

Electron transfer kinetics of the reduction of bis(dihydrogentellurato)cuprate(III) in an alkaline medium

Kalyan K. Sen Gupta^a and Biswajit Pal^{b*}

^aDepartment of Chemistry, Jadavpur University, Kolkata-700 032, India

^bDepartment of Chemistry, St. Paul's C. M. College, 33/1, Raja Rammohan Roy Sarani, Kolkata-700 009, India

E-mail : palbiswajit@yahoo.com

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Abstract : This review highlights the reactivity of bis(dihydrogentellurato)cuprate(III) towards different inorganic and organic substrates reported during the period 1989 until 2007. The inorganic substrates are reducing nitro compounds, phosphorus, organophosphorus compounds and reducing organic substrates like alkanols, aryl alcohols, diols, aldehydes (aliphatic, aromatic, heterocyclic) and a,b-unsaturated compounds. All these reactions were studied in alkaline medium and the reactions exhibit diverse mechanistic behavior. Kinetics and mechanistic aspects of the reactions have been analyzed. An attempt has been made to correlate the results of different redox processes involving bis(dihydrogen-tellurato)cuprate(III).

Keywords : Review, oxidation-reduction reactions, bis(dihydrogentellurato)cuprate(III), reducing substrates.

Macrocyclic nickel(II) and copper(II) complexes of the deca- and tetradecaaza ligands

Anurag, Ankur Rastogi and Ram Nayan*

Department of Chemistry, Hindu College, Moradabad-244 001, Uttar Pradesh, India

E-mail : ramnayan_2003@yahoo.co.in Fax : 91-591-2440070

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Abstract : Template condensation reactions between the dinuclear nickel(II) or copper(II) complexes of the hexaaza macrocycles 1,4,7,9,12,15-hexaaza-8,8,16,16-tetrachlorocyclohexadecane (HTCH) or 1,4,7,10,13,16-hexaaza-8,9,17,18-tetrachlorocyclooctadecane (HTCO) and triethylenetetramine have yielded products of three new macrocyclic ring systems : 1,4,7,10,12,15,18,20,23,26,29,30,33,36-tetradecaazadispiro[10.7.10.7]hexatriacontane (TDSH), 2,5,8,11,14,17,19,22,25,28-decaaza-9,10-dichlorobicyclo[16.10.0]octacosane (DDCO) and 2,5,8,10,13,16,19,21,24,27,29,32,35,38-tetradecaazatri-cyclo[26.10.0.0²⁰]octatriacontane (TTCO). Formulation of these products as [Ni₄(TDSH)(H₂O)₁₀]Cl₈·5H₂O, [Cu₄(TDSH)(H₂O)₂]Cl₈, [Ni₃(DDCO)(H₂O)₈]Cl₆ and [Ni₄(TTCO)(H₂O)₁₀]Cl₈ and the metal-free TDSH.14HCl has been supported by elemental analyses, conductivity measurements, melting points and spectroscopic studies.

Keywords : Copper(II), nickel(II), macrocyclic, ligand.

Synthesis and spectral studies of nitrogen-oxygen donor macrocyclic metal complexes of Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II} and Pt^{II}

Sulekh Chandra^{a*}, Shweta Verma^a and P. Meera^b

^aDepartment of Chemistry, Zakir Husain College (University of Delhi), JLN Marg, New Delhi-110 002, India

E-mail : schandra_00@yahoo.com; shweta_verma@rediffmail.com Fax : 91-11-23215906

^bPhysical & Materials Chemistry, National Chemical Laboratory, Pune-411 008, Maharashtra, India

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Abstract : The complexes of Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II} and Pt^{II} with a nitrogen-oxygen donor macrocyclic ligand, viz. 5,6,13,14-dibenzo[1,4,8,11]dioxadiazas-5,7,11,13-cyclotetradecin have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, spectral and electrochemical studies. The molar conductance measurements of the complexes in DMF solution correspond to non electrolytic nature for M(L)X₂ complexes and 1 : 2 electrolytes for M(L)X₂ complexes [where M = Mn^{II}, Cu^{II}; M = Zn^{II}, Pd^{II} and Pt^{II}; X = Cl⁻, NO₃⁻ and L = ligand]. Thus, the complexes may be formulated as [M(L)X₂] and [M(L)]X₂ respectively. Mn^{II}, Cu^{II} complexes were of the high-spin type whereas the complexes of Zn^{II}, Pd^{II} and Pt^{II} were diamagnetic. On the basis of spectral studies an octahedral geometry has been assigned for Mn^{II}, tetragonal for Cu^{II}, tetrahedral for Zn^{II} complexes whereas square planar for Pd^{II} and Pt^{II} complexes.

