQUAD75. The best-fit chemical models were selected based on statistical parameters like crystallographic R factor and sum of the squares of residuals in mass-balance equations. The models for binary complex systems contain the chemical species ML, ML_2, MLH, ML_2H and ML_2H_2 for Co(II), Ni(II) and Cu(II) in acetonitrile-water and DMF-water mixtures. The trend in the variation of stability constants with change in the mole fraction of the medium was explained based on electrostatic and non-electrostatic forces. Distribution of the species with pH at different compositions of acetonitrile-water and DMF-water mixtures was also presented.

KEY WORDS:

MSA, Acetonitrile, DMF, MINIQUAD75, stability constants, best-fit chemical model

1. INTRODUCTION:

Cobalt(II), nickel(II) and copper(II) are associated with several enzymes [1-2] and any variation in their concentration leads to metabolic disorders [3]. Hence speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ions. In biological fluids, metal ions exist in non-exchangeable form as in metallo-proteins or loosely bound to some bioligands as in metal-activated proteins. The loosely bound metal ions are in equilibrium with simple metal ions present in the bio-fluids. These simultaneous equilibria involving a variety of metal ions and ligands are important in bio-fluids [4].

Mercaptosuccinic acid (MSA) or thiomalic acid (HOOC–CH(SH)-CH2-COOH) is a dicarboxylic acid containing a thiol functional group (-SH group) instead of an –OH group in malic acid[5]. MSA is a tridentate ligand which has the ability to form strong complexes with many metal ions in natural environment and within cells [6] and it has three replaceable hydrogen ions (two from the carboxylic and one from the sulfhydryl functional groups). Sodium salt of the anionic Au(I) complex of 2-mercaptosuccinic acid is an effective antiarthritic drug.[7-10] MSA is widely applied in industry and technology as corrosion inhibitor, electrolyte for electroplating bath, and components of bleach-fixing baths for photographic films and as active materials for depilatories and hair straightening.

Acetonitrile (AN) is a weak base [11] and a much weaker acid [12] than water. Anions have lower solvation energies in AN than in water, except in those cases where there is specific interaction with the solvent, thus cations are reduced at considerably more positive potential [13] in AN than in water. It is a protophobic dipolar aprotic solvent and it does not form any hydrogen bond with solute species. The protophobic character of AN may arise from the possible formation of dimers which are shown to exist from IR studies [14]. Acid-base equilibria and dissociation behavior of various acids in AN medium have been studied using spectrophotometer and conductivity meter [15]. Proton acceptor power and homo conjugation of mono- and diamines in AN as solvent was studied [16]. *N, N*-Dimethylformamide (DMF) was first prepared in 1893 by the French chemist Albert Verley. It is a clear, transparent, high-boiling point liquid with a light amine flavor and a relative density of 0.9445 (25°C). It is soluble in water and most organic solvents [17] that used as a common solvent for chemical reactions.

Since the dielectric constant at the active site cavities is very small compared to that at biofluids, low dielectric constant is mimicked by using a water soluble organic solvent like acetonitrile (AN) and dimethylformamide (DMF). Very few studies have been reported in the literature on effect of dielectric constants in organic solvent- water mixtures [18-19]. Hence, speciation studies of the title systems have been undertaken based on their involvement in various physiological reactions.

pH-Dependent Investigations Of 1,10-Phenanthroline Protonation Constant Values In Dimethylformamide And Acetonitrile -Water Mixtures

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ABSTRACT

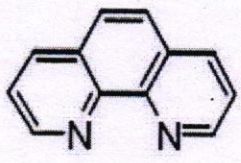
The protonation constants for the isoelectric reaction $LH^+ \rightleftharpoons L + H^+$ (where L = 1,10-phenanthroline) were determined pH-metrically in Dimethylformamide and Acetonitrile -water mixtures. The changes in the pK values are interpreted in terms of solvent basicity and ion-solvent interactions. The free energies of transfer of the H^+ ion from water to Dimethylformamide and Acetonitrile -water mixtures were also calculated. The protonation constants were calculated with the computer program MINIQUAD75 and selection of the best fit chemical models was based on the statistical parameters. The log K values were found to increase with increase of the organic solvent content. Its proton dissociation constants are reported to be pKa_1=0.70 and pKa_2=4.98 (μ=0.1, 25°C). Distribution of species, protonation equilibria and effect of influential parameters on the protonation constants have also been presented.

