

THE STUDY OF 2-ACETYLAMINOTOLUENE OZONOLYSIS IN ACETIC ACID (p. 4-8)

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The kinetics and mechanism of ozone reaction with 2-aminotoluene and its acylated derivative in acetic acid were studied in order to determine the possibility of obtaining 2-aminobenzoic acid.

It is shown that the 2-aminotoluene ozonolysis reaction in acetic acid solution runs at high speed, and preferably on the free electron pair of the amino group to form mainly resinous compounds; oxidation products by the methyl group of the substrate are not formed under these conditions. The ozone attack direction changes towards oxidation of the methyl group and the aromatic ring by N-acylation of the amino group. 2-Acetylaminotoluene reacts with ozone to form mainly degradation products of the aromatic ring – aliphatic peroxides (80.7 %), and oxidation products by the methyl group – 2-acetylaminobenzaldehyde at early stages and at deeper stages – 2-aminobenzoic acid (14.0 %), which if necessary can easily be hydrolyzed to the corresponding 2-aminobenzoic acid.

Ozone is consumed in the reaction in two ways: non-chain ozone consumption mechanism prevails at temperatures of up to 20 °C, and chain ozone consumption along with non-chain is observed at higher temperatures.

These data will be useful to develop a method of catalytic oxidation of 2-acetylaminotoluene by ozone to the corresponding benzoic acid.

Keywords: ozonolysis, 2-acetylaminotoluene, ozone, acetic acid, oxidation, 2-acetylaminobenzaldehyde, 2-aminobenzoic acid.

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AMINO ACIDS AND THEIR DERIVATIVES IN CATALYTIC CYCLOHEXANE OXIDATION (p. 8-13)

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Homogeneous catalytic oxidation of cyclohexane can be improved by using additives to industrial catalysts that are based on variable valence metals. Recent studies have been much focused on enzymatic catalysis with protein-based enzymes that consist of amino acids of various structures. We assume that the presence of two functional groups in amino acids enables them to form complexes with catalysts, function as modifiers, and influence the composition of reaction products. The present study reveals how the liquid-phase homogeneous catalytic oxidation is affected by binary catalyst systems that are composed of cobalt naphthenate and amino acids of various origins (glycine or aminosulfonic acid) as well as individual catalyst, which is cobalt salt 2 (heptadecane olamine) of pentadion acid (CSHPA). The research determines and compares qualitative and quantitative impacts of amino acid additives and individual CSHPA on the oxidation process. The study identifies the regular dependence of CSHPA catalyst on the nature of its previous ultrasound processing. It has been found that the origin of an additive and the alteration of its concentration in a catalytic system permit regulating the quantitative composition of reaction products that result from the liquid-phase oxidation of cyclohexane. The researched catalytic systems can be applied in production to improve its technical and economic indices.

Keywords: amino acids, catalytic systems, liquid-phase oxidation, catalysis, cyclohexane, cyclohexanol, cyclohexanone.

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THE RESEARCH OF THE KINETICS OF SUNFLOWER CAKE EXTRACTION BY ETHYL ALCOHOL (p. 13-18)

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The present paper deals with theoretical and experimental substantiation of the basic process laws of the sunflower cake extraction by unconventional solvent – ethyl alcohol. Industrial samples of sunflower cake in the form of granules and grits, for which the porosity parameters (porosity and filtration ratios) were defined, were subjected to the test. Physical model of the 8-step extractor, operating by the countercurrent irrigation principle was developed using a specially designed laboratory setup. The influence of some technological factors (duty of water, extraction time and oilseed material structure) on the sunflower oil extraction kinetics (original cake oil content variation in time) and miscella concentration at each extraction stage was experimentally found. Based on the experimental results, internal diffusion coefficient for ethanolic extraction of sunflower cake, depending on the porosity and filtration indicators was calculated using MathCad and Microsoft Excel application package. It was shown that improved ethyl alcohol percolation in the granule is confirmed by the higher value of the coefficient of internal diffusion in the granule. The latter is about 2 times higher than that for the hexane extraction. New scientific data for the formulation of the values of process parameters for future technology were obtained.

Keywords: ethanolic extraction, sunflower cake, kinetics, internal diffusion, oil content, miscella concentration.

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MATHEMATICAL MODEL OF SORPTION PROCESS OF LIQUID ORGANIC SUBSTANCES BY POLYMERIC MEMBRANE ELEMENTS (p. 19-23)

Inessa Burtina, Ludmila Ruzhinska, Mikhail Murashko, Lesia Rudenko

The results of the study of pharmaceutical wastewater treatment from organic impurities through sorption and desorption of organic solvents by polymeric membrane elements are presented in the paper.

The processes of sorption by membrane elements are characterized by high efficiency, energy saving, possibility of fine separation of mixtures with obtaining high-quality products and their undeniable environmental safety.

Sorption process lies in passing of certain organic compounds (solvents) of wastewater to the body of nonporous polymeric membrane elements (adsorbent), with the possibility of further desorption of absorbed compounds. Using such membrane technology allows to achieve a significant impurity concentration reduction, high wastewater treatment efficiency and raw materials consumption coefficient reduction due to the return of organic solvents in the production process.