Keywords : Macrocyclic, Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II}, Pt^{II}.

Studies on the solubilities and dissociation constants of substituted benzoic acids in 2-propanol-water mixtures and ion-solvent interactions

Rupasri Mandal (Karan) and Sujit Chandra Lahiri*

Department of Chemistry, University of Kalyani, Kalyani-741 235, West Bengal, India

E-mail : sujitclahiri@yahoo.com

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Abstract : The solvational behaviour of 2- and 3-substituted bromo- and iodo-benzoic acids have been examined from the solubility of the acids and the dissociation constants for the reaction



determined conductometrically using Fuoss-Kraus method in 2-propanol + water mixtures (0–87 mass% of 2-propanol). The changes in the solubility values depend on the hydrophobic character and the dielectric constant of the solvent medium. The Gibbs energy of transfer for anions have been determined from the relation

$$DG^\circ_{\text{t(dissn)}} = DG^\circ_{\text{t(H}^+)} + DG^\circ_{\text{t(A}^-)} - DG^\circ_{\text{t(HA)}}$$

using the previously determined values of $DG^\circ_{\text{t(H}^+)}$. $DG^\circ_{\text{t(A}^-)}$ values have been found to be increasingly positive in aquo-organic mixtures and the $DG^\circ_{\text{t(A}^-)}$ values of the 3-compounds are considerably different from those of 2-compounds. The results are discussed in the light of solute-solvent interactions. The effects of substitution on the interaction energies of anions have been determined.

Keywords : Ion-solvent interaction, dissociation constant, benzoic acid, conductivity measurement.

Fullerene-DBP conjugates : Their co-occurrence in meteorites, ammonites and Shilajit, and application in systemic drug delivery

Shibnath Ghosal* and Muruganandam A. V.

R & D Centre, Indian Herbs Ltd., Saharanpur-247 001, Uttar Pradesh, India

E-mail : vishnu20024@rediffmail.com

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Abstract : A unified manifestation of the macrocosmic and microcosmic actions is expressed by the co-occurrence of C₆₀-fullerene-dibenzo-a-pyrone (DBP) conjugates in meteorites, ammonites, and Shilajit. The crystal forms of mineral (aragonite) deposition in ammonites (the major marine precursors of Shilajit), are distinctly different in many respects from the inorganic mineral, aragonite. The mineral deposition in the living ammonite shells is under strict biological control and involves organo-mineral complexes received from meteorites. These constituents in ammonites are eventually transformed into Shilajit by humification. Hence, the supramolecular assemblies of complex chemical constituents of ammonites, in many respects, show striking similarities with the humic constituents (FAs, HAs and HMs) of meteorites and of Shilajit. Some selected assemblies, viz. fusoms and DCPs, of Shilajit, comprising of fullerene-DBP conjugates in their inner core, were found to confer facile water-solubility, stability and superior bioavailability (*Yogabahi* in Ayurveda) to a host of chemical agents that are ordinarily water-insoluble, thermolabile, autoxidizable, and/or prematurely biodegradable before reaching the target site. The potential of this superior drug delivery system is evaluated.

Keywords : Meteorites, ammonites, Shilajit, fullerene-DBP conjugates, drug delivery.

Comparative rate study on the oxidation of nicotinamide and isonicotinamide by permanganate in acidic medium

Ashok Sharma^a, Punit K. Mudgal and K. S. Gupta*

Department of Chemistry, University of Rajasthan, Jaipur-302 004, Rajasthan, India

E-mail : guptaks14@rediffmail.com

^aGovernment College, Dausa, Rajasthan, India

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Abstract : A comparative rate study on the oxidation of nicotinamide and isonicotinamide by potassium permanganate has been carried out in acidic solutions over an extended [H⁺]-range (1 × 10⁻⁵–1.0 mol L⁻¹). Under the similar reaction conditions, the oxidation of pyridine is imperceptible. Further, in the absence of acid none of the two amides is oxidized and in both cases, the N-protonated amide species appears to be reactive. For nicotinamide, the results are in agreement with the two-term rate law (A). The oxidation product was corresponding N-oxide.

$$-d[\text{MnO}_4^-]/dt = (k_0K + k_1K_1[\text{H}^+]) [\text{S}]_0 [\text{MnO}_4^-]_t [\text{H}^+]/(1 + K[\text{H}^+]) \quad (\text{A})$$