Keywords: 1,10-phenanthroline, Dimethylformamide, Acetonitrile, protonation constant, dielectric constant

1. INTRODUCTION

1,10-Phenanthroline(phen) is a colorimetric reagent for iron detection. It is also used as a reagent for the solvent extraction of anions. phen is an organic compound. It is a bi-dentate ligand in coordination chemistry, it forms strong complexes with many metal ions. Phen, an N-donor ligand with planar aromatic rings is known [1-7] to form protonated species in acidic solution .i.e., $H(phen)^+$ and $H(phen)^{2+}$ in the pH range of 2.0-9.0,and $H_2(phen)^{2+}$ at $[H^+]>1$ mol dm^{-3}. Due to hydrophobicity of aromatic rings in phen, the solubility of the neutral species is low in water which remarkably increases in organic solvents and also in aqua-organic mixtures. This reagent is slightly soluble in water (3.3 g/l at room temperature) and benzene (14 g/l at room temperature), and fairly soluble in alcohol (540 g/l), acetone, and diluted mineral acids. Its proton dissociation constants are reported to be pKa_1=0.70 and pKa_2=4.98 (μ=0.1, 25°C). phen which occurs in coal tar can be produced by the degradation of certain alkaloids. It is used as a starting material to prepare dyes and drugs. It is a good metal chelator used in metallocene industry as a redox mediator in biosensors, coordination of organometallic compounds, and as a catalyst for the oxidative organic synthesis. Phen is a well known chelating agent [8] and has been reported to be biologically active either alone or in the presence of metal ion. The bacteriostatic effects of phen and its metallic chelates have been studied of which the mixed ligand complexes have been found to be more effective.

phen or 4,5-diazaphenanthrene is a tricyclic compound. Phen is a metal chelator. As a bidentate ligand in coordination chemistry, it forms strong complexes with many metal ions through N-atoms. Due to hydrophobicity of aromatic rings of phen, the solubility of the neutral species is low in water which remarkably increases in organic solvents and also in aqua-organic mixtures. Protonation equilibria of phen have been studied in varying concentrations (0-60% v/v) of ACETONITRILE - water mixtures maintaining an ionic strength of 0.16 mol dm^{-3} at 303 K using pH metric method. The protonation constants have been calculated with the computer program MINIQUAD75 and the best fit models are arrived at based on statistical grounds employing crystallographic R factor, χ^2 ,skewness and kurtosis. Phen has two dissociable protons. It exists as LH_2^{2+} at low pH and gets deprotonated with the formation of LH^+, L successively with increase in pH.The protonated species $Hphen^+$ and H_2phen^{2+} were reported in the pH range 3.8-5.5 and < 1.0, respectively.



H_2O

Structure of 1,10-Phenanthroline

In this experiment, the protonation constants of 1,10-phenanthroline have been determined pH-metrically in aqueous solutions

CHEMICAL SPECIATION OF BINARY COMPLEXES OF Co(II), Cu(II) AND Ni(II) WITH L-DOPA IN ACETONITRILE-WATER AND DMF-WATER MIXTURES

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ABSTRACT:

A computer assisted pH-metric investigation has been carried out on the speciation of complexes of Co(II), Ni(II) and Cu(II) with L-Dopa. The titrations were performed in the presence of different relative concentrations with sodium hydroxide in varying concentrations (0–60% v/v) of acetonitrile–water mixtures and DMF-water mixtures at an ionic strength of 0.16 mol L^{-1} and at a temperature of 303.0 K. Stability constants of the binary complexes were refined using MINIQUAD75. The best-fit chemical models were selected based on statistical parameters like crystallographic R factor and sum of the squares of residuals in mass-balance equations. The models for binary complex systems contain the chemical species ML, ML_2, MLH, ML_2H and ML_2H_2 for Co(II), Ni(II) and Cu(II) in acetonitrile-water and DMF-water mixtures. The trend in the variation of stability constants with change in the mole fraction of the medium was explained based on electrostatic and non-electrostatic forces. Distribution of the species with pH at different compositions of acetonitrile-water and DMF-water mixtures was also presented.