Membrane sorption with the subsequent desorption is a multifactorial process that is associated with the dissolution of organic

components in polymeric membranes, which is accompanied by swelling of the membrane materials in organic solvents.

The results of experimental studies of the dissolution kinetics of polar and nonpolar molecules in nonpolar membranes, swelling processes of polymeric membrane materials in organic solvents, diffusion coefficients of the most common solvents in polymeric membranes are given in the paper.

Based on the experiments, the mathematical model of the adsorption process of organic solvents by polymeric membrane elements was developed. Mathematical model adequately describes the concentration distribution over the polymeric membrane element thickness. The model takes into account all process peculiarities, including swelling. Based on the model, concentrations of the most common organic solvents in industry were calculated in different sections of membrane elements.

The results of experimental and theoretical research can be used in designing plants for water treatment from organic solvents, particularly, in selecting the fixed-bed adsorber design in the form of membrane attachment.

Keywords: sorption, desorption, polymeric membrane, diffusion, swelling, wastewater, mathematical model, mass transfer.

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NON-EMULSION COPOLYMERIZATION IN OBTAINING SILICONE-ACRYLIC SURFACTANT (p. 24-28)

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The experiment-based paper presents non-emulsion hybride copolymerization of acrylic acid and polydimethylsiloxane in making the most pure silicone acrylic polymeric surfactant. We have determined optimal conditions for the synthesis. The study of copolymerization kinetics by means of identifying the acid number has determined the best reasonable time and temperature for the reaction—2 hours and 120 respectively, since after 2 hours the acid conversion makes up 78 %, whereas polymer yield is 66 %.

The synthesized silicone acrylic polymeric surfactant is a viscous transparent liquid that has no pungent smell and dissolves in organic solvents. We have identified and characterized the properties—mo-

lecular mass, viscosity and surface tension—of the obtained silicone acrylic polymer. The polymeric surfactant can be used as surface modifier in lacquer and paint products.

Keywords: silicone acrylic polymer, polydimethylsiloxane, acrylic acid, non-emulsion copolymerization, surfactants.

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REGULARITIES OF OBTAINING POLYMER-SILICATE COMPOSITES FROM WATER-SOLUBLE SILICATES AND POLYMERS (p. 29-33)

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Based on the studies, the influence of nature, concentration and method of administration of polymer modifier and precipitant

on physicochemical regularities of obtaining the modified polymer-silicate materials was determined. It was found that the nature and concentration of the precipitant and polymer significantly affect the output of metal-containing polymer-silicate formations. Thus, the optimum polymer concentration in the reaction medium is 0.2–0.3 mol/L. It was found that PVP dissolution should be conducted in a solution of sodium silicate solute and PVA – a metal chloride solution. This order provides the maximum polymer sedimentation degree and modification efficiency. Based on IR spectroscopic, potentiometric and sorption studies, it was found that the process of obtaining polymer-silicate material is accompanied by intermolecular interactions between the active silicate groups and functional polymer groups that promotes the uniform distribution of macromolecules in salicylic frame. The modified silicate formations are characterized by significantly lower moisture absorption value than unmodified, which is connected with the blocking of surface groups of silicate formations by PVA and PVA macromolecules and fine particle porosity reduction. The obtained metal-containing polymer-silicate materials will be characterized by high affinity for the polymer matrix when creating composites on their basis and are aimed at affecting their morphology and providing the complex with specific properties depending on the nature of the modifier and the metal cation.

Keywords: composite, sodium silicate solute, polyvinyl alcohol, polyvinylpyrrolidone, precipitant, silicate, modification.

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DEVELOPMENT OF METHODS FOR THE GAS CHROMATOGRAPHIC DETERMINATION OF THE CONTENT OF DISSOLVED COMPONENTS IN THE ENERGY OILS (p. 34-42)

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The paper presents the results of the development of methods for the gas chromatographic determination of the content of dissolved components: gases (H₂, CH₄, C₂H₆, C₂H₄, C₂H₂, CO, CO₂, C₃H₈, C₃H₆, H₂S); ionol; furan compounds (furfural; acetylfuran; 5-methyl-furfural; 2-furan-methanol) in the energy oils (transformer, cable, condenser, turbine). The purpose of the paper was to reduce the errors of measurement methods and improve the accuracy of measurement results in determining the content of dissolved components in the energy oils by the static version of the extraction-gas chromatographic measurements using gas chromatographic analysis of equilibrium phases - gaseous or liquid extracts. For modern energy oils, the values of the distribution coefficients in the system "energy oil – dissolved gas – gas-extractant" using static and dynamic variants of extraction-gas chromatographic measurements were defined; formulas for calculating the concentrations of ionol and furan compounds in the energy oils based on accepted mathematical models of extraction processes for measurements were obtained; optimum procedures of extraction-gas chromatographic determination of the content of dissolved gases, ionol and furan compounds in the energy oils for developing optimal gas scheme of multichannel gas chromatograph were selected. The conditions for implementing the extraction-gas chromatographic measurements using appropriate adsorbents in packed chromatographic columns in determining the content of dissolved gases – by the absolute calibration using the distribution coefficients for these gases instead of the corresponding Ostwald coefficients; ionol or furan compounds – by adding corresponding pure component or various extractant volumes in the energy oils. In the presence of emulsion water in the energy oil, oil is dried by silica gel (in determining ionol) or sodium sulfate (in determining furan compounds). The results of the calculations are assessed). It was found that it is necessary to perform temperature programming of the corresponding chromatographic column after the evolution of the chromatographic peak of the last determined component. The developed techniques can be used in determining the concentrations of dissolved components in the energy oils for technical diagnostics of oil-filled electrical equipment; quality indicators of the energy oils; compatibility of mixed energy oils and sensitivity of these oils to ionol.

Keywords: gas chromatography, extraction, energy oil, ionol, dissolved gas, furan compound.

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ELECTROCHEMICAL CHLORINE SENSOR BASED ON THE HALIDE ELECTROLYTE WITH MEDIATOR FOR ACCIDENTAL RELEASES (p. 42-47)

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An amperometric chlorine sensor with matrix electrolyte based on LiI, surpassing existing domestic and foreign samples by a range of specifications was developed. Implementation of the gas diffusion indicator electrode with iodine-iodide mediator system has allowed to increase the upper limit of measurement by more than an order of magnitude. Optimization of the indicator electrode with regard

to the background current has allowed to expand the measurement range by 7 times compared with existing samples, which with the possibility of the 0,17 ppm chlorine concentration measurement (at the maximum allowable concentration of 0,3 ppm) allows to reach the upper limit of measurement of 100 ppm or more. The duration of the transition process (τ_{90}) of defining the transitional signal of the developed sensor is within 30–60 s. Balanced electrochemical system of the sensor ensures its stable operation by several times longer than the warranty period.

Keywords: amperometric chlorine sensor, measurement range, selectivity, mediator catalysis, iodine-iodide system.

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DEVELOPMENT OF HIGHLY PRODUCTIVE CURRENT MODES FOR COPPER ELECTROWINNING AS A DENSE METAL (p. 48-55)

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Electrochemical studies of copper planting from sulfuric acid solutions, the composition of which varies during the electrowinning process in order to increase its productivity and reduce power consumption for copper production were carried out in the paper.

It was found that at reducing the copper sulfate concentration (Cc) from 200 to 40 g/dm² and increasing acid concentration (Ca) from 30 to 90 g/dm², the role of migration of copper ions in the mass transfer is low, but the solution acidity does affect the limiting current of copper deposition i_L . The dependences of i_L on two variables – Cc and Ca were experimentally found and mathematically described, which was the basis for selecting the working current densities (i_p) of the copper electro-winning process. The influence of the solution composition and the current density on the cathode copper morphology was investigated. It is shown that the compact deposits without dendrites and powder can be obtained at a ratio of $i_p/i_L=0,825$. Electrolysis modes with cathodic current density reduction in time were developed, which allow to combine the high speed of the process, a high metal current efficiency and obtaining a dense copper precipitate with the quality, acceptable for hydrometallurgy. Results and proposed approach to optimizing copper electro-winning parameters can be used in hydrometallurgy for metallic copper production, in processes of copper extraction from production wastes, wastewater purification from metal ions.

Keywords: limited current density, migration, copper sulfate, polarization curves, deposit morphology, productivity of the process.

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PARALLEL-SERIAL ADSORPTION OF PHOSPHATE IONS BY NATURAL SORBENTS (p. 56-60)

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The process of adsorption of phosphorus compounds on natural sorbent – zeolite, which shows adsorption and ion exchange properties is considered. Phosphates belong to anthropogenic environmental pollutants. They are present in the wastewater of industrial and utility enterprises. Static activity of phosphates in zeolite in their pollution limits in wastewater is investigated. It is shown that they are in low concentrations. This process is described by Henry linear adsorption equation.

The presence of other components in the wastewater, especially ammonium compounds, complicates the adsorption process. The absorption of ammonium ions occurs mainly through ion exchange, replacing sodium, potassium and ammonium cations in the zeolite.

The absorption of phosphorus compounds proceeds due to adsorption and formation of compounds with calcium and magnesium ions in zeolite pores. Parallel adsorption of two components slightly reduces static activity in relation to phosphorus compounds, but the total adsorption of the two components is higher.

The second investigated mechanism of adsorption of components from aqueous solutions by zeolite was serial adsorption. Primarily, adsorption of copper ions, for example, when treating electroplating wastewater was conducted. This process allows to modify sorbent and change its adsorption properties. The next stage was adsorption of phosphate compounds by the modified zeolite, on which these compounds form persistent connections with copper, calcium and magnesium ions, and adsorption capacity of the modified zeolite significantly increases.

The studies of parallel and serial sorption indicate the feasibility of these purification methods.

Keywords: natural zeolite, modified zeolite, phosphate ions, heavy metals, adsorption, wastewater.

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