On the other hand, the oxidation of isonicotinamide follows a simpler rate law (B).

$$-d[\text{MnO}_4^-]/dt = k_0K[\text{S}]_0 [\text{MnO}_4^-]_t [\text{H}^+]/(1 + K[\text{H}^+]) \quad (\text{B})$$

The values of k_0 , K and k_1K_1 for nicotinamide were found to be $5.5 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$, 1.8×10^4 and $1.0 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively at 35 °C. And for isonicotinamide, the k_0 and K values were $4.4 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ and 5.6×10^3 respectively at 35 °C. The oxidation of nicotinamide is faster than the oxidation of isonicotinamide. It appears that the presence of -CONH₂ group at position 3 activates the ring nitrogen more for oxidation than the presence of this group at position 4.

Keywords : Permanganate, nicotinamide, isonicotinamide, oxidation, kinetics, N-protonation.

Spectral and equilibrium studies on some new derivatives of 4-amino-5-phenyl-3-mercapto-1,2,4-triazole

Aliya, B. Sireesha, Ch. Venkata Ramana Reddy and Ch. Sarala Devi*

Department of Chemistry, Nizam College, Osmania University, Hyderabad-500 001, India

E-mail : dr_saraladevich@yahoo.com

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Abstract : 4-Amino-5-phenyl-3-mercapto-1,2,4-triazole (APMT), 4-(4-methoxy)benzylideneamino-5-phenyl-3-mercapto-1,2,4-triazole (PMBPMT), 4-benzylideneamino-5-phenyl-3-mercapto-1,2,4-triazole (BPMT), 4-(2-hydroxy)benzylideneamino-5-phenyl-3-mercapto-1,2,4-triazole (HBPMT) and 4-amino-5-(4-nitro)phenyl-3-mercapto-1,2,4-triazole (ANPMT) were synthesized and characterized by elemental analyses, IR, ^1H NMR, ^{13}C NMR, DEPT and Mass spectral studies. Proton dissociation constants of these compounds in 70% v/v dioxan-water medium at 303 K and 0.1M (KNO_3) ionic strength were measured. The order of the pK_a corresponding to mercapto group follows the sequence : PMBPMT > BPMT > HBPMT > APMT > ANPMT.

Keywords : 1,2,4-Triazoles, IR, ^1H NMR, ^{13}C NMR, DEPT, dissociation constants.

Extraction chromatographic studies of uranium(VI) with crosslinked poly(acrylic acid) coated on silica gel

Bhabatosh Mandal*, Pranesh Chowdhury* and Susanta K. Pandit

Analytical Laboratory, Department of Chemistry, Visva-Bharati, Santiniketan-731 235, West Bengal, India

E-mail : bhabatosh_mandal@yahoo.co.in

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Abstract : A selective method has been developed for extraction and separation of U^{VI} with the chemically synthesized high molecular mass crosslinked poly(acrylic acid) coated on silanized silica gel. The coated materials act as a stationary phase for the extraction chromatographic studies. The structure and thermal stability of crosslinked poly(acrylic acid) has been elucidated with the help of FTIR and TGA. The optimum pH range for quantitative extraction of uranium was found to be 4 to 6. The effects of pH and stripping agent on extraction and elution of U^{VI} have been investigated. Ion exchange and break-through capacity of the exchanger (polymer coated on silanized silica gel) have been determined at room temperature. Surface morphology of the exchanger was studied by SEM. U^{VI} has been separated quantitatively from various synthetic aqueous mixtures containing metal ions (V^{IV} , Th^{IV} , Ce^{IV} , Pb^{II} , Hg^{II} , In^{III} , Fe^{III} and Zr^{IV}) commonly present in uranium ores and fission products. The method permits pre-concentration and sequential separation of U^{VI} from Ce^{VI} , Th^{IV} and Zr^{IV} of the same analytical group. A plausible mechanism for uranium ion exchange has been suggested.

Keywords : Poly(acrylic acid), silanized silica gel, metal ion, ion-exchange, solid phase extraction.