KEY WORDS:

L-Dopa, Acetonitrile, DMF, MINIQUAD75, binary species, Distribution

1. INTRODUCTION:

Metals by themselves and in proper balance to one another have important biochemical and nutritional functions [1-2]. The bioavailability of these minerals is also a very important factor, depending on the food source and also upon the pH of intestine [3-4]. Co(II), Cu(II) and Ni(II) are associated with several enzymes [5-6] and any variation in their concentration leads to metabolic disorders [7]. Hence speciation study of essential metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ions. In biological fluids, metal ions exist in non-exchangeable form as in metallo-proteins or loosely bound to some bioligands as in metal-activated proteins. The loosely bound metal ions are in equilibrium with simple metal ions present in the bio-fluids. These simultaneous equilibria involving a variety of metal ions and ligands are important in bio-fluids [8]. The formation of metal complexes of L-Dopa was reviewed by Gergely [9] and Pettit [10]. L-Dopa is a naturally occurring dietary supplement and psychoactive drug found in certain kinds of food and herbs. Besides its natural and essential biological role L-Dopa is a popular drug in the treatment of manganese poisoning and Parkinson's disease [11-12] which are accompanied by neurologically similar sequels [13]. L-Dopa is also a popular drug in the treatment of dopamine-reponsive dystonia and to increase dopamine concentration, since it is capable of crossing the blood brain barrier, where Dopamine itself cannot. Once L-Dopa enters the central nervous system (CNS) it is converted into dopamine by the enzyme aromatic L-amino acid decarboxylase, also known as dopa decarboxylase. However, conversion to dopamine also occurs in the peripheral tissues, causing adverse effects and decreasing the availability of dopamine to the CNS; so it is the standard practice to co-administer a peripheral dopa decarboxylase inhibitor. L-Dopa, when oxidized, can form bonds with sulfur containing compounds (such as cysteine) to polymerize with other amino acids and lower bioavailability of protein when L-Dopa is consumed via foods [14].

Cobalt is an essential trace element that is an integral part of vitamin B_{12}, which is essential in the metabolism of folic acid and fatty acids. Cobalt is essential for the production of red blood cells and cobalamin and it acts as the substrate for the final enzymatic reaction that yields the active coenzyme derivatives of cyanocobalamin and aqua cobalamin. Although cobalt is an essential element for life in minute amounts (10 mg/day), at higher levels of exposure it shows mutagenic and carcinogenic effects [15]. Minot and Murphy [16] discovered that pernicious anemia can be treated by feeding the patient with large amounts of liver which contains vitamin B_{12}. Trace amounts of vitamin B_{12} are essential for the synthesis of hemoglobin. Its deficiency causes anemia. Besides cobalt is involved in the production of red blood cells and is important for the proper functioning of the nervous system as it can help in creating a myelin sheath. Nickel plays numerous roles in the biology of microorganisms and plants [17-18]. Urease, an enzyme which assists in the hydrolysis of urea, contains nickel. The NiFe-hydrogenases contain nickel in addition to iron-sulfur clusters [19]. A nickel-tetrapyrrole coenzyme, F430, is present in the methyl coenzyme M reductase which powers methanogenic archaea. Other nickel-containing enzymes include a class of superoxide dismutase [20] and a glyoxalase [21]. Copper is essential in all plants and animals. The human body contains copper at a level of about 1.4 to 2.1 mg/kg weight of human body [22].

INFLUENCE OF DIELECTRIC CONSTANT ON PROTONATION EQUILIBRIA OF L-DOPA IN ACETONITRILE-WATER AND DMF-WATER MIXTURES

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Abstract: Solute-solvent interactions of L-Dopa have been studied in 0–60% v/v Acetonitrile-water and DMF–water media using pH-metric method. The protonation constants have been calculated with the computer program MINIQUAD75. The best fit chemical model of the protonation equilibria have been selected based on standard deviation in protonation constants and residual analysis using crystallographic R-factor and sum of squares of residuals in all mass balance equations. Linear variation of protonation constants with inverse of dielectric constants of the solvent mixture has been attributed to the dominance of the electrostatic forces. Distribution of species, protonation equilibria and effect of influential parameters on the protonation constants have also been presented.

