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Articles and Statements

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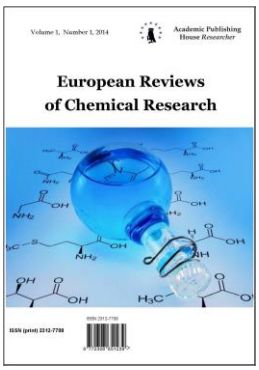

Articles and Statements

UDC 544

Synthetic Methods and Exploring Biological Potential of Various Substituted Quinoxalin-2-one Derivatives

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Abstract

Substituted quinoxaline have considerable interest in chemistry, biology and pharmacology. Quinoxaline derivatives are capable with variety of biological activities and possess different biological activities, of which the most potent are anti-microbial, analgesic and anti-inflammatory activities. It facilitated the researchers to develop various methods for their synthesis and their applications. In this review represented different methods of synthesis, reactivity and various biological activities of quinoxaline derivatives.

Keywords: Quinoxaline, reactivity, biological activities, synthetic methods.

Introduction

Quinoxaline and its derivatives are important nitrogen containing heterocyclic compounds of various biologically properties. Quinoxaline and its derivatives are mostly of synthetic origin. Substituted quinoxalines are an important class of benzoheterocycles, which constitute the building blocks of wide range of pharmacologically active compounds having antibacterial [1-4] antifungal [5], anticancer [6, 7], antitubercular [8], antileishmanial [9], antimalarial [10] and antidepressant activities [11]. Also, some quinoxalin-2-ones and quinoxaline-2,3-diones have been reported to show antimicrobial [12, 13], potent antithrombotic [14], anti-pain and anti-inflammatory [15] activities. The quinoxaline is described as a bioisoster of quinoline, naphthalene, benzothiophene and other aromatic rings such as pyridine and pyrazine. Because of the similarity between some antitubercular drugs and quinoxaline, as well as the presence of the quinoxaline moiety in some broad spectrum antibiotics, it was hoped that quinoxaline analogs would exhibit antitubercular activity [16]. The quinoxaline antibiotics are agents of bicyclic desipeptide antibiotic that have been reported activity against gram-positive bacteria and certain tumors and to inhibit RNA synthesis [17]. Quinoxaline has also been used in reactive dyes and pigments, azo dyes, fluroscein dyes and it also forms a part of certain antibiotics. Quinoxaline m.p. 29-30°C and is miscible with water. It is weakly basic (*p*ka 0.56) and thus considerably weaker base than the isomeric diazonapthalenes namely cinnoline (*p*ka 2.42), pthalizine (*p*ka 3.47) or quinazoline (*p*ka 1.95). 2-Hydroxy-but not 2-amino quinoxaline exist in tautomeric forms.

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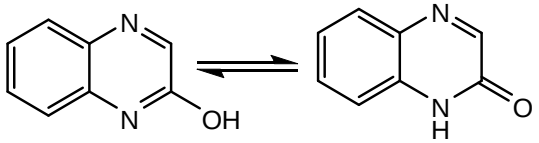
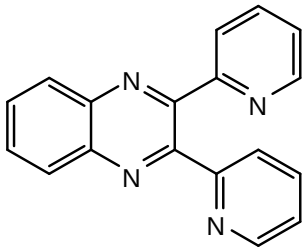
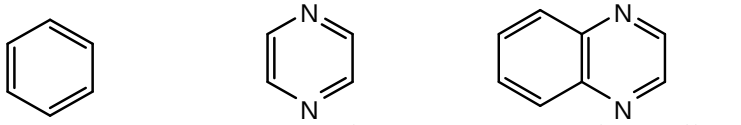


Some of quinoxaline analogues, such as 2,3-bis (2-pyridyl)-quinoxaline (DPQ) complexed with transition metals are of current interest in view of its binding to DNA. This may suggest that conjugation of biologically active peptides with quinoxaline analogs can lead to new therapeutic agents possessing interesting anticancer properties [18].



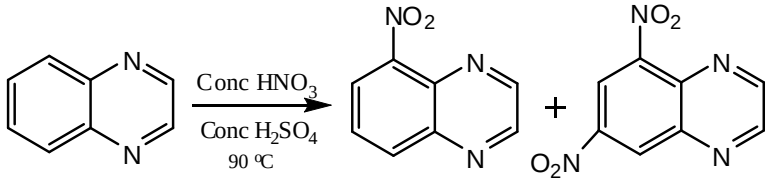
2,3-bis(2-pyridyl)-quinoxaline (DPQ): Quinoxaline derivatives constitute the basis of many insecticides, fungicides, herbicides, as well as being important in human health and as receptor antagonists. Although rarely described in nature, synthetic quinoxaline moiety is a part of number of antibiotics such as echinomycin, levomycin and actinomycin which are known to inhibit the growth of Grampositive bacteria and also active against various transplantable tumors. In addition, quinoxaline derivatives are reported for their application in dyes, efficient electroluminescent materials, organic semiconductors and DNA cleaving agents [19].

History: Quinoxaline is also called as benzopyrazine. It is heterocyclic compound containing benzene ring and pyrazine ring. Pyrazine are stable, colorless compound which are soluble in water. Unlike pyridine, they are expensive, not readily available and so are seldom used as starting material for synthesis of their derivative. Diazines are fused to benzene ring to form quinoxaline. The pyrazine ring system is found in the fungal metabolite aspergillic acid and in dihydro form in luciferin of several bettles including the fire fly is responsible for the chemiluminescence of this ostracod. Methoxy pyrazine are very important component of aroma of many fruits and vegetable such as Peas and Capsicum peppers and also of wines [20].



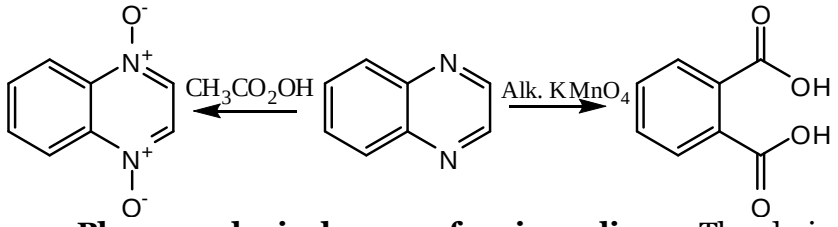
Benzene **Pyrazine** **Quinoxaline**

Quinoxaline is a low melting solid, m.p 29-30˚C and is miscible with water. It is weakly basic pKa 0.56. Quinoxaline forms salts with acids. Nitration occurs only under forcing conditions (Conc. HNO_3, Oleum, 90◦C) to give 5-nitroquinoxaline (1.5%) and 5,7-dinitro- quinoxaline (24%).



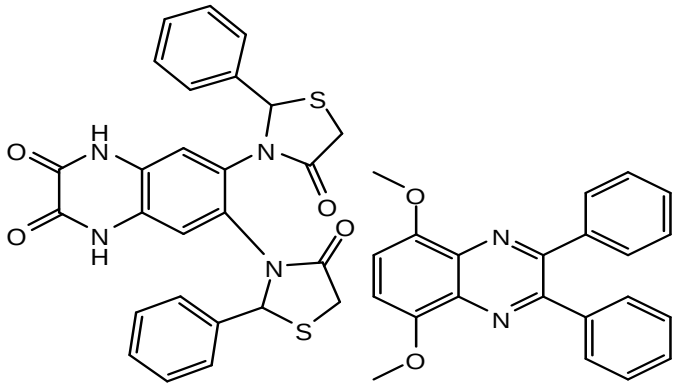
1.5% **24%**

Oxidation of quinoxaline results in the formation of the product depending on the nature of the oxidizing agent employed. With alkaline potassium permanganate pyrazine 2,3-dicarboxylic acid is formed, while with peracid quinoxaline di-N-oxide results [52].



