Multiwavelength Spectrophotometric Determination of Protolytic Constants of 4-(2-Pyridylazo)resorcinol (PAR) in Binary Dioxane + Water Mixtures

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Acid-base properties of 4-(2-pyridylazo)resorcinol (PAR) in 1,4-dioxane (DX)-water binary mixture were investigated using a multiwavelength spectrophotometric method. The protolytic equilibrium constants, spectral profiles, concentration diagrams and also the number of components have been calculated from the fitting of the pH-absorbance data with appropriate mass balance equations by an established factor analysis model. The binary mixture of water-DX is a good system to study changing in the donating ability and permittivity of mixed solvent components in comparison to each other, considering the fact that variation in the permittivity from pure water to pure DX is 76 units. A linear relationship is observed between pKa's of the PAR molecule and the mole fraction of DX in different solvent mixtures. A glass electrode calibration procedure based on a four-parameter equation aided Gran's method was used to obtain pH readings based on the concentration scale (p_cH). It has been observed that there is an inverse relationship between second and third protolytic constants and mole fraction of DX. The effect of the solvent on the protolytic constants was discussed.

Key words: PAR, DATAN, acidity constants, binary solvents, multiwavelength, spectrophotometry, chemometrics, dioxane + water mixtures

Synthesis, Characterization and Magnetic Studies of Oxamido-Bridged Copper(II)–Iron(III) Heterobinuclear Complexes

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Two new oxamido-bridged Cu(II)–Fe(III) heterobinuclear complexes of formulae $[Cu(dmoxpn)Fe(bpy)_2](ClO_4)_3$ (**1**) and $[Cu(dmoxae)Fe(bpy)_2](ClO_4)_3$ (**2**) have been synthesized, where bpy denotes 2,2′-bipyridine; while dmoxpn and dmoxae represent N,N′-bis[3-(dimethylamino)propyl]oxamido and N,N′-bis[2-(dimethylamino)ethyl]oxamido dianions, respectively. Based on elemental analyses, molar conductivity measurements, IR and electronic spectral studies, it is proposed that the two complexes have oxamido-bridged structures consisting of a copper(II) and an iron(III) ions, which have a square planar environment and a distorted octahedral environment, respectively. The two heterobinuclear complexes were further characterized by variable-temperature magnetic susceptibility (4.2~300 K) measurements and the observed data were simulated by the equation based on the spin Hamiltonian operator, $\hat{H} = -2J\hat{S}_1 \hat{S}_2$, giving the exchange integral J = –18.2 cm^{-1} for (**1**) and J = –26.5 cm^{-1} for (**2**). The results revealed the occurrence of an intramolecular antiferromagnetic interaction between the adjacent iron(III) and copper(II) ions through the oxamido- -bridge within each molecule. The influence of the chelate ring arrangement around the copper(II) in the copper(II)–iron(III) heterobinuclear complexes on magnetic interactions between the metal ions of this kind of complexes is preliminarily discussed.

Key words: μ-oxamido-bridge, copper(II), iron(III), heterobinuclear complexes, magnetic properties

Geometry of α-Diaryl Type CH–NH Acids of Pharmacological Interest. Crystal Structures of α-(4-Chlorophenyl)- and α-(2,4-Dichlorophenyl)-α-2-pyrazilideneacetonitriles

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α-Diarylacetonitriles represent a very interesting model for studying the structure-activity relationship, due to restricted freedom of conformational diversity and, on the other hand, a very wide range of biological activities, including analgesic, non-narcotic antiinflammatory and antirheumatic. The two studied representatives have in the crystal state very uniform molecular structures, which may be characterized by a dihedral angle between the two aromatic rings, being 77° in 4-chlorophenyl; 74° and 80° in 2,4-dichlorophenyl derivative, respectively. Despite the presence of groups capable of weak C–H hydrogen bonds formation there is only one short C–H...X contact (X = N in 4 position of the pyrazinyl ring) of 2.40 Å, being significantly shorter than the sum of van der Waals radii of respective atoms. The contact found in the 2,4-dichlorophenyl derivative crystal is in accord with CH–NH proton transfer observed in these compounds.