Keywords: *MINIQUAD75, Acetonitrile, DMF, L-Dopa*

1. INTRODUCTION:

2-Amino-3-(3,4-dihydroxyphenyl) propanoic acid (L-Dopa) is a naturally occurring dietary supplement and psychoactive drug found in certain kinds of food and herbs. Its richest natural source is from plant kingdom like the seeds of Mucuna Pruriens **[1]**. L-Dopa is an important neurotransmitter that is found in the brain and as a hormone in the circulatory system. Besides its natural and essential biological role L-Dopa is a popular drug in the treatment of Manganese poisoning and Parkinson's disease **[2, 3]**. It is also a popular drug in the treatment of dopamine-reponsive dystonia and to increase dopamine concentration, since it is capable of crossing the blood brain barrier, where dopamine itself cannot. Once L-Dopa enters the central nervous system (CNS) it is converted into dopamine by the enzyme aromatic L-amino acid decarboxylase, also known as dopa decarboxylase. However, conversion to dopamine also occurs in the peripheral tissues, causing adverse effects and decreasing the availability of dopamine to the CNS. So it is the standard practice to co-administer a peripheral dopa decarboxylase inhibitor. Potentiometric titrations of L-Dopa with Al^{3+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, and Zn^{2+} are studied and compared with UV-Vis-spectroscopy **[4]**. L-Dopa possesses four protonation constants (H_4L). Out of these four protons, two of these will be phenolate (catecholate) protons. The first proton to coordinate (a phenolate proton) has a very high affinity for the LH_3^- ion. The next two protons to coordinate bond to the other phenolate oxygen and the amine nitrogen.

Acetonitrile (AN) is a weak base **[5]** and a much weaker acid **[6]** than water. Anions have lower solvation energies in AN than in water, except in those cases where there is specific interaction with the solvent, thus cations are reduced at considerably more positive potential **[7]** in AN than in water. It is a protophobic dipolar aprotic solvent and it does not form any hydrogen bond with solute species. The protophobic character of AN may arise from the possible formation of dimers which are shown to exist from IR studies **[8]**. Acid-base equilibria and dissociation behavior of various acids in AN medium have been studied using spectrophotometer and conductivity meter **[9]**. Proton acceptor power and homo conjugation of mono- and diamines in AN as solvent was studied **[10]**. Dielectric constants of water + AN have been measured from 308.15 to 278.15 K over the entire composition range. Their deviations from ideality have been determined **[11]**.

N, *N*-Dimethylformamide (DMF) was first prepared in 1893 by the French chemist Albert Verley. It is a compound formed by the substitution of the hydroxyl group of formic acid with dimethyl amino group and the molecular formula $HCON(CH_3)_2$. It is a clear, transparent, high-boiling point liquid with a light amine flavor and a relative density of 0.9445 (25°C). It is soluble in water and most organic solvents **[12]** that used as a common solvent for chemical reactions. In Petroleum Industry DMF can be used as a gas absorbent for separating and refining gases. In Pesticide and Pharmaceutical industries DMF finds application as an intermediate of organic synthesis. It is also used as a catalyst in carboxylation reactions, in organic synthesis, as a quench and cleaner combination for hot-dipped tin parts (e.g., for high-voltage capacitors), as an industrial paint stripper and in inks and dyes in printing and fibre-dyeing applications **[13-14]**.

The aim of the present study is to determine the protonation- deprotonation equilibria of L-Dopa in low dielectric media. AN and DMF are commonly used in complex equilibria to maintain low dielectric constant. Hence AN–water and DMF-water

A pH METRIC DETERMINATION OF PROTONATION CONSTANTS OF MERCAPTOSUCCINIC ACID IN DIMETHYLFORMAMIDE AND ACETONITRILE -WATER MIXTURES

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ABSTRACT

The protonation constants values of mercaptosuccinic acid were determined in Dimethyl formamide and Acetonitrile - water mixtures (0–60% v/v) at 303.0 K at an ionic strength of 0.16 M using pH-metric technique. The protonation constants were calculated with the computer program MINIQUAD75 and selection of the best fit chemical models was based on the statistical parameters. The log K values were found to be an increase with increase of the organic solvent content. The linear variations of the protonation constants with the reciprocal of the dielectric constant of the medium have been attributed to the dominance of electrostatic forces. Distribution of species, protonation equilibria and effect of influential parameters on the protonation constants have also been presented.

Keywords: Mercaptosuccinic acid, Dimethylformamide, Acetonitrile, protonation constant, dielectric constant

INTRODUCTION:

Mercaptosuccinic acid as a ligand, has been of interest because of its versatility in coordinate modes due to two carboxylic acids and sulfhydryl groups (1). More recently, it has been used in the synthesis of novel polyanionic inhibitor of HIV and other viruses (2).Thiomalic acid is used as a brightening agent of metal plating.