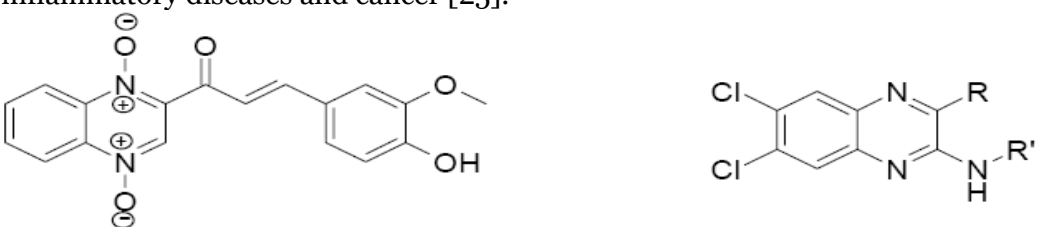
Pharmacological uses of quinoxalines: The derivatives of quinoxalinone occupy a significant place in several areas, particulary in pharmacology. Also, the modifications in the basic structure of the quinoxalinone, have enabled the emergence of new derivatives with a wide spectrum of biological activity. These derivatives have shown that structural modification can improve its pharmacological profile conferring antibacterial, anticancer, anti-HIV, tranquilizers and sedative properties. The anticancer and antidepressant activities are the most encouraging activities for the pharmacists.

Antimicrobial agent shows activity against bacteria, fungi, mycobacterium species, called antibacterial, antifungal, antituberculer activity respectively. There are various quinoxaline derivatives showing antimicrobial activity. Some new condensed bridge head nitrogen heterocycles of quinoxalines were evaluated for antimicrobial activity against the gram positive bacteria *Staphyllococus aureus* and *Bacillus subtilis*, the gram-negative *Psudomonas aeruginosa* and *proteus vulgaris*, the fungi *Aspergillus niger* and the *Mycobacterium tuberculosis* H37Rv species. The pyrrolo[3,4-*b*]quinoxalines were tested for their antibacterial activity against *S. aureus, Escherichia coli* and their antifungal activity against *Candida albicans* at a concentration of 3mg/mL. Steptomycin (25 µg) and Mycostatin (30 µg) were used as reference for the antibacterial and antifungal activities, respectively [1]. A series of 6,7-Bis[2-(substituted Phenyl)-4-oxothiazolidin-3-yl]quinoxaline-2,3-(1*H*,4*H*)-diones (1) were screened for anti-TB activity against H37Rv strains of *M. tuberculosis* at a concentration of 6.250 g/ml. Isoniazid (0.0250 g/ml) and Rifampicin (0.1250 g/ml) were used as standards [21,22]. Antiamoebic activity of 2,3-diaryl-5,8-dimethoxy-quinoxalines (**2**). The *in vitro* activity of the compounds against *Entamoeba histolytica* was determined. Most of the compounds displayed *in vitro* activity at 50-200 µg/ml concentrations. Standard drugs Nitroimidazole and Diloxanide furoate showed *in vitro* activity at 2-5 µg/ml concentrations [23].



1 **2**

Various studied the anti-inflammatory and antioxidant activity of several quinoxalines. Compound **3** presented the most interesting activity [24]. Similarly, in anti-inflammatory activity of the quinoxaline B **(4)** by varying R and R substituents. Compounds B_1 and B_2 were found to be non-peptide antagonists of the interleukin-8 molecule receptor, which is involved in several inflammatory diseases and cancer [25].



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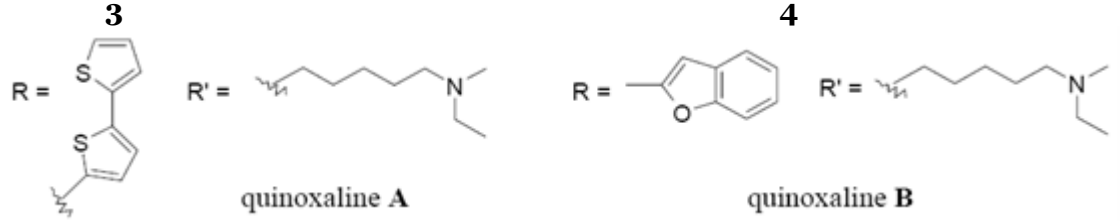
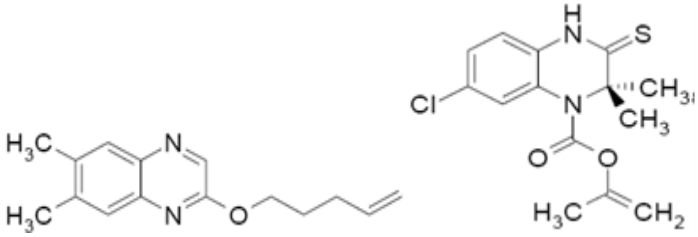


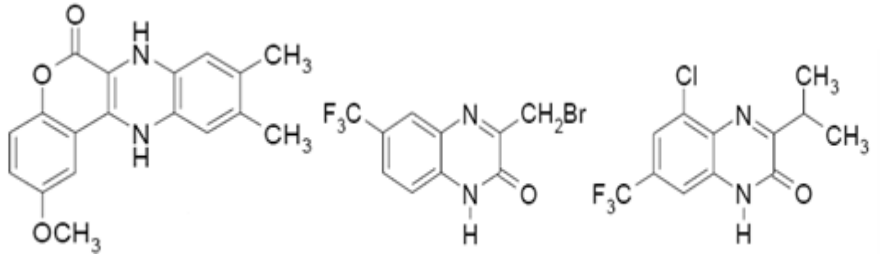
quinoxaline **A** quinoxaline **B**

Similarly, the quinoxalinone derivatives have antiviral properties [26, 27]. Many studies have shown the activity of a few quinoxaline compounds towards the human immunodeficiency virus (HIV-1), including the 6,7-dimethyl-2-(pent-4-enyloxy)quinoxaline **5**, [29] and S-2720 **6**, which not only inhibit HIV-1 RT, but prevent its replication at the cellular membrane [30].