Electron Ionization Mass Spectrometric Study of 5-Benzylidene Rhodanines Differentially Substituted in the Phenyl Ring and 3-Phenyl Rhodanine

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The electron ionization behaviour of 5-benzylidene rhodanines (**1–10**) and 3-phenyl rhodanine (**11**) was studied. For each of the **1–10** an efficient loss of mass 87, namely the loss of HNCS and CO molecules, was observed. The compounds containing a hydroxy group at the *ortho* position to the rhodanine moiety showed also an abundant fragment ion formed by the loss of HNCS. The other phenyl ring substituents did not affect this fragmentation pathway. On the other hand, decomposition of the [M-87]$^{+\cdot}$ fragment ion strongly depends on the phenyl ring substitution, *e.g.* for **5** having a methoxy group at the *meta* position to the rhodanine moiety, in contrast to its *ortho* and *para* correspondents **4** and **6**, the loss of the fragments HCO$^{\cdot}$ and H$_2$CO proceeded. 3-Phenyl rhodanine lost the ketene molecule yielding the fragment ion of *m/z* 167. On the grounds of its decomposition and comparison with reference compound decomposition it was deduced that this ion had the structure of 2-mercaptobenzothiazole.

Key words: 5-benzylidene rhodanines, 3-phenyl rhodanine, electron ionization, fragmentation pathways

Stachyfloroside E: A New Acylated Flavone Glycoside from *Stachys parviflora*

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Phytochemical investigations of the whole plant of *Stachys parviflora* (Lamiaceae) resulted in the isolation of a new acylated flavone glycoside. The structure of the new compound, named stachyfloroside E, was established as 6,8-dihydroxy-2-(4′,5′-dihydroxy)-7[-6-*O*-acetyl-β-D-galactopyranosyl(1→2)-β-D-glucopyranosyl)oxy]-4H-1-benzopyran (**1**). The structure elucidation of the new compound was based primarily on 1D and 2D NMR analysis, including COSY, HMBC and HMQC correlations.

Gas Phase Kinetics of the Reaction System of $2NO_2 \leftrightarrow N_2O_4$ and Simple Alcohols Between 293–358 K

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The reversible reactions between nitrogen dioxide and alcohols (CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, $CH_3CHOHCH_3$) have been studied in the gas phase, using the spectrophotometric method. RONO ($R = CH_3$, CH_3CH_2, $CH_3CH_2CH_2$, CH_3CHCH_3) were identified by UV spectra. The equilibrium constants as well as the bimolecular rate constants were determined by computer modeling, using the programme MINICHEM. We calculated the following values for the forward rate constants k_3^{av}: $(3.0\pm0.9)\times10^{-18}$, $(8.0\pm2.4)\times10^{-18}$, $(5.4\pm1.6)\times10^{-18}$, $(2.0\pm0.6)\times10^{-18}$ cm^3 $molec^{-1}$ s^{-1} and the equilibrium constants K_{av}: 100 ± 30, 40 ± 12, 109 ± 33, 39 ± 12 at 298 K for the reactions with methanol, ethanol, 1-propanol and 2-propanol, respectively. The temperature dependence of the rate constants and the equilibrium constants were studied and it allowed to obtain the activation energy for the forward and for the reverse reaction, as well as thermochemical parameters. The equilibrium constants and the rate constants suggest that symmetrical N_2O_4 is the reactive species.

Key words: nitrogen dioxide, dinitrogen tetroxide, simple alcohols

Isothermal Sections of the Y_2Se_3–Cu_2Se–Sn(Pb)Se Systems at 870 K and Crystal Structure of the $Y_{4.2}Pb_{0.7}Se_7$ Compound