Mercaptosuccinic acid (MSA) or thiomalic acid (HOOC-CH(SH)-CH_2-COOH) is a dicarboxylic acid containing a thiol functional group (-SH group) instead of an -OH group in malic acid (3). It is an important organic compound with multifunctional intermediate in organic synthesis. It is widely used in the synthesis of various biologically active sulfur containing compounds such as the antileukemic spiro [indoline-3,2'-thiazolidine]-2,4'-diones (4), antimicrobial (5,6) and antitubercular 4-thiazolidinones. It is also used as a building block in the synthesis of novel polyanionic inhibitors of human immunodeficiency virus and other viruses (7) and as a starting material in the synthesis of isocysteine, an important non-proteinogenic amino acid in a potent peptide inhibitor of stromelysin (8). In addition, sodium salt of the anionic Au (I) complex of 2-mercaptosuccinic acid is an effective antiarthritic drug (9). MSA is widely applied in industry and technology as corrosion inhibitor, electrolyte for electroplating bath and components of bleach-fixing baths for photographic films and as active materials for depilatories and hair straightening (10).

The composition and stability of zinc complexes of thiomalic acid was studied by using potentiometer and conductivitymeter (11).

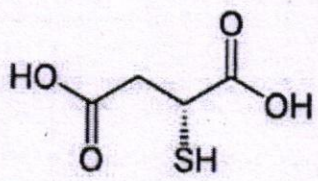

Fig: Structure of 2-mercaptosuccinic acid

The dicarboxylic reductant, MSA was one of the thiols chosen since there are three species existing in solution with different charges over the pH range. It may exist as double or singly protonated form or as the dianion having the two carboxylates deprotonated (12). The determination of protonation constants of MSA is important in understanding its physico-chemical

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Synthesis and Photocatalytic Studies of Fe_3O_4 Nanoparticles

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ABSTRACT

Advances in nanoscience and nanotechnology are centered in the control of size and shape of nanoparticles, as well as attainment of the extended arrangement of nanoparticles in different structures. One dimensional nanostructured magnetic materials are interesting because of their enhanced magnetic properties and potential applications such as information storage and gas sensor. The advanced electronic applications of Fe_3O_4 magnetic nanomaterials are considered to require improvement in the powder processing, particularly, meticulous particle control in the nanometer range and phase purity. Structural properties of Fe_3O_4 nanoparticles were synthesized via sol-gel protocol, the morphology and particles size were determined by X-ray diffraction, scanning electron microscope, transmission electron microscope, energy dispersive X-ray, UV- diffuse reflectance spectrophotometer and particle size analyzer. The structure of as prepared Fe_3O_4 nanoparticles was used for photocatalytic applications.

1. Introduction

Nanomaterials are the most challenging areas of current scientific and technological research because of their tremendous possibilities in novel shapes, structures and the unusual phenomena associated with materials. The field of nanotechnology is one of the most popular areas for current research and development in all technical disciplines. Nanostructured II–VI semiconductors have been studied very intensively in recent time due to their industrial implementation in nanoelectronic devices [1]. The n-type metal oxide semiconductor gas sensors are popular for monitoring caused by toxic and inflammable gases. They exhibit changes in electrical resistance in the presence of toxic and inflammable gases in the ambient atmosphere. The basis of this change in resistance lies in the reaction between the adsorbed oxygen on the oxide surface and a reducing gas, thus causing a decrease in resistance by releasing electrons back into the oxide [2].

Nanostructures of metal oxides have great attention due to their unique properties in novel applications. The devices based on inorganic materials such as metal oxide semiconductors, which works on principle of the change in conductivity with interaction of molecules [3]. Metal oxides nanostructures offer functionality from electrically conducting to insulating and from highly catalytic to inert propertites. One-dimensional nanostructured materials have attracted great attention over the past decade because of their important and often exhibit novel applications such as magnetic, electrical and optical properties. The unique and novel size dependent properties of magnetic oxides have initiated current worldwide intense research on magnetic nanomaterials [4].

Magnetic particles with sizes in the nanometer scale are now of interest because of their many technological applications and unique magnetic properties which differ considerably from those of bulk materials. Below a critical size, magnetic particles become single domain in contrast with the usual multi domain structure of the bulk magnetic materials exhibiting unique phenomena such as super paramagnetic and quantum tunneling of the magnetization [5].

Iron oxides are one of the most important transition metal oxides of technological importance [6]. Fe_3O_4 is a traditional magnetic material used in wide variety of applications such as electronic ignition systems, generators, vending machines, medical implants, wrist watches, inductor core, transformer circuits, magnetic sensors and recording equipment, telecommunications, magnetic fluids, microwave absorbers and other high-frequency applications [7]. Nanoparticles with novel morphologies and desired compositions have drawn immense attention due to their unique morphology and composition-dependent physicochemical properties and their importance in basic scientific research and potential technology applications [8].

