

Experimental results and theoretical validation for the antioxidant mechanism of bilirubin[†]

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Abstract : The present study demonstrates that hydroxyl, 1-hydroxy ethyl and glutathiyyl radicals abstract hydrogen atom from bilirubin and forms a carbon-centered radical. The bimolecular rate constant for the reaction of ·OH, 1-hydroxy ethyl and glutathiyyl radicals with bilirubin are 1.0×10^{10} , 2.0×10^8 and $6.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. The transient absorption spectra obtained in these reactions have two peaks at 350 nm and 540 nm with bleaching in absorption at 450 nm. Both the absorption peaks form and decay with same rate constants showing that they are due to the same species. The bilirubin radical thus produced, decays with first order rate constant of $1.13 \times 10^4 \text{ s}^{-1}$. In presence of oxygen the decay becomes faster confirming it to be a carbon-centered radical. Linoleic acid peroxy radical also reacts with bilirubin via hydrogen abstraction. In the case of NO_2^- radical reaction, bilirubin produces absorption peak at 590 nm assigned to be the radical cation formed via single electron transfer from bilirubin. The bimolecular rate constant for this reaction is $2.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Corrected absorption spectra have been shown in few cases of these oxidation reactions. These results show that the oxidation of bilirubin can occur in two ways, either via hydrogen atom transfer or via single electron transfer depending on the nature of the oxidizing radical. *Ab initio* molecular orbital calculations have been performed to investigate the structure and energetics of radicals and radical cation produced by removal of hydrogen and electron, respectively from bilirubin molecule. It has been found that hydrogen abstraction from central methylenic group is most probable whereas pyrrole radical cation is most stable.

Keywords : Bilirubin, antioxidant mechanism, free radicals, hydrogen atom transfer, single electron transfer, pulse radiolysis, *ab initio* calculation.

A brief account on radiation chemical studies of antioxidants : Examples from natural phenols, sulfur and selenium compounds[†]

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Abstract : Reactive oxygen species (ROS) is a collective term used for a group of oxidants, which are either free radicals or molecular species capable of generating free radicals. Excessive production of ROS in living cells is a pathological condition known as oxidative stress. These species, depending on their reactivity and oxidizing ability, participate in a variety of chemical reactions and their reactions often cause irreversible chemical changes in biomolecules. Antioxidants are employed to protect the biomolecules from the damaging effects of such free radicals, primarily by their direct reaction. Although free radical reactions involving ROS with antioxidants are studied by several indirect methods, their direct monitoring is possible only by employing fast kinetic methods. Radiation chemistry of aqueous solutions and pulse radiolysis technique in particular has been found to be well suited to probe such reactions. Thus in this article, contributions from radiation chemistry section of BARC on the reactions of biologically important free radicals involved in oxidative stress with antioxidants have been discussed. Reactions of such radicals with curcumin, an antioxidant from

turmeric, which was studied extensively in this laboratory using pulse radiolysis technique, has also been presented. In the last three decades, the section has contributed significantly to the understanding of sulfur and selenium based antioxidants. A few recent highlights on these systems using pulse radiolysis have also been compared.

Keywords : Radiation, antioxidant, selenium compounds, sulfur.

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Pulse radiolysis studies at NCFRR : Recent research projects[†]

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Abstract : This article is an account of the pulse radiolysis facility at the National Centre for Free Radical Research, Department of Chemistry, University of Pune and a description of the recent research work at the centre. The features and functioning of the linac system along with the issues related to its maintenance are briefly described. The pulse radiolysis studies undertaken by various groups are diverse in nature with topics ranging from antioxidants, organic sulphur systems, dyes, nucleobases, nanoparticles, metal complexes etc. and some of them are briefly reviewed.

Keywords : Pulse radiolysis, metal complex, dye, nanoparticle.

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A technique for charge density measurement in laser-cluster interaction studies[†]

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Abstract : Ethyl bromide clusters have been irradiated with 532 nm laser pulses at gigawatt intensity condition. The time-of-flight mass spectra consist of multiply charged atomic ions of carbon and bromine along with mono-positively charged molecular and cluster fragments. To determine the charge density associated with the laser-cluster interaction, a new and simple technique has been devised for the time-of-flight configuration. In the new configuration, repeller grid has been changed to a thin plate and the electrical biasing arrangement has been modified. This new configuration allows measurement of charge densities as well as time-of-flight mass spectra without disturbing the experimental arrangement.

Keywords : Laser-cluster interaction, charge density, time-of-flight mass spectrometer (TOFMS), Coulomb explosion.