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Interactions between the components in the Y_2Se_3–Cu_2Se–SnSe and Y_2Se_3–Cu_2Se–PbSe systems at 870 K were determined using X-ray powder diffraction. The existence of the compound with composition $YCuSe_2$–$Y_{2/3}Cu_2Se_2$ ($Er_{2/3}Cu_2S_2$ structure type, space group $P\bar{3}$, $a = 0.40660$–$0.40370(1)$ nm, $c = 0.64640$–$0.65906(2)$ nm) was confirmed in the Y_2Se_3–Cu_2Se section. The existence of the compounds $Y_6Pb_2Se_{11}$ ($Y_6Pb_2Se_{11}$ structure type, space group $Cmcm$, $a = 0.40620(8)$ nm, $b = 1.3467(2)$ nm, $c = 3.7624(7)$ nm) and $Y_{4.2}Pb_{0.7}Se_7$ (Y_5Se_7 structure type, space group Cm, $a = 1.3357(1)$ nm, $b = 0.40469(3)$ nm, $c = 1.22356(8)$ nm, $\beta = 104.529(3)°$) in the Y_2Se_3–PbSe section was observed. No quaternary compounds exist in the Y_2Se_3–Cu_2Se–SnSe system. The existence of the compounds $Y_{3.33}CuPb_{1.5}Se_7$ ($Y_{3.33}CuPb_{1.5}S_7$ structure type, space group Cm, $a = 1.35675(7)$ nm, $b = 0.40959(2)$ nm, $c = 1.26026(6)$ nm, $\beta = 104.661(2)°$) and $YCuPbSe_3$ (β-$BaLaCuSe_3$ structure type, space group $Pnma$, $a = 1.05438(5)$ nm, $b = 0.40524(2)$ nm, $c = 1.33840(5)$ nm) in the Y_2Se_3–Cu_2Se–PbSe system was confirmed.

Key words: X-ray analysis, isothermal section, crystal structure, phase diagram

Electrochemical Studies of N,N′-Bis-(β-phenylcinnamaldehyde) Phenylenediimine in Dimethylformamide

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The electrochemical reduction mechanism of novel ligand N,N′-bis(β-phenyl-cinnamaldehyde) phenylenediimine has been investigated in the potential range –1.1 V to –2.7 V on glassy carbon (GC) and mercury (Hg) electrodes. Reduction of >C=N bonds was studied in dimethylformamide using direct current (DC) voltammetry, differential pulse (DP) voltammetry, cyclic voltammetry (CV), chronoamperometry, chronocoulometry and coulometry. The studied process consists of two irreversible 2-electron transfers attributable to the reduction of azomethine bonds. The diffusion and transfer coefficients are reported. Adsorption characteristics of the molecule on a mercury electrode were studied and the maximum surface excess was found to be about 1.8×10^{-10} mol cm^{-2}.

Key words: cyclic voltammetry, electrochemistry, diimine, Schiff bases, coupled chemical reaction, reduction

Measurements of Phase Equilibria in Asymmetric Mixtures at High Pressures. Experimental Setup and Introductory Measurements

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An apparatus for measuring high-pressure phase equilibria up to 453 K and pressures up to 2000 bar is presented. The applied method of the construction of a phase diagram for a fluid mixture requires the determination of families of P-T diagrams of constant composition (isopleths). The equipment consists of a variable volume cell, a temperature stabilizing system, pressure generation system and a system that makes the loading of the cell with a gas possible. Measurements of liquid – liquid, liquid – vapour and solid – liquid equilibria were performed for two binary systems: ethylene + eicosane and carbon dioxide + squalane.

Key words: phase equilibria, high pressure, experimental setup

The Havriliak-Negami Dielectric Response in Time Domain

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The subject of this paper is to show how to transform the Havriliak-Negami function, which has its analytical representation in frequency domain only, into the time domain. We present some results of numerical calculations of the time-domain dielectric response function *f(t)* and analyse the time dependence of this function in respect of the power-laws.

Estimation of Consecutive and Parallel Reactions During Ethane Dehydrogenation with Carbon Dioxide over Co-MCM-41

by Y.-N. Li, X.-H. Guo, G.-D. Zhou, X. He, Y.-L. Bi, W.-X. Li, T.-X. Cheng,
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The main reactions between C_2H_6 and CO_2 and their thermodynamics were studied, which indicated that there exist very complicated reactions between them. CO_2 can enhance the equilibrium conversion of C_2H_4 formation *via* dehydrogenation of C_2H_6 and react with the surface deposited carbon, resulting in stabilization of the activity and the prolongation of lifetime of the catalyst. Thus, the exploration of catalyst with desired C_2H_4 selectivity from oxidative dehydrogenation of ethane (ODE) is most important. In this study, the possible reactions of ODE with CO_2 on Co-MCM-41 catalyst are discussed.