The energy gap (*Eg*) is an important feature of semiconductors which determines their applications in optoelectronics [9-12]. The UV-Vis absorption spectroscopy is frequently used to characterize semiconductors materials [13], it is easy to extract the *Eg* values from their absorption spectra knowing their thickness. However, in colloidal samples, the scattering effect is enhanced since more superficial area is exposed to the light beam. In normal incidence mode, dispersed light is counted as absorbed light and the technique does not distinguish between the two phenomena. On the other hand, it is common to obtain powdered materials, frequently UV-Vis absorption spectroscopy is carried out dispersing the sample in liquid media like water, ethanol or methanol. If the particle size of the sample is not small enough, it precipitates and the absorption spectrum is even more difficult to interpret. In order to avoid these complications, it is desirable to use diffuse reflectance spectroscopy (DRS), which enables to obtain *Eg* of un-supported materials [14]. The theory which makes possible to use DRS was proposed by Kubelka and Munk [15].

2. Experimental Methods

2.1 Synthesis of Fe_3O_4 Nanoparticles

During the sol-gel protocol of iron nanoparticles, 3.2 g of poly ethylene glycol (PEG) taken in 25 mL of distilled water and stirred for 30 min. Later 3.3 g of $FeSO_4.7H_2O$ in 10 mL of distilled water, 9.6 g of $Fe_2(SO_4)_3$ in 20 mL of distilled water are stirred separately. Now both $FeSO_4.7H_2O$ and $Fe_2(SO_4)_3$ solutions were added drop by drop into the poly ethylene glycol solution. Then the solution was stirred for 30 min, ammonia solution is added to maintain pH-10. The mixture was further stirred for 4 h and filtered, washed with distilled water and finally rinsed with acetone and dried in hot air oven at 60 °C for 8 h. The dried compound was calcined at different temperatures at 400 °C, 600 °C and 800 °C for 4 h to get Fe_3O_4 nanoparticles.

2.2 Characterization Techniques

X-ray powder diffraction data were recorded on Siemens (D5000)

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FS-COMPLEMENT OPERATOR –A SYMMETRIC DIFFERENCE OPERATION BETWEEN FS-SUBSETS

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Abstract : In this paper ,we define a symmetric difference operation between two given Fs-subsets of a given Fs-set and prove collection of all Fs-subsets of a given Fs-set with this symmetric operation is a commutative group with some conditions

Keywords:Fs-set, Fs-subset, Fs-union, Fs-intersection , Fs-Complement, symmetric difference operation .

I. INTRODUCTION

Ever since Zadeh [8] introduced the notion of fuzzy sets in his pioneering work, several mathematicians studied numerous aspects of fuzzy sets.

Recently many researchers put their efforts in order to prove collection of all fuzzy subsets of a given fuzzy set is Boolean algebra under suitable operations [21].VaddiparthiYogeswara ,G.Srinivas and BiswajitRath[11] introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions. In this paper, we define a binary operation namely ,symmetric differenceoperation between to Fs-subsets and prove collection of all Fs-sub sets of a given Fs-set under this operation is a commutative group along with some conditions. For smooth reading of the paper, the theory of Fs-sets is introduced briefly in the section-II. All other relevant results are proved in the next section. We denote the largest element of a complete Boolean algebra $L_A[1.1]$ by M_A or $1or1_A$. For all lattice theoretic, set theoretic properties and Boolean algebraic properties one can refer Szasz [3], Garret Birkhoff[4],Steven Givant• Paul Halmos[2] and Thomas Jech[5].

II.THEORY OF FS-SETS

2.1 Fs-set: Let U be a universal set, $A_1 \subseteq U$ and let $A \subseteq U$ be non-empty. A four tuple $\mathcal{A} = (A_1, A, \bar{A}(\mu_{1A_1}, \mu_{2A}), L_A)$ is said be an Fs-set if, and only if

(1) $A \subseteq A_1$
(2) L_A is a complete Boolean Algebra
(3) $\mu_{1A_1}: A_1 \longrightarrow L_A$,$\mu_{2A}: A \longrightarrow L_A$,are functions such that $\mu_{1A_1}|A \geq \mu_{2A}$
(4) $\bar{A}: A \longrightarrow L_A$ is defined by $\bar{A}x = \mu_{1A_1}x \wedge (\mu_{2A}x)^c$,for each $x \in A$

