Self-Assembling Systems in Restricted Geometry

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Results obtained within Ciach-Høye-Stell model of oil-water-surfactant mixtures in restricted geometry are reviewed. Special attention is paid to ordering effects of a surface (or two parallel surfaces) close to phase boundaries between lamellar and microemulsion or water-rich phases. Relations between the structure of the confined self-assembling system and the measurable quantities are discussed. Predictions of the Ciach-Høye-Stell model are compared with Landau-Ginzburg and membrane theories and with experimental results.
Synthesis and Characterization of a New Thiazole Schiff Base
5-Bromo-2-hydroxybenzylidene-2-aminobenzothiazole
and Its Complexes with Co(II), Cu(II) and Ni(II)

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A new ligand 5-bromo-2-hydroxybenzylidene-2-aminobenzothiazole has been synthesized from 2-aminobenzothiazole and 5-bromosalicylaldehyde by condensation in ethanol. Metal complexes of the ligand were prepared from chloride salts of Co(II), Cu(II), and Ni(II) in ethanol. Characterization of the ligand and its complexes were carried out by microanalyses, magnetic susceptibility measurements, FT-IR, $^{13}$C, $^1$H NMR, and UV-Visible spectroscopy. It was suggested that two ligands with two water molecules coordinate to each metal atom by hydroxy oxygen and imino nitrogen to form high spin distorted octahedral complexes with Co(II), Ni(II) and Cu(II).
Metal-Ion-Directed Synthesis of Homo- and Heteronuclear Dimetallic Schiff Base Podates

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Homodinuclear complexes of lanthanum(III), zinc(II), cadmium(II) and mercury(II) ions and heterodinuclear complexes of lanthanum(II) and zinc(II) ions containing Schiff base open-chain ligands terminated by two carbonyl groups or one amine and one carbonyl group were prepared as a result of the partial Schiff base condensation reaction between 2,6-diacetylpyridine and 4-methyl-1,2-phenylenediamine or 2,6-diaminopyridine in the presence of the appropriate ions acting as templates. The complexes were characterized by spectroscopic methods (IR, $^1$H NMR, FAB-MS) and elemental analysis.
Spectral and Thermal Investigations of Y(III) and Lanthanide(III) Complexes with 3,3-Dimethylglutaric Acid

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Conditions for the preparation of Y(III) and lanthanide(III) (La–Lu) 3,3-dimethylglutarates were investigated and their quantitative composition and solubility in water at 293 K were determined \((10^{-7}–10^{-5} \text{ mole dm}^{-3})\). The IR spectra of the complexes prepared with the general formula \(\text{Ln}_2\{\text{C}_5\text{H}_{10}\text{(COO)}_2\}_n\cdot n\text{H}_2\text{O} (n = 2–15)\) were recorded and their thermal decomposition in air were investigated. During heating the hydrated 3,3-dimethylglutarates are dehydrated in one (La, Ce, Pr, Sm, Gd, Lu), two (Y, Nd, Eu, Dy, Ho, Tm) or three (Tb, Er) steps and next the anhydrous complexes and dihydrated Yb(III) complex decompose to oxides \(\text{Ln}_2\text{O}_3\), CeO_2, Pr_6O_11 and Tb_4O_7 with intermediate formation \(\text{Ln}_2\text{O}_2\text{CO}_3\) except of Ce(III) complex, which decomposes directly to CeO_2. The carboxylate groups in the complexes studied are bidentate.
Carbohydrates Dithiocarbonic Acid Esters and Their Application in Glycosylation Reactions

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Allyl dithiocarbonic acid esters are used as efficient glycosyl donors in the presence of soft activators. Different glycosides are obtained in good yields, isomer α being the main product.
The Ritter Reaction of Terpenes. Part 3.
Investigation of Carvone and Related Compounds

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The Ritter reaction of (R)-carvone (1), cis-carveol (2) and carvyl ethers 3 and 4 was investigated. For ketone 1 formation of 8-amido-6-p-menthen-2-ones (7–12) in moderate yields was observed. Alcohol 2 gave, depending on the reaction conditions, 2-amido-6,8(9)-p-menthadienes, 2-amido-4(8),6-p-menthadienes and/or 2,8-diamido-6-p-menthadienes. Ethers 3 and 4 underwent cleavage to almost the same amides as it was observed for cis-carveol (2). Additionally, tertiary phenylcarveol (5) under similar conditions furnished 6-acetamido-2-phenyl-1,8(9)-p-menthadiene (28) as a result of dehydration, followed by migration of a double bond. The proposed mechanisms of the reactions are presented.
Acid-Catalyzed Cleavage of Some Chromone, Coumarin and Pyrone Derivatives of Aminomethylphosphonic Acid. Products and Kinetics of the Reaction

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Treatment of chromone-2, coumarin-4 and pyrone-2 derivatives of N-benzylamino- methylphosphonic acid with strong mineral acids leads to formation of the corresponding heterocyclic amines and phosphoric acid. Kinetic studies of this cleavage reaction demonstrate that protonation has a remarkable influence on a cleavage of C–P bonds. In aq. H₂SO₄, cleavage of the acids 1–3 exhibits a kinetic dependence on [H⁺]. The measured solvent isotope effect (k/₃/k/D) was about 1.5 for the 1 and 2 and only 1.1 for the 3. The existence of the isotope effect shows that protons are involved on the rate-determining step. The data obtained suggest that the protonated phosphonate molecule is split by a dissociative mechanism with A-S₁E₂2 character and this is combined with an elimination of the phosphonate group as a positive-charged phosphorus moiety.