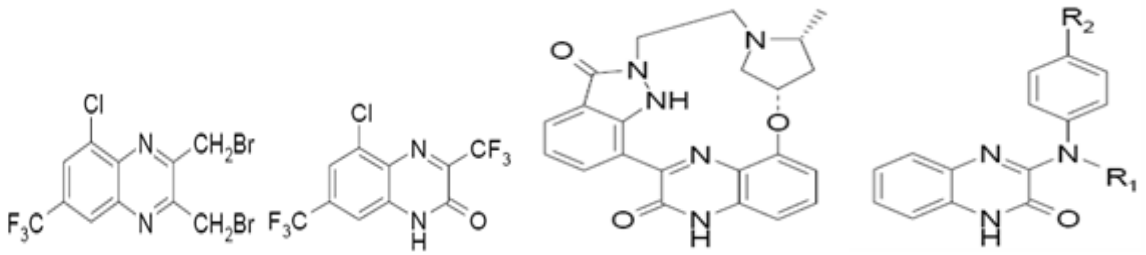


4 **5**

Another activity of quinoxalines is the anti-microbial one. The 9,10-dimethyl-2-methoxy-6-oxo-7,12-dihydro–chromo-[3,4-b]quinoxaline **6** has both, antibacterial and antifungal activities [31]. The quinoxalines **7**, **8**, **9**, and **10** possess the same activities [32]. The compound **11** is a molecular macrocycle derived from the quinoxalin-2-one inhibitor of cyclin-dependent kinases CDK1, 2, 4 and 6 [33]. While the compound **12** [34] inhibiting glycogen phosphorylase is the enzyme responsible for the metabolism of glycogen to glucose since glucose is over produced in patients suffering from diabetes.

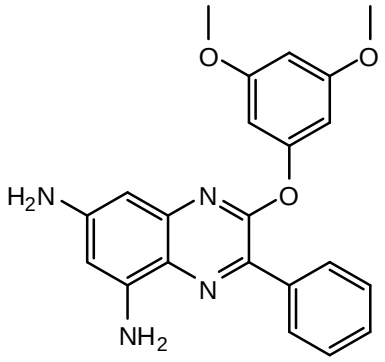


6 **7** **8**



9 **10** **11** **12**

Some quinoxaline derivatives which showed antitumor activity, 5,7-diamino-3-phenyl-2-[(3,5-dimethoxy)phenoxy]quinoxaline **13** has an antitumor activity in vitro, towards several types of tumors [36]. Also the 3-(4-bromophenyl)-2-(ethylsulfonyl)-6-methylquinoxaline-1,4-dioxide **14**, has an activity against the tumor in the hypoxia stage, which is a phase where the tumor shows a resistance during chemotherapy and radiotherapy [37]. Various results are showing activities of quinoxaline, as an inhibitor of the kinase protein [38], or as antagonists of bradykinin, which is a peptide responsible for the dilatation of blood vessels, thus leading to the lowering of blood pressure [39]. A series of quinoxaline derivatives **15**, which could act as modulators of the AMPA receptor mediators of synaptic responses [40].



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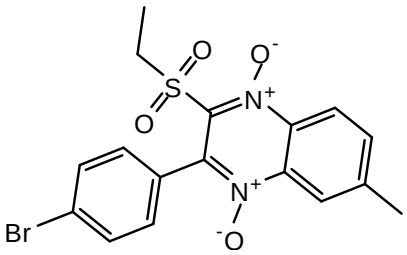

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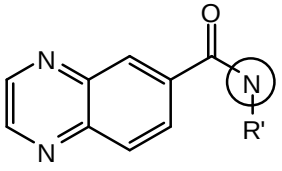
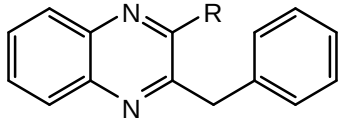


15

The circle containing nitrogen designates a heterocycle of 5 to 8 rings, the group R' may be a group 2- or 3-alkyl, cycloalkyl, hydroxy, alkoxy, alkoxy-alkyl, hydroxy-alkyl, or carbamoyl.

The 3-benzyl-2-substituted quinoxalines as novel monoamine oxidase A (MAO-A) inhibitors. MAO inhibitors is useful for the treatment of several neurological diseases such as Parkinson's disease and depression. MAO-A inhibitors are used as antidepressant and anti-anxiety drugs. The compounds (**16**) were evaluated for their MAO-A inhibitory activity *in vitro* using serotonin as substrate. All these compounds were used at a concentration of 1×10^{-4} M [41]. Methyl [4-(substituted 2-quinoxalinyloxy) phenyl] acetates (**17**) and ethyl N-{[4-(substituted-2-quinoxalinyloxy) phenyl] acetyl} glutamate analogs of Methotrexate were evaluated for *in vitro* anti cancer activity by bioisosteric replacement [42].



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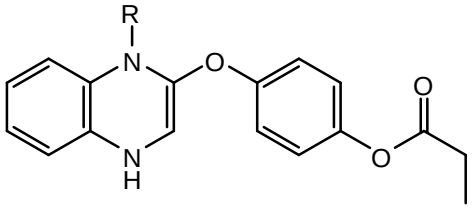
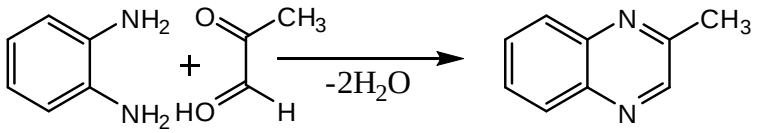


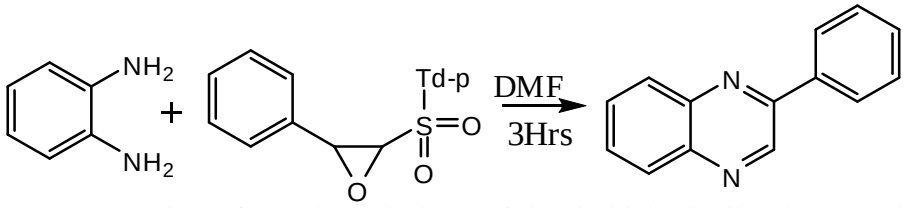
17

The ring substituted 3-phenyl-1-(1,4-di-N-oxide quinoxaline-2-yl)-2-propen-1-one derivatives and of their 4,5-dihydro-(1H)-pyrazole analogues. Synthesized compounds were evaluated for anti-inflammatory and antioxidant activity [43].

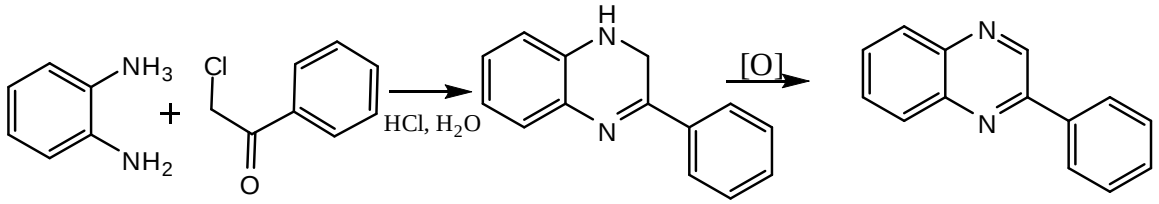
Synthesis of quinoxalines: The synthesis methods proposed can be divided into two categories. The first one involves cyclocondensation reactions between *o*-phenylenediamines and aliphatic electrophile compounds, in conventional terms, or in the presence of metal salts in solution or solid support under microwaves. The pyrazine nucleus may also be formed using derivatives of *o*-substituted aniline. Another class of reactions involves nitrogen heterocycles which has different links likely to opening reactions or rearrangements in different conditions, leading to opened intermediates that, later, cyclize to give the quinoxaline derivatives. The fusion of one or two benzene rings in quinoxaline and phenazine increases the number of resonance structure, which are available to these systems. It posses the dipole moment of zero. Quinoxaline itself is prepared by the reaction of *o*phenyldiamine and glyxol [44]. Simillarly 2-Methyl Quinoxaline has been prepared by the reaction of *o*-phenyldiamine and pyruvaldehyde.