2.2 Fs-subset: Let $\mathcal{A}=(A_1, A, \bar{A}(\mu_{1A_1}, \mu_{2A}), L_A)$ and $\mathcal{B}=(B_1, B, \bar{B}(\mu_{1B_1}, \mu_{2B}), L_B)$ be a pair of Fs-sets. $\mathcal{B}$ is said to be an Fs-subset of $\mathcal{A}$, denoted by $\mathcal{B} \subseteq \mathcal{A}$, if, and only if

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HOW IMAGE IS IN THE IMAGES OF FS-SUBSETS UNDER THE FS-COMPLEMENT OPERATOR

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(1) **Abstract:** In this paper we search the nature of an image of an Fs-subset under an Fs-function whenever this Fs-function acts on complement of an Fs-subset .Also we provethat the image of the complemented Fs-subset contains complement of the image under some condition. An Fs-set is $\mathcal{A} = \left(A_1, A, \bar{A}\left(\mu_{1A_1}, \mu_{2A}\right), L_A\right)$with following condition

(1) $A \subseteq A_1$
(2) L_A is a complete Boolean Algebra
(3) $\mu_{1A_1}: A_1 \longrightarrow L_A$,$\mu_{2A}: A \longrightarrow L_A$,are functions such that $\mu_{1A_1}|A \geq \mu_{2A}$
(4) $\bar{A}$:$A \longrightarrow L_A$ is defined by $\bar{A}x = \mu_{1A_1}x \wedge \left(\mu_{2A}x\right)^c$,for each $x \in A$

andFs-function is a triplet (f_1, f, Φ) denoted by $\bar{f}$,between two Fs-subsets $\mathcal{B} = \left(B_1, B, \bar{B}\left(\mu_{1B_1}, \mu_{2B}\right), L_B\right)$ and $\mathcal{C} = \left(C_1, C, \bar{C}\left(\mu_{1C_1}, \mu_{2C}\right), L_C\right)$ of $\mathcal{A}$, denoted by$\bar{f}$: $\mathcal{B} = \left(B_1, B, \bar{B}\left(\mu_{1B_1}, \mu_{2B}\right), L_B\right) \longrightarrow \mathcal{C} = \left(C_1, C, \bar{C}\left(\mu_{1C_1}, \mu_{2C}\right), L_C\right)$ if, and only if

(a) $f_1: B_1 \rightarrow C_1$ is function
(b) $f = f_1|_B^C: B \rightarrow C$ be onto
(c) $\Phi: L_B \longrightarrow L_C$ is complete homomorphism

Here $A \subseteq A_1$ is crisp set and L_A complete Boolean algebra,L_B is a complete Subalgebra of L_A and $B_1 \subseteq A_1, A \subseteq B$.

Keywords: Fs-set, Fs-subset, Fs-empty set ,Fs-Complement, Fs-function, Image of an Fs-subset.

I. INTRODUCTION

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Recently many researchers put their efforts in order to prove collection of all fuzzy subsets of a given fuzzy set is Boolean algebra under suitable operations [21].VaddiparthiYogeswara ,G.Srinivas and BiswajitRath[11] introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions. Also VaddiparthiYogeswara, BiswajitRathintroduced the concept of the Fs-function between Fs-set and image of an Fs-subset under an Fs-function studied some properties [17]. The concept of inverse image of an Fs-subset under an Fs-function was introduced by VaddiparthiYogeswara, BiswajitRath, Ch.RamasanyasiRaoetc [23,24,25]. In this paper we describe complement of an image of an Fs-subset under an Fs-function and study the corresponding Fs-subset properties and prove some results. For smooth reading of the paper, the theory of Fs-sets and Fs-functions and images in brief is dealt with in first three sections. We denote the

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Preservation of Arbitrary Fs-Unions and Fs-Intersections by the Inverse of an Fs-function

Vaddiparthi Yogeswara* Biswajit Rath Ch. Ramasanyasi Rao*** K.V. Umakameswari*** and Raghu Ram*****

Abstract : In this paper we prove that inverse of an Fs-function preserves arbitrary Fs-unions and Fs-intersections

Keywords : Fs-set, Fs-subset , Fs-function, Image of an Fs-subset, Inverse image of an Fs-set.

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2. THEORY OF FS-SETS

1. Fs-set : Let U be a universal set, $A_1 \subseteq U$ and let $A \subseteq U$ be non-empty. A four tuple

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is said be an FS-set if, and only if

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3. $\mu_{1A_1} : A_1 \to L_A$, $\mu_{2A} : A \to L_A$, are functions such that $\mu_{1A_1} \mid A \geq \mu_{2A}$
4. $\overline{A} : A \to L_A$ is defined by

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Theory of Inverse Images of Fs-Subsets under an Fs-Function – Some Observations

Vaddiparthi Yogeswara* Biswajit Rath and Ch. Ramasanyasi Rao*** K.V. Umakameswari*** and Raghu Ram*****

Abstract : In this paper we introduce the concept of inverse image of an Fs-subset under an Fs-function and prove some results.
Keywords : Fs-set, Fs-subset, Fs-empty set , Fs-function, Image of an Fs-subset, Inverse image of an Fs-set.