Novel Buspirone-Like 5-HT\textsubscript{1A} Receptor Ligands

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Four novel buspirone-like compounds were synthesized and their affinity to the serotonin 5-HT\textsubscript{1A} receptor was determined. Two compounds bind to 5-HT\textsubscript{1A} receptor with a high affinity and two other compounds exhibit a low affinity to this receptor. A simple two-parameter polynomial correlation was suggested to express the structure-activity relationships.
Effect of Partially Aqueous Solutions of Different pH’s on the Hydrolysis Rate of Some Schiff Bases

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The mechanism of the hydrolysis of a series of Schiff bases derived from p-phenylene diamine and various aromatic aldehydes has been examined in aqueous media containing 40 wt% methanol, in the presence of NaOH. The base hydrolysis reaction of these compounds is strictly second-order kinetics, first-order with respect to the Schiff base and also to hydroxide ion, and the hydroxide ion attack on the free base becomes the rate-determining step under these basic conditions. The work is extended to include a systematic kinetic study on the hydrolysis reaction of the Schiff bases under investigation, in partially aqueous solutions of different pH’s, in media containing 40 wt% methanol. A rate profile diagram of pH versus hydrolysis rate constant for all of the Schiff bases shows that the rate is minimal at alkaline region (pH > 8.96), and too rapid at strongly acidic media (pH < 3.53).
Non-Typical Influence of Adsorbed 1-Octanol on Electroreduction of 1-Nitropentane on Mercury Electrodes

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The electroreduction of 1-nitropentane in the absence and in the presence of 1-octanol was studied. In the absence of inhibitor, 1-nitropentane at concentrations near to saturation is adsorbed weakly on mercury electrodes. In the presence of smaller concentrations of inhibitors, such as 1-octanol, 1-nitropentane electroreduction is inhibited less than that of nitromethane under comparable conditions. This difference was explained by the larger affinity of 1-nitropentane to the alcohol-rich surface phase and nitromethane to the aqueous solution phase. The increased affinity of the reactant to the electrode surface phase at the 1-octanol relative concentration, c/c0, exceeding 0.7, may explain the independence of the electroreduction rate constant of 1-nitropentane and, even, its increase when the bulk concentration of inhibitor approached the saturation.
Analyzing a Sequence of Reactions by the De Donder Equation

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In the kinetic analysis of the mechanism postulated simplified assumptions are often made. These assumptions are generally verified by comparing the simplified kinetic description with experimental data. In this study consideration is given to the idea of constructing a “quantitative” measure for the “qualitative” assessment of the assumption (approximation), which makes it possible to examine its adequacy at an arbitrary moment of the reaction. The adopted measures are defined as criteria for steady-state and equilibrium (quasi-equilibrium) approximations.
Influence of H/D Isotope Substitution on Physicochemical Properties of Aqueous Solutions of Urea and Thiourea

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The influence of the H/D isotope substitution on excess volumes, partial molar volumes, viscosity and ultrasound speed in aqueous solutions of urea and thiourea are studied at 20°C. The excess volume of the solutions studied is relatively small—however, it is negative in urea and positive in thiourea solutions. On the other hand, the deuteration affects the excess volume in both solutions in the same way: deuterated systems show smaller deviation from additivity than regular ones. The speed of sound in the systems studied increases monotonously with concentration, but its isotope effect decreases as the concentration increases. The curves of viscosity are monotonous too, but isotope effect of kinematic viscosity is practically the same in the whole concentration range studied. The present results for urea and thiourea aqueous solutions are compared with those previously obtained for amide–water systems.
Study of the Stability of Some Ion-Pairs in Non-Aqueous Solutions by Potentiometric and Spectrophotometric Methods

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Changes in selected complexes caused by photodissociation were studied potentiometrically by measuring the time dependence of electromotive force of suitable cells and spectrophotometrically by measuring the time dependence of absorbance to evaluate the stability constants. Ion pairs labetalol (LAB)-reineckate (REINE) in nitromethane and crystal violet (CV)-tetrachloroferrate(III) (FeCl₄) in tetrachloroethane were used. The concentration ranges were determined, in which the EMF variations are greatest: the 4–5.5 × 10⁻⁴ mol l⁻¹ range for the LAB–REINE complex and the 0.9–3 × 10⁻⁶ for the CV–FeCl₄ complex. Linear dependence of the EMF variation on the intensity of radiation, as well as a slight effect of temperature on irradiated solution were found. The stability constants of the studied complexes in chloroform, determined directly from spectrophotometric measurements are log βₐᵥ = 6.6 for LAB-REINE complex and log βₐᵥ = 7.3 for the CV–FeCl₄ complex.
Electrochemical Studies on the Thallium(I) Telluride – Mercury(II) Telluride Solid System

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The concentration cell-EMF measurement method was employed in verifying two phase diagrams published earlier for the system Tl₂Te – HgTe. The thermodynamic characteristics of the system in solid state has been determined at 373 and 453 K.
A New Taraxastane-Type Triterpenoid and Sesquiterpene Lactones from *Picris evae*

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Bond Valence Sum Analysis (BVS) of Metal Ligand Bond Lengths in Some Zn(II), Cd(II) Dithiocarbamate Complexes and Their Adducts

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Rietveld Refinement of the Structure of Nd$_2$Zn$_{15}$Ge$_2$

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