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Tuning the appearance of Marcus inversion region for intermolecular electron transfer (ET) reactions in micellar media[†]

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Abstract : In this mini-review we present a concise account of the results of our research on photoinduced electron transfer (ET) processes in micellar media, which we have been actively pursuing in our group for last one decade. Though Marcus inversion behavior is easy to observe for intramolecular ET reactions as well as for charge recombination reactions in contact ion pairs, the difficulty of observing such inversion behavior for intermolecular ET reactions under diffusive condition is a long lasting problem. The two most important factors that act against the observation of Marcus inversion for intermolecular ET reactions are : (i) diffusion of the reactants, which imposes a maximum limit for the observed reaction rate such that the true ET rates, which are faster than the diffusional rate of the reactants, are not possible to be estimated for such systems, and (ii) the non-availability of suitable donor and acceptor series to reach a very high reaction exergonicity ($-DG^0$) such that it is difficult to reach the farthest part of the inverted region where the true ET rates in the donor-acceptor encounter pairs become inherently slower than the diffusional rate of the reactants. In our studies, different micellar systems have been judiciously used as the reaction media to overcome the above limiting factors and accordingly the Marcus inversion behavior for the intermolecular ET reactions could be observed very easily. In these studies, the advantages of the micellar systems have been taken with respect to the following considerations, i.e. (i) the diffusion of the reactants inside the micelles will be highly retarded such that the ET reactions can effectively be considered as occurring under a non-diffusive condition of the reactants and (ii) the solvent relaxation dynamics in micellar media will be substantially slow such that the ET reactions in micelles will effectively occur under a situation of non-equilibrium solvent reorganization where the effective contribution of the solvent reorganization energy towards the activation barrier for the ET reactions will be reduced significantly and accordingly the onset of the Marcus inversion will be shifted towards the lower exergonicity region in comparison to that under very fast solvent relaxation condition. In fact, our studies in different micellar media using various donor-acceptor systems have unequivocally established for the first time the easy observation of Marcus inversion region for intermolecular ET reactions. Besides the observation of Marcus inversion region, we have also investigated other important aspects that might change the kinetics of ET reactions in micellar media, namely the effect of intervening surfactant chain, effect of temperature, distant dependence of the reactants, etc. In this short review we briefly present the results of these studies, with special emphasis to the observation of Marcus inversion and its tuning using micellar systems.

Keywords : Intermolecular electron transfer, micelles, electron transfer dynamics, Marcus inversion.

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Inhibitive effect of some Schiff base ligands for corrosion of mild steel in acidic media[†]

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Abstract : Schiff bases are widely used in complex formation as organic ligands. The effectiveness of some Schiff bases as corrosion inhibitors for mild steel in acid media has been studied by both weight loss and electro-chemical methods. Studies on the effect of inhibitor concentration and temperature on the corrosion of mild steel have been made. The inhibitor appears to function through adsorption following Langmuir adsorption isotherm. The thermodynamic parameters such as activation energy and free energy of adsorption were calculated. With the addition of methyl group in the ligand, +I effect increases, causing increase in the p-electron density on the azomethene group giving increased inhibitive effect. More effective inhibition was found due to increased adsorption caused by greater p-electron cloud when a phenyl group is added to the ligand. The polarization studies show that the inhibitors act as mixed inhibitors blocking both anodic and cathodic sites.

Keywords : Schiff bases, corrosion inhibitors, mild steel, acid media, inhibition mechanism.

Science and Technology of isotope enrichment[†]

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Abstract : One of the toughest scientific challenges has been to effectively - and inexpensively - separate a desired isotope of an element from the remaining isotopes for uses ranging from medicine to energy to weapons applications. In this account, after briefly dealing with important basics of separation physics, the various separation methods broadly classified as physical and chemical methods are described. Emphasis has been given to the advanced separation processes using lasers and some results from our laboratory have been described in detail. It is quite clear that there is a continuous massive effort by scientists and engineers around the world for developing isotope enrichment technologies.

Keywords : Isotope enrichment, laser, AVLIS, MLIS, IRMPD.

Excess adsorption of b-lactoglobulin on the soft surface of casein powder[‡]

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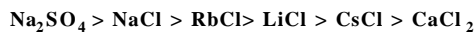
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Abstract : Extents (G_2^1) of adsorption of globular milk protein b-lactoglobulin (blg) from salt solution onto the soft surface of casein powder have been measured as functions of blg concentration at pH 6.5 keeping ionic strength and temperature constants. Ionic strengths were maintained by using neutral salts LiCl, NaCl, KCl, RbCl, CsCl, CaCl₂ and Na₂SO₄. Six molar concentration of denaturant urea was also used for the study of adsorption. Except KCl and KCNS, G_2^1 in the presence of other salts and urea respectively are positive. Values of G_2^1 in all cases increases with increase of C_2 for blg concentration in the bulk phase. G_2^1 also increases with increase of C_2 until at a critical value C_2^m , it attains the maximum value G_2^m at the state of surface saturation. Values of G_2^m stands in the order :



This order is partly agreeing with lyotropic or Hoffmeister series effect. G_2^1 for KCl and KCNS are negative in sign at all values of C_2 due to the excess positive hydration of blg in the presence of these salts. The maximum affinities of adsorption at the state of surface saturation represented by the free energy decrease $-DG^0$ calculated from the use of integrated form of the Gibbs adsorption equation in kJ per kg of casein varies linearly with increase of G_2^m and average values of the free energy change $-DG_B^0$ calculated from the slope of this plot is 38 kJ per mole of adsorbed blg in all cases.