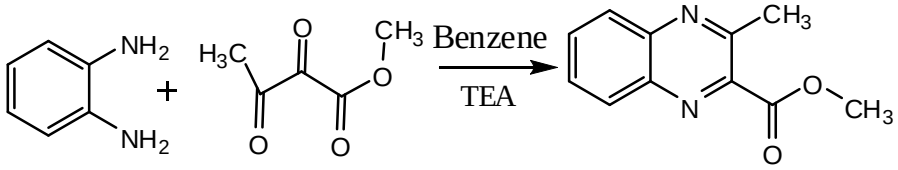
The 1-(*p*-tolysulfonyl)-2- phenyloxirane, obtained from the condensation of chloromethyl *p*-tolysulfone with benzaldehyde, on reaction with *o*-Phenylenediamine yields 2-phenyl quinoxaline in good yield [45].



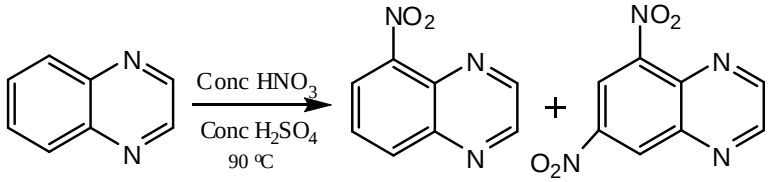
A number of simple variations of the dialdehyde diamine reaction appear to work well. Thus replacement of the dialdehyde with a α-halogenketone results in the formation of 2- substituted quinoxaline.2-phenylquinoxaline has been prepared in this manner from phenacyl chloride and *o*-phenylenediamine [46].



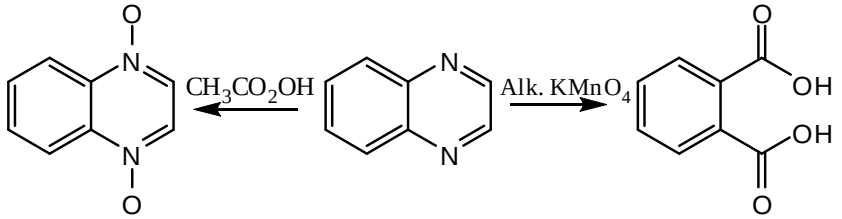
Compounds containing 1,2,3-tricarbonyl functionality have been used in the synthesis of a variety of Heterocyclic derivatives [47]. The tricarbonyl group containing compounds can be prepared by treating 3-keto ester with *p*-nitro sulphonyl peroxide 6, to give 2-(p-nitro phenyl)-sulfonyl) oxy)-3-keto esters.



Treatment of the resulting 2-(nosyloxy)-3-ketoesters with triethyl amine (TEA) in benzene at roosm temperature results in *vic* tricarbonyl compound. The tricarbonyl compound can be trapped *in situ* with *o*-phenylenediamine to give quinoxaline derivatives. Quinoxaline forms salt with acids. Nitration occurs only under forcing conditions (Conc.HNO_3, Oleum) to give 5-nitro-quinoxaline (1.5%) and 5,-7-dinitroquinoxaline (95%) [48].

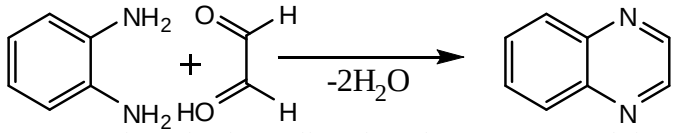


The 2-chloroquinoxaline has been prepared by the action of phosphorous oxychloride on quinoxaline -2-one or quinoxaline-1- oxide [49]. Oxidation of quinoxaline results in the formation of the product depending upon the nature of the oxidizing agent employed. With alkaline potassium permagnate pyrazine 2, 3-dicarboxylic acid is formed, while with peracid quinoxaline *di*-N-oxide results. 2-methylquinoxalineon selenium dioxide oxidation affords quinoxaline 2-carboxaldehyde.

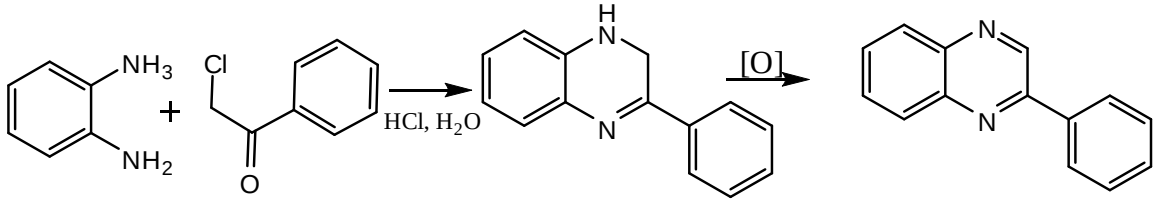


Alkyl radicals produced from acyl peroxide or alkyl hydro peroxide give high yields of 2-substituted alkyl derivatives. Reduction (Na, C_2H_5OH) of quinoxaline gives a 1,2,3,4-tetrahydro Derivatives [50, 51].

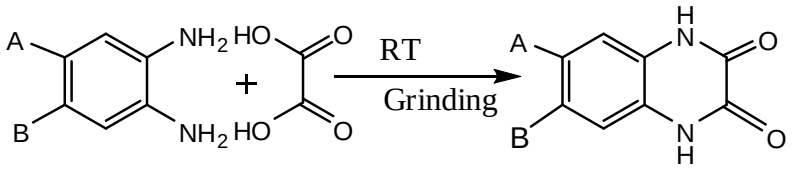
Quinoxaline itself is prepared by the reaction of o-phenylenediamine and glyoxal.



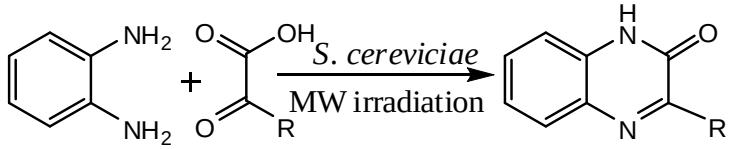
2-Phenylquinoxaline has been prepared in this manner from phenylacylchloride and *o*-phenylenediamine [52].

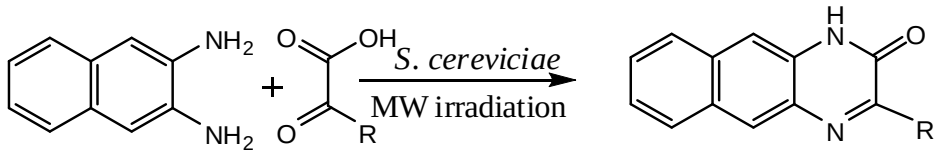


Several methods for synthesis are available in literature which involves conventional one pot, and microwave synthesis methods [53]. One-pot efficient green synthesis of 1,4-dihydro-quinoxaline-2,3-dione derivatives has reported by potential pharmacophore 1,4-dihydro-quinoxaline-2,3-dione has been achieved in a one-pot reaction at room temperature from substituted *o*-phenylene diamine and oxalic acid under solvent free conditions by a simple grinding method. Thermal and powder X-ray diffraction analysis was carried out for some crystals [54].