1. INTRODUCTION

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Recently many researchers put their efforts in order to prove collection of all fuzzy subsets of a given fuzzy set is Boolean algebra under suitable operations [21]. Vaddiparthi Yogeswara , G.Srinivas and Biswajit Rath[11] introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions. They are successful in their efforts in proving that result with some conditions. In this paper we introduce the concept of inverse image of an Fs-subset under an Fs-function and prove some results. For smooth reading of the paper, the theory of Fs-sets and Fs-functions in brief is dealt with in first two sections. We denote the largest element of a complete Boolean algebra L_A[1.1] by M_A or 1_A. For all lattice theoretic properties and Boolean algebraic properties one can refer Szasz [3], Garret Birkhoff [4], Steven Givant • Paul Halmos [2] and Thomas Jech [5]. For results in topology one can refer [10].

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is a complete Boolean Algebra

(*a*) $A \subseteq A_1$

(*b*) L_A is a complete Boolean Algebra

(*c*) $\mu_{1A_1} : A_1 \to L_A$, $\mu_{2A} : A \to L_A$, are functions such that $\mu_{1A_1} \mid A \geq \mu_{2A}$

2. Fs-subset : Let $A = (A_1, A, \overline{A}\ (\mu_{1A_1} \times \wedge (\mu_{2A}), L_A)$ and $B = (B_1, B, \overline{B}\ (\mu_{1B_1}, \mu_{2B}), L_B)$ be a pair of Fs-sets. B is said to be an Fs-subset of A, denoted by $B \subseteq A$, if, and only if

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Some Properties of Associates of Subsets of FSP-Points Set

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ABSTRACT

In this paper, based upon Fs-set theory [1], we define a crisp Fs-points set FSP($\mathcal{A}$) for given Fs-set $\mathcal{A}$ and establish a pair of relations between collection of all Fs-subsets of a given Fs-set $\mathcal{A}$ and collection of all crisp subsets of Fs-points set FSP($\mathcal{A}$) of the same Fs-set $\mathcal{A}$ and prove one of the relations is a meet complete homomorphism and the other is a join complete homomorphism and search properties of relations between Fs-complemented sets and complemented constructed crisp sets via these homomorphisms.

Key word: Fs-set, Fs-subset, Fs-complement, Fs-function, Fs-point

1 Introduction:

Ever since Zadeh [17] introduced the notion of fuzzy sets in his pioneering work, several mathematicians studied numerous aspects of fuzzy sets.

Murthy[7] introduced f-sets in order to prove Axiom of choice for fuzzy sets. The following example shows why the introduction of f-set theory is necessitated. Let A be non-empty and consider a diamond lattice $L = \{0, \alpha \parallel \beta, 1\}$. Define two fuzzy sets f and g from A into L such that $f(x) = \alpha$ and $g(x) = \beta$. Here both f and g are nonempty fuzzy sets. The Cartesian product of f and g from A into L is given by $(f \times g)(x) = f(x) \wedge g(x) = \alpha \wedge \beta = 0$. That is, $f \times g$ is a empty set. Even though both f and g are non-empty fuzzy sets, their fuzzy Cartesian product is empty showing that the failure of Axiom of choice in L-fuzzy set theory [10]. The collection of all f-subsets of a given f-set with Murthy's definition [7] f-complement [10] could not form a compete Boolean algebra. Vaddiparthi Yogeswara , G.Srinivas and Biswajit Rath introduced the concept of Fs-set and developed the theory of Fs-sets in order to prove collection of all Fs-subsets of given Fs-set is a complete Boolean algebra under Fs-unions, Fs-intersections and Fs-complements. The Fs-sets they introduced contain Boolean valued membership functions .They are successful in their efforts in proving that result with some conditions. In papers [2] and [3] Vaddiparthi Yogeswara, Biswajit Rath and S.V.G.Reddy introduced the concept of Fs-Function between two Fs-subsets of given Fs-set and defined an image of an Fs-subset under a given Fs-function. Also they studied the properties of images under various kinds of Fs-functions.

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