Keywords : Excess adsorption, beta-lactoglobulin, casein powder, lyotropic series, adsorption on soft surface, adsorption free energies.

Interactions of therapeutically active plant flavonols with biological targets: Insights from fluorescence spectroscopic studies[†]

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Abstract : Plant flavonols have attracted much recent attention in view of their novel therapeutic properties (effective against various free radical mediated and other diseases) which make them promising alternatives to conventional therapeutic drugs. However, till date, not much is known, regarding their mode of interactions and binding affinities with relevant biological targets. This article presents perspectives highlighting the usefulness of the exquisitely sensitive 'two color' fluorescence behavior of flavonols (which arise due to highly efficient photoinduced excited state intramolecular proton transfer (ESIPT) reactions) for exploring their interactions, at the molecular level, with biomembranes and proteins, which are the principal biological targets of such drug molecules. In this context, we made exploratory studies on the interactions of some representative therapeutically important flavonols with model and natural membranes (composed of phosphatidylcholine liposomes and red blood cell ghost membranes respectively) and serum albumin proteins. Since the ESIPT process is highly sensitive to external hydrogen bonding perturbation effects, the relative contribution between the two colors is strongly modulated by the local environment of the fluorophore, with dramatic changes in the emission yield, energy, anisotropy (r), lifetime (τ) and related parameters of both ESIPT tautomer and normal fluorescence bands. This provides multiparametric fluorescence probing opportunities, revealing salient details about the nature and location of binding sites as well as quantitative estimates of partition coefficients/binding constants. This promising new approach may be expected to open up new avenues for the 'screening' of the most appropriate flavonoid derivatives, from among numerous structural variants found in nature, as well as the design of relevant synthetic derivatives with improved features.

Keywords : 3-Hydroxyflavone, fisetin, robinetin, quercetin, fluorescence spectroscopy, excited -state intramolecular proton transfer, phosphatidylcholine liposome, bovine serum albumin.

Stilbenoids and sesquiterpene derivatives of the orchids *Gastrochilum calcoelaria* and *Dendrobium amoenum*: Application of 2D NMR spectroscopy in structural elucidation of complex natural products[†]

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Abstract : Systematic chemical investigation of the Indian orchid *Gastrochilum calcoelaria* D. Don for the first time afforded two new bibenzyl derivatives, designated gastrochilin and gastrochilinin, besides the compounds confusarin [2,7-dihydroxy-3,4,8-trimethoxyphenanthrene] and 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene. The orchid *Dendrobium amoenum* Wall was chemically investigated earlier. Further chemical investigation of this Indian orchid has resulted in the isolation of yet another new bibenzyl derivative amoenylinin, besides the previously reported stilbenoids amoenylin [4-hydroxy-3,4,5-trimethoxybibenzyl], isoamoenylin [3,4-hydroxy-3,4,5-trimethoxybibenzyl], moscatilin [4,4c-dihydroxy-3,3c,5-trimethoxybibenzyl], batatacin-III [3,3c-dihydroxy-5-

methoxybibenzyl], 3,4-dihydroxy-5-methoxybibenzyl, the two phenanthrenes confusarin and 2,7-dihydroxy-3,4,6-trimethoxyphenanthrene, the two phenanthropyran derivatives imbricatin [2,7-dihydroxy-6-methoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran] and flaccidin [2,6-dihydroxy-7-methoxy-9,10-dihydro-5*H*-phenanthro[4,5-*bcd*]pyran], the two sesquiterpenoids amotin and amoenin, *p*-hydroxybenzaldehyde and *b*-sitosterol. The structures of gastrochilin, gastrochilin and amoenylinin are established as 2-hydroxy-3,3-dimethoxy-4,5-methylenedioxybibenzyl, 2,3,3-trimethoxy-4,5-methylenedioxybibenzyl and 3,3,4,4,5-pentamethoxybibenzyl, respectively, from spectral and chemical evidence. Additional spectral evidence for 3,4-dihydroxy-5-methoxybibenzyl and detailed 2D NMR spectral analysis of amotin are provided for further confirmation of their assigned structures.

Keywords : *Gastrochilum calcoelaria* D. Don, *Dendrobium amoenum* Wall, Orchidaceae, gastrochilin, gastrochilin, amoenylinin, 3,4-dihydroxy-5-methoxybibenzyl, bibenzyl derivatives, 2D NMR spectral analysis of amotin, amoenin, sesquiterpene derivatives.