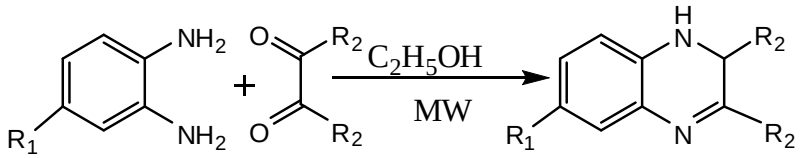


The microwave-assisted Hinsberg reaction of quinoxalinone derivatives by reacting *o*-phenylenediamine or 2,3-diaminenaphthalene with a variety of α-ketoacids through enzymatic catalysis or microwave irradiation [55].

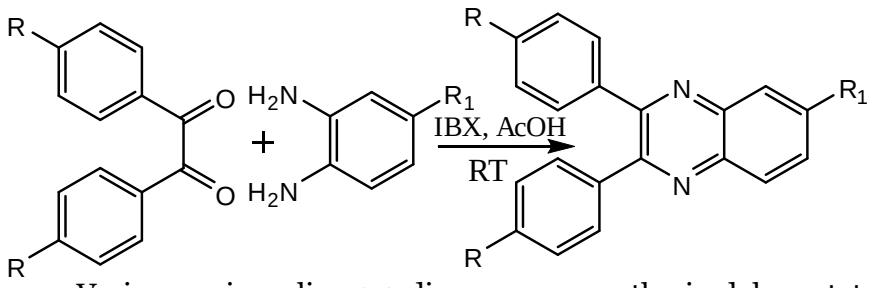




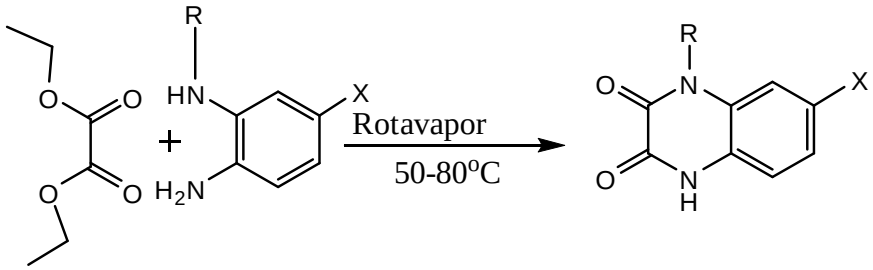
Quinoxalines are effectively synthesized in a few min by the condensation reaction of *o*-phenylenediamine with α-dicarbonyl compounds in ethanol under microwave irradiation [56]. High yield, short reaction time, pure products without purification and using only ethanol instead of toxic and expensive solvents for isolation of the products, are the advantages of this method.



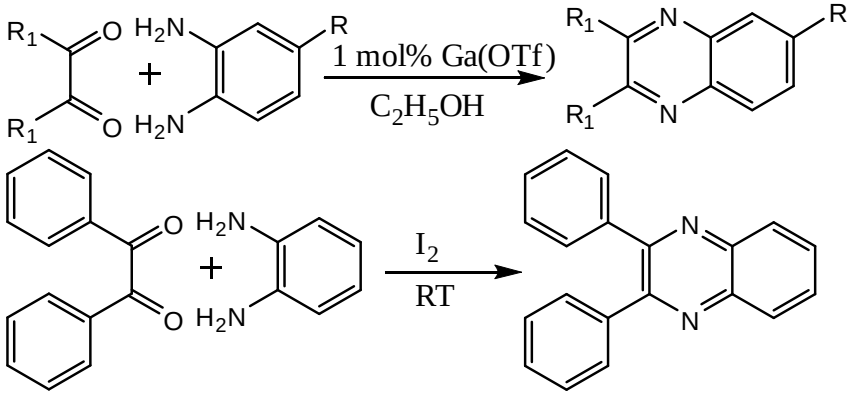
A facile synthesis of quinoxaline derivatives and quinoxaline-2, 3-diones as NMDA receptor antagonists 32 were also reported. *o*-Iodoxybenzoic acid (IBX), a readily available hypervalent iodine reagent, was found to be highly effective in synthesis of quinoxaline derivatives, from 1,2-diketones and *o*phenylenediamines at room temperature in very high yield [57].



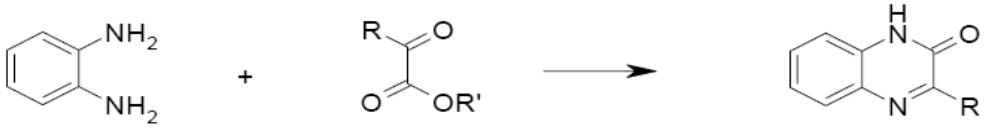
Various quinoxaline-2,3-diones were synthesized by rotatory evaporation of 1,2-diamino aromatic compounds in diethyl oxalate at 50-800C [58].



Gallium (IIII) triflate-catalyzed reactions of phenylene-1,2-diamines and 1,2-diketones produce quinoxalines in excellent to quantitative yields. The reactions proceed with 1 mol% catalyst in ethanol at room temperature. The catalyst can be recycled for at least 10 times. Attempt to synthesize quinoxaline derivatives at room temperature using molecular iodine as the catalyst are present in the literature as reported by several aromatic as well as aliphatic 1,2-diketones and aromatic 1,2-diamines, such as substituted phenylene diamines, tetra amines were further subjected to condensation using catalytic amounts of iodine to afford the products in excellent yield [59].

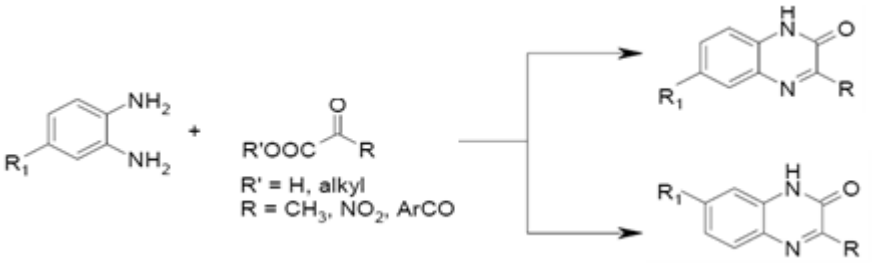


Condensation of *o*-phenylenediamine with α-ketocarboxylic acid and ketoesters: The 1,2-dihydroquinoxalin-2-ones and their derivatives substituted in position 3 were obtained by condensation of *o*-phenylenediamine with α-ketocarboxylic acid and ketoesters or their correspondents in accordance with the method of Hinsberg [60-62].

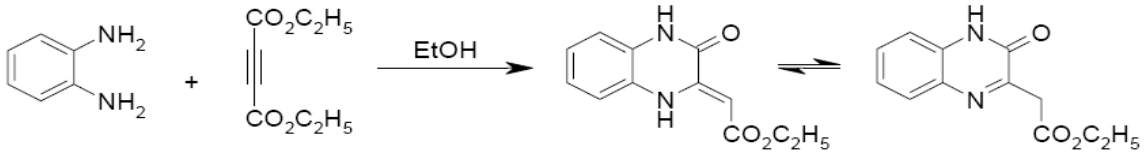


R' = H, alkyl

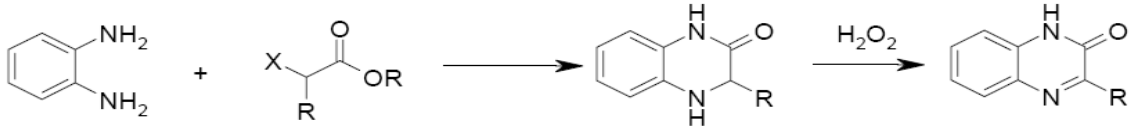
It should be noted that when the reaction involves the monosubstitued *o*-phenylendiamines, it was possible to obtain a mixture of two isomers [63-65].