Key words: ethane, carbon dioxide, ethene, thermodynamics

Segregation in CuPd Alloys Studied by X-ray Photoelectron Spectroscopy Using Lineshape Analysis by the Fuzzy *k*-Nearest Neighbour Rule

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The surface segregation process in polycrystalline Cu75Pd25 alloy is investigated. Quantitative and qualitative analyses of selected CuPd alloys with atomic composition Cu25Pd75, Cu50Pd50 and Cu75Pd25 are based on the multiline (ML) approach and the spectra lineshape analysis with the use of a statistical pattern recognition method, called the fuzzy *k*-nearest neighbour rule (f*k*NN). The analyzed X-ray photoelectron spectra (XPS), recorded using AlK_{α} radiation from 280 eV to 1450 eV, exhibit a varying mean escape depth depending on the investigated photoelectron kinetic energy. The lineshape analysis, allowing to identify qualitatively and quantitatively the atomic composition and structure within the selected electron sampling depth, was shown to be consistent with the results of conventional quantitative analyses, based on measured binding energy shifts and intensities, and applicable for the layer segregation processes.

Key words: CuPd alloys, segregation, quantitative and qualitative analyses, multiline (ML) approach, pattern recognition, the fuzzy *k*-nearest neighbour rule, f*k*NN

Electrochemical and Computational Studies of Some 9,10-Anthraquinone Derivatives in Acetonitrile Solution

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The electrochemical behavior of some recently synthesized 9,10-anthraquinone derivatives on Au electrode in acetonitrile was investigated. In the absence of proton donors, the anthraquinones reduced in two successive one-electron steps. The first step is reversible or nearly reversible, while the second step is quasi-reversible. The influence of molecular structure on the reduction potential is addressed. The diffusion coefficients of the anthraquinone derivatives were determined from chronoamperometry and rotating disk electrode measurements. The heterogeneous electron transfer rate constants and charge transfer coefficients were evaluated from rotating disk voltammetry measurements. An *ab-initio* quantum mechanical method was carried out at the DFT-B3LYP level to compute the electrode's formal potentials for the four anthraquinones AQ1-AQ4 in acetonitrile solution. A nice linear relationship was observed between the theoretically predicted values and experimentally determined formal electrode potentials of the 9,10-anthraquinone derivatives.

Syntheses, Properties and Crystal Structures of One-dimensional Transition Metal-Azide Coordination Polymers *via* Hydrogen Bonds

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Three novel mononuclear transition metal-azide compounds, $Mn(Pz^{Bu-t})_4(N_3)_2$ (**1**), $Co(Pz^{Bu-t})_4(N_3)_2$ (**2**) and $Co(Pz^{Bu-t})_3(N_3)_3$ (**3**) (Pz^{Bu-t} = 3-*tert*-butyl pyrazole), have been synthesized and characterized by elemental analysis, IR and UV-Vis spectra, and the crystal structures of compounds **1** and **3** have been determined. Crystal data for **1**: triclinic, space group $P\bar{1}$ with a = 8.0844(9), b = 10.1230(12), c = 12.1046(13) Å, α = 91.854(3)°, β = 108.495(2)°, γ =101.598(2)°, V = 915.33(18) Å^3 and Z = 1. Crystal data for **3**: monoclinic, space group $P2(1)$ with a = 10.3286(9), b = 23.593(2), c = 12.7735(10) Å, β = 106.659(2)°, V = 2982.0(4) Å^3 and Z= 2. The azide ions in compound **1** are coordinated to manganese(II) ions in *trans* centrosymmetric octahedral configuration. However, compound **3** shows two unsymmetrical molecules with distorted octahedral geometry ligated by three azide anions and three 3-*tert*-butyl pyrazole ligands in crystal cell. The compounds are aggregated to form one-dimensional chain through (pyrazole)N–H···N(azide) hydrogen bonds, respectively. In aqueous solution, the reaction of compound **2** with azide excess (2 equivalents) and H_2O_2 was investigated, and the product was isolated and identified to be homogeneous as compound **3**. The result suggests that the compound **3**, as the oxidation product of compound **2**, was formed by the change of the coordination geometry around cobalt ion in the reaction process, due to the binding of peroxides to the cobalt ion *via* the removal of the pyrazole ligand.

Key words: azide complexes, crystal structures, hydrogen bonds

Microwave-assisted Synthesis of Hydrated Sodium Uranyl Oxonium Silicate

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