Synthesis of dl-DOPA functionalized chelating resin : Its application in separation of metal ions from environmental samples

Suparna Dutta and Arabinda K. Das*

Department of Chemistry, The University of Burdwan, Burdwan-713 104, West Bengal, India

E-mail : arabindakdas@rediffmail.com

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Abstract : Chloromethylated polystyrene-divinylbenzene has been functionalized with 3-(3,4-dihydroxyphenyl) dl-alanine (dl-DOPA). The resulting chelating resin has been characterized by its elemental analyses, infrared spectroscopy, thermogravimetric analysis and metal ion sorption capacities. It has been used for the preconcentration and separation of Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} and Pb^{II} and their determination by FAAS. Parameters such as the amount of resin, effect of pH, equilibration rate, sorption and desorption of metal ions and effect of diverse ions have been studied. The sorption capacities increase with increase in pH. Recoveries of the metal ions were 96 ± 5, 97 ± 6, 96 ± 5, 95 ± 8 and 96 ± 5 at 95% confidence level whereas the limits of detection (LOD) are 4.0, 5.0, 0.5, 1.3 and 25.0 mg L⁻¹ for Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} and Pb^{II} respectively. The calibration curves were linear up to 8 mg L⁻¹ (R² = 0.998), 10 mg L⁻¹ (R² = 1.000), 2 mg L⁻¹ (R² = 0.998), 2 mg L⁻¹ (R² = 1.000) and 5 mg L⁻¹ (R² = 0.979) for Ni^{II}, Co^{II}, Zn^{II}, Cd^{II} and Pb^{II} respectively. The reliability of the environment friendly method has been tested by analyzing certified samples.

Keywords : 3-(3,4-Dihydroxyphenyl) dl-alanine (dl-DOPA), chelating resin, solid phase extraction, Ni^{II}, Co^{II}, Zn^{II}, Cd^{II}, Pb^{II}.

Lutein content, fatty acid composition and enzymatic modification of lutein from marigold (*Tagetes patula* L.) flower petals

Sugata Bhattacharyya^a, Anadi Roychowdhury^b and Santinath Ghosh^{b*}

^aQuality Control Division, Dey's Medical Stores (Mfg.) Limited, Bondel Road, Kolkata-700 019, India

E-mail : subbhatt2003@gmail.com

^bDepartment of Chemical Technology, University College of Science and Technology, University of Calcutta, 92, Acharya Prafulla Chandra Road, Kolkata-700 009, India

E-mail : santinathghosh@yahoo.com.hk Fax : 91-33-23519755

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Abstract : Marigold flower (*Tagetes patula* L.) is a very good source of carotenoid mainly lutein. The marigold flowers of three varieties (orange, yellow and red) are utilized to extract the lutein present in it by using various solvents like hexane, acetone, petroleum ether and methanol. Among these solvents methanol showed the highest extractability (52.51%). Among the various marigold, orange variety content the maximum amount of lutein of 154.96 mg per gram of extract. The fatty acid composition of the ester fraction was determined and saturated fatty acid content was maximum (about 75%) and unsaturated fatty acid was about 25%. The lutein ester was also reacted with capric acid (C₁₀) in presence of *M. miehei* immobilized lipase and about 17.5% C₁₀ fatty acid was incorporated to produce modified lutein for application in various functional foods.

Keywords : Lutein, fatty acid, marigold petals, *Tagetes patula* L.

Equilibrium studies of Cu^{II} and Ni^{II} ternary complexes with anthranilic acid derivatives and *N,N*-donor ligands

B. Krishna Rao^a, Ch. Sarala Devi^b and Ch. Venkata Ramana Reddy^{c*}

^aDepartment of Chemistry, K. U. College of Engineering, Kothagudem-507 101, Andhra Pradesh, India

^bDepartment of Chemistry, Nizam College, Osmania University, Hyderabad-500 001, India

^cDepartment of Chemistry, Chaitanya Bharathi Institute of Technology, Gandipet, Hyderabad-500 075, India

E-mail : vrr9@yahoo.com

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Abstract : Equilibrium studies of (1 : 1 : 1) ternary, MAL complexes where, M = Cu^{II} and Ni^{II}, L = *N*-methyl anthranilic acid (NMAA), *N*-butyl anthranilic acid (NBAA) and *N*-phenyl anthranilic acid (NPAA) and A = 2,2-bipyridyl (bipy) and 1,10-phenanthroline (phen) were carried out pH -metrically at 30 °C and 0.1 M (KNO₃) ionic strength in aqueous-ethanol (50% v/v) medium. The formation constants of the binary (ML) and ternary complexes were determined under identical conditions for better correlation. The relative stabilities of the ternary complexes are quantified in terms of the parameter, $D \log K$. The stabilities of the complexes with respect to the ligand, L follow the order, NBAA > NMAA > NPAA. Various factors influencing the formation and stability of the complexes are discussed.