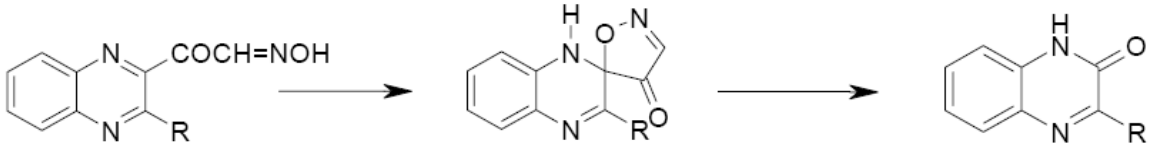
The condensation of *o*-phenylenediamine with diethyl acetylenedicarboxylate in ethanol, used to prepare a compound with quinoxaline structure which exist in two tautomeric forms [66].



From quinoxaline intermediates: The quinoxaline by condensing the α-halogenoesters with *o*-phenylenediamine and creating an oxidation by means of hydrogen peroxide [67].

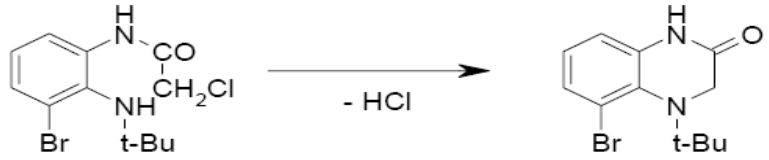


Several examples have been described in the literature on the hydrolysis of 2-aminoquinoxalines leading to quinoxalinones. Thus, the 2,3-diaminoquinoxaline is hydrolyzed by hydrochloric acid (2.5M) at 100 °C, for 5 minutes to give 3-aminoquinoxalin-2-one [68]. In the same way, the treatment of 2-amino-3-phenylquinoxaline by nitric acid, give 3-phenylquinoxalin-2-one with an excellent performance [69]. By leading the oxime quinoxalinylglyoxal to reflux of dimethylaniline, it was possible to prepare the quinoxalinone from a spiro intermediate [70].

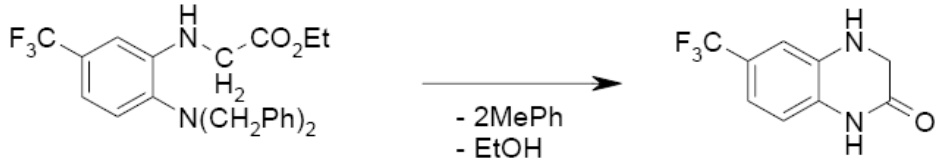


R = Me ou Ph

From derivatives of aniline: The 2-bromo-*N*-tert-butyl-6-(2-chloroacetamido) aniline leads in reflux of acetonitrile for 24 hours to 5-bromo-4-tertbutyl-3,4-dihydro-2(1*H*)-quinoxalinone with a yield of 79% [71].

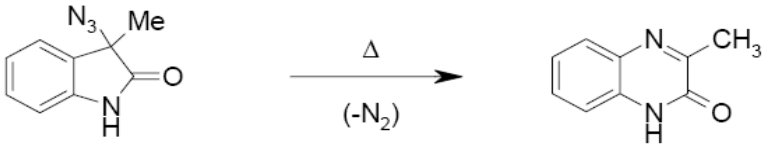


By subjecting the *N*,*N*-dibenzyl-2-(ethoxycarbonylmethyl)amino-4-(trifluoromethyl) aniline to a reduction under a pressure of 3 atmospheres, which induces a spontaneous cyclization, giving the 6-trifluoromethyl-3,4-dihydro-2(1*H*)-quinoxalinone with good yield [72].

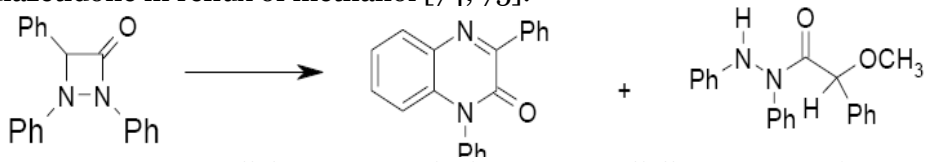


From heterocyclic systems-by cycle extension

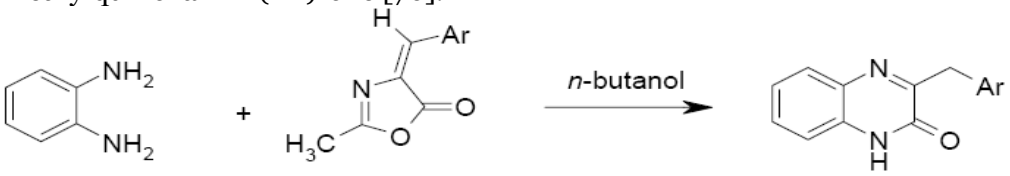
From indolinone: The 3-methylquinoxalinone may also be prepared by an extension of cycle [73]. Thus the 3-azido-3-methyl-2-indolinone is transformed into quinoxalinone in xylene at reflux.



From diazetidone: The quinoxaline was obtained with a yield of 34% by heating diazetidone in reflux of methanol [74, 75].

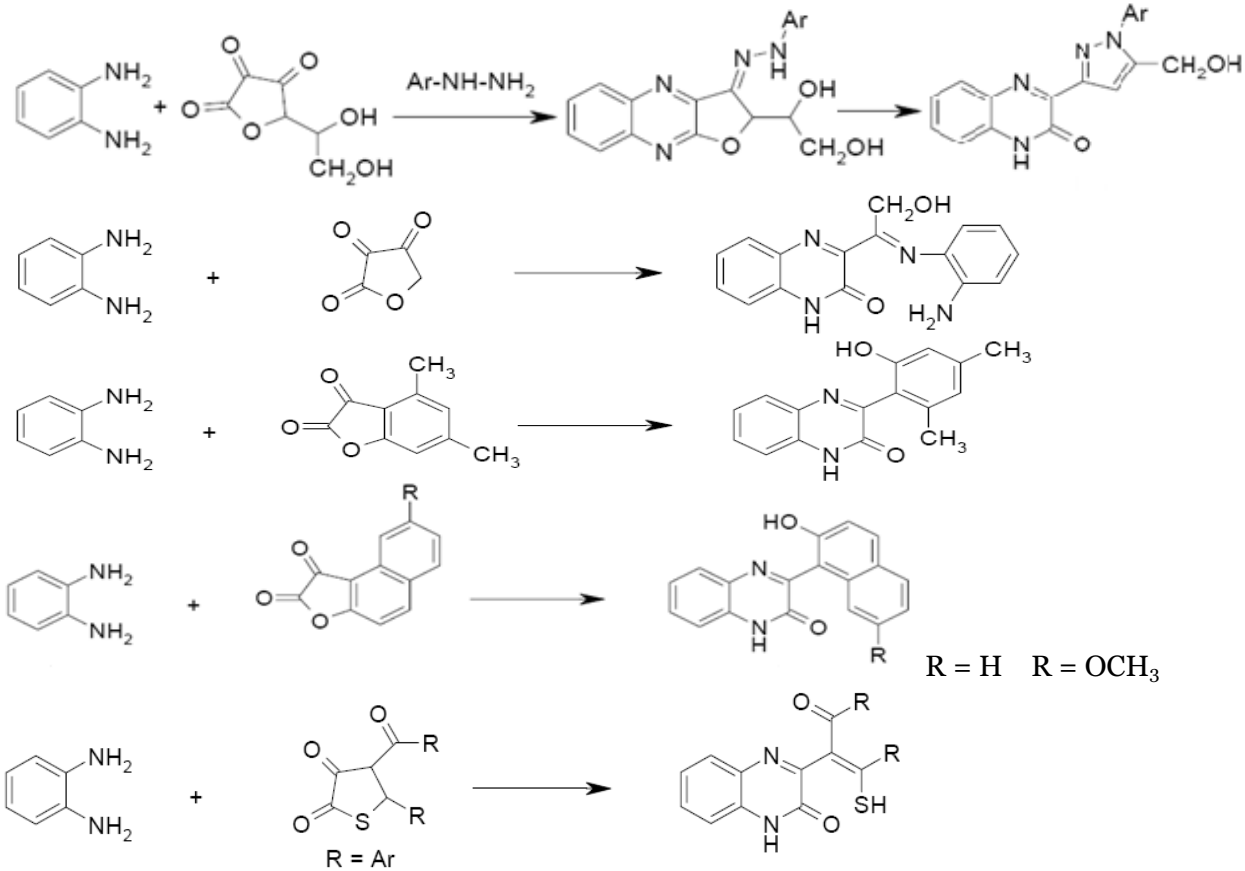


From 4-arylidene-2-methyl-1,3-oxazolidin-5-one: The condensation in *n*-butanol at reflux, *o*-phenylenediamine and 2-arylidene-methyloxazolin-5-one, for accessing the 3-aryl-methylquinoxalin-2(1*H*)-one [76].



From dehydroascorbic acid: Similarly, the condensation of dehydroascorbic acid with *o*-phenylenediamine, led to compound which turns into pyrazolylquinoxalinone in the presence of arylhydrazines [77].

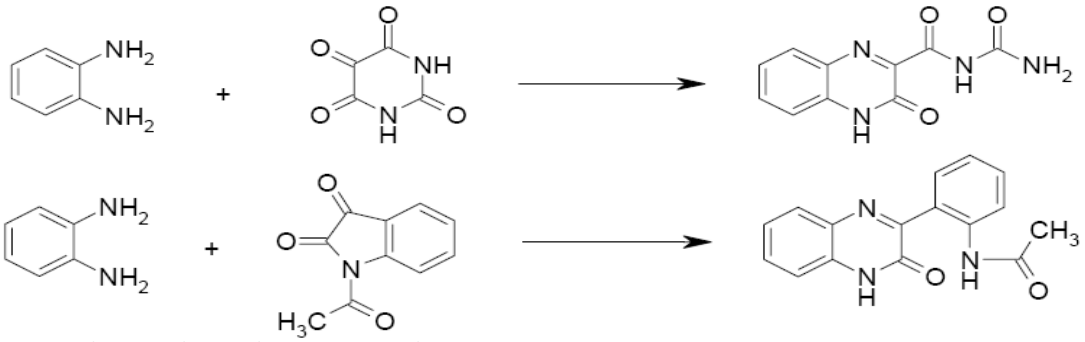
From dicarbonylated five-membered ring compounds: In a similar way, the quinoxalines by condensing *o*-phenylenediamine with heterocyclic dicarbonyl compounds [78].



R = H R = OCH_3

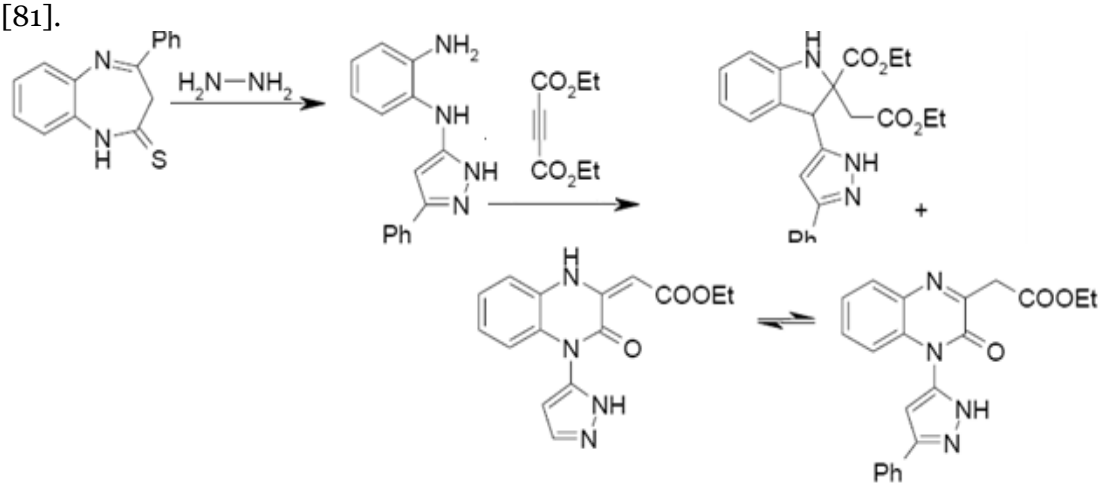
R = Ar

From nitrogenous polycarbonylated heterocycles: Other compounds containing function lactams and were also used as agents of cyclization for the preparation of quinoxalinones and [79-80].

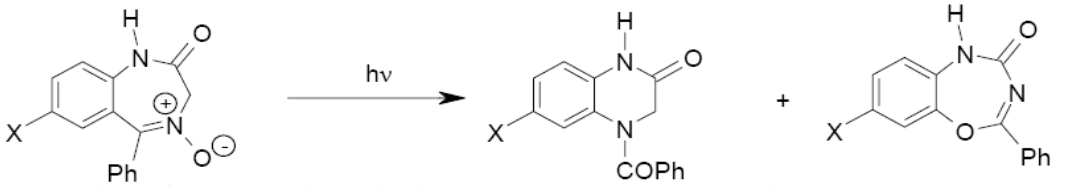


Through cycle contraction

From 1,5-benzodiazepin-2-one: The quinoxaline from benzodiazepine-2-thione in two steps. First, they made an opening round of the seven membered ring, by reacting hydrazine on benzodiazepine-2-thione, obtained by sulfuration of 1,5-benzodiazepin-2-one. The *o*-amino-phenylaminopyrazole obtained undergoes condensation with diethyl acetylene dicarboxylate, gave benzimidazoline, beside of a new quinoxaline derivative which takes form in two tautomeric forms [81].

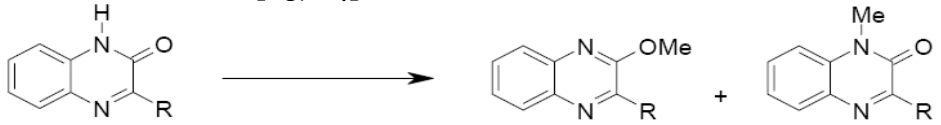


From 1,4-benzodiazepin-2-one N-oxide: Irradiation of 1,4-benzodiazepine gives quinoxaline when (X=Cl). Conversely, we note the formation of oxadiazocine, when (X = SMe) [82].



Reactivity of quinoxaline derivatives: The chemistry of the quinoxaline derivatives with great opportunities due to the presence of different reactive sites: the lactam function involving the nitrogen atom and the carbonyl group; and is involved in alkylation reactions, amination, chlorination, and the sulfuration and in 1,3-dipolar cycloaddition.

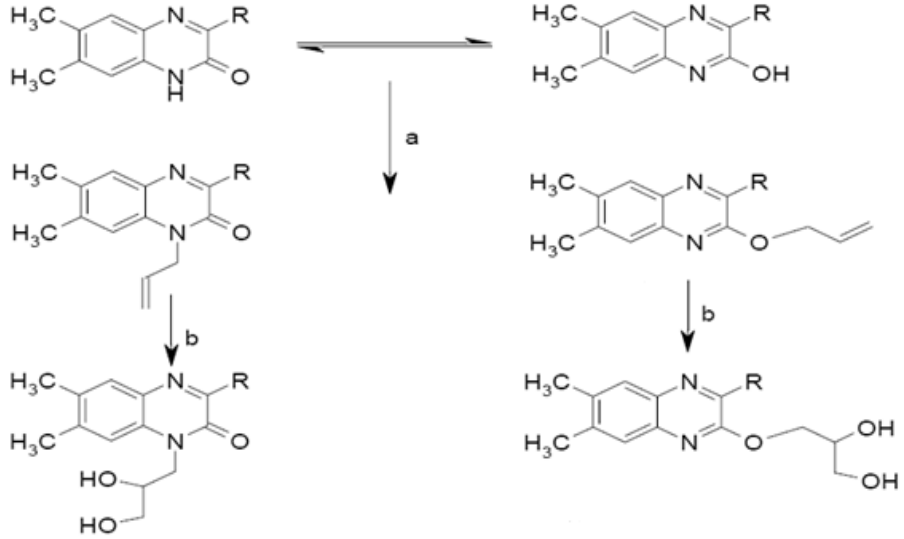
Alkylation: The alkylation reaction of quinoxalin-2-one gives a mixture of *O*-alkyl and *N*-alkyl derivatives. Thus the methylation of quinoxaline by diazomethane involved the two centers of the lactam function [83, 84].



This reaction has been generalized to other alkylating agents, using phase transfer catalysis conditions, to lead to the *N* and *O* alkyl compounds [85].

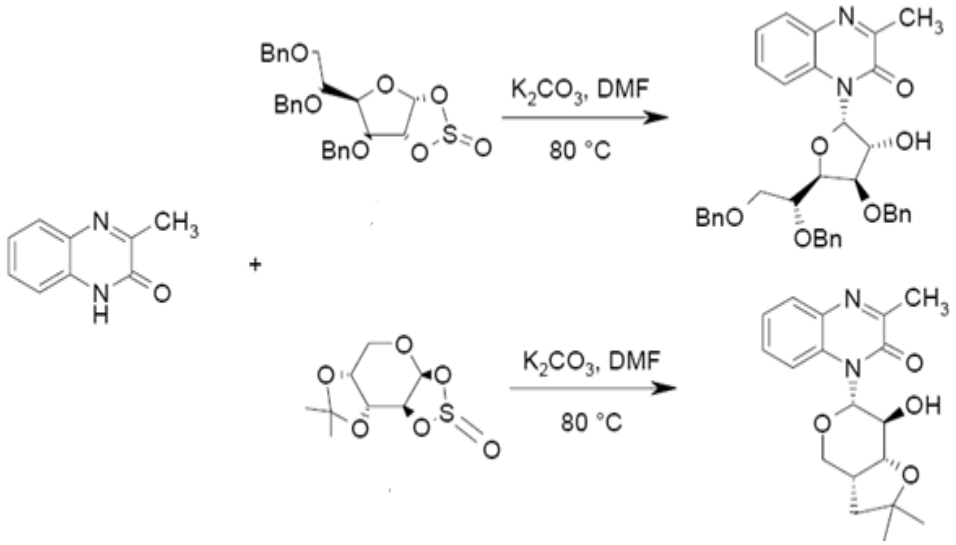
The alkylation reactions have been exploited to prepare quinoxalines differently functionalized in position 1 and 2. Thus, a protocol of using allyl bromide as an alkylating agent

and sodium hydride in dimethylformamide at 100 °C. The dihydroxylation of *N* and *O* alkyl derivatives and compound, was performed with AD-mix β in a mixture *t*-butanol-water [86].

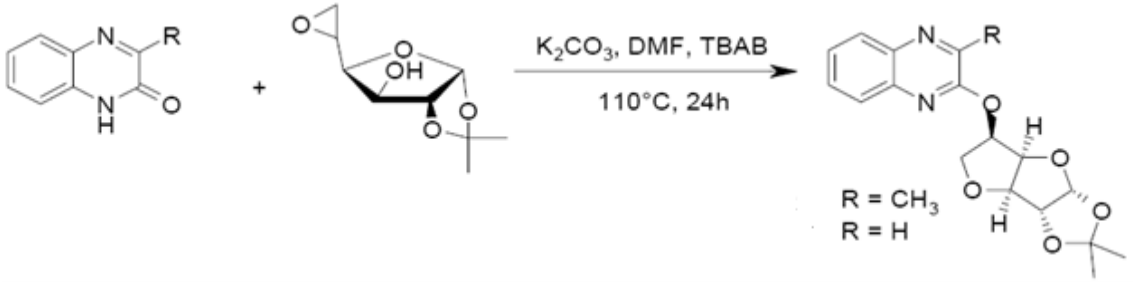


a) Allyl bromide, NaH, DMF, 100 °C b) AD-mixβ. *t*BuOH, H_2O, 0 °C

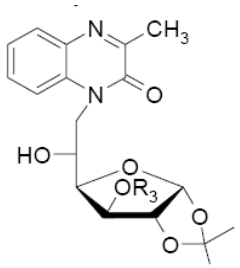
An efficient synthesis method for obtaining nucleoside analogues and, from the quinoxalinone by reacting derivatives1,2-*O*sulfonyl of gluco- and arabino- structure with 3-methylquinoxalin-2(1*H*)-one in the presence of a weak base K_2CO_3 in DMF at 80 °C [87].



The condensation of quinoxalinone with 5,6-anhydro-1,2-*O*-isopropylidene-α-Dglucofuranose, leads to *O*-glucoquinoxalines. In a reaction involving the rearrangement of the 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose to the corresponding 3,6-anhydro, which preferentially reacts with the oxygen atom of the lactam function of quinoxaline. The *O*-glucoquinoxalines obtained were identified [88].

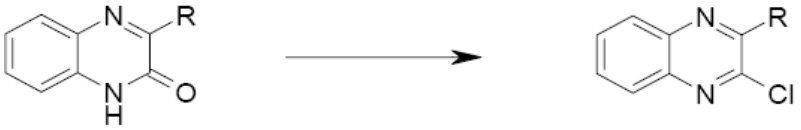


It should be noted that when the hydroxyl group of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose, is protected by an alkyl group, the same reaction is used to isolate the compound of *N*-alkylation beside the compound of *O*-alkylation.