Keywords : Ligand, ternary complexes, formation constants, stability, $D \log K$.

Theoretical estimation of viscosity of quinary and its constituent quaternary liquid mixtures

Vinay Sangur^a, Nidhi Singh^a, Tanu Srivastava^a, Prakash Chandra^a, Niti Pandey^b and J. D. Pandey^{a*}

^aDepartment of Chemistry, University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

E-mail : jdpandey@rediffmail.com; drvsanguri@rediffmail.com

^bDepartment of Chemistry, Kamla Nehru Institute of Science, Sultanpur-228 118, Uttar Pradesh, India

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Abstract : The present work is concerned with the theoretical analysis of quite new and rare data on viscosity of a regular quinary and its quaternary subsystems at 308.15 K and 313.15 K (Nhaesi and Asfour, *J. Chem. Eng. Data*, 2005, 50, 149). For the first time, six different relations, viz. Wassiljewa relation, Sutherland-Wassiljewa (S-W) relation, Arrhenius model, Bingham relation, Kendall-Munroe (K-M) relation and Croenauer-Rothfus-Kermore (C-R-K) relation have been applied to the quinary system (toluene + octane + ethylbenzene + tetradecane + hexadecane) and its quaternary subsystems.

The theoretical results are compared with experimental viscosity data reported in the aforementioned papers. Quite interesting results are obtained.

Keywords : Quinary liquid system, viscosity, Wassiljewa relation, Arrhenius model.

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New *N*-galactosides : Synthesis of *N*-galactosylated thiocarbamides, benzothiazolyl thiocarbamides and thiocarbamates

Prashant R. Mahalle, Gajanan V. Korpe and Shirish P. Deshmukh*

P.G. Department of Chemistry, Shri Shivaji College, Akola-444 001, Maharashtra, India

E-mail : prmahalle@rediffmail.com

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Abstract : The title compounds were prepared by the condensation of tetra-*O*-acetyl- β -D-galactopyranosyl isothiocyanate with several amines, 2-aminobenzothiazole/substituted benzothiazoles and alcohols respectively. The structure of these new *N*-galactoside has been established on the basis of usual chemical transformations and IR, NMR and Mass spectral studies of some typical cases.

Keywords : *N*-Galactosides, galactosyl isothiocyanate, galactosyl thiocarbamides, galactosyl benzothiazolyl thiocarbamides, galactosyl thiocarbamates.

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Microwave-assisted Vilsmeier-Haack formylation of aromatic substrates

Kumaresh Ghosh* and Suman Adhikari

Department of Chemistry, University of Kalyani, Kalyani-741 235, Nadia, West Bengal, India

E-mail : ghosh_k2003@yahoo.co.in; *Fax* : 91-33-25828282

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Abstract : A microwave-assisted Vilsmeier-Haack formylation reaction has been studied on various amines, phenols and polynuclear hydrocarbons under solvent free condition that rapidly affords higher yield of products compared to traditional thermal condition.

Keywords : Aromatic compounds, microwave, Vilsmeier-Haack formylation.

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Trace determination of Pb, Cu, Cd and Zn in Ayurvedic drug, "Mahayograj Guggulu" via polarographic technique

Shweta Sharma, Priyanka Dhingra and R. S. Pandey*

Department of Chemistry, University of Rajasthan, Jaipur-302 064, Rajasthan, India

E-mail : shweta19sharma@rediffmail.com; pandey-rajshree@uniraj.ernet.in

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Abstract : Ayurveda is predominant among India's traditional health systems and Ayurvedic medicine constitutes around 84% of the sector. However, claims of several Ayurvedic products are often being criticized for not having any scientific evidence and general lack of standardization of raw materials. A D.C. polarographic method has been proposed for the determination of heavy metals like Pb, Cd, Zn, Cu etc. in Ayurvedic drug – "Mahayograj Guggulu" at mg/L level. The drug was digested with HCl + HNO₃. The analysis was performed using 0.1 M HCl (for Zn), 0.25 M acetate buffer (pH = 4.4 ± 0.1) for Cd, Cu, 0.1 M LiClO₄ (pH = 2.2 ± 0.1) for Pb. The concentration of metals were in the order Zn > Cd > Cu > Pb. The results were satisfactory and the developed method is simple, rapid and sensitive and can be applied to the microdetermination of the heavy metals in various Ayurvedic drugs.

Keywords : Mahayograj Guggulu, D.C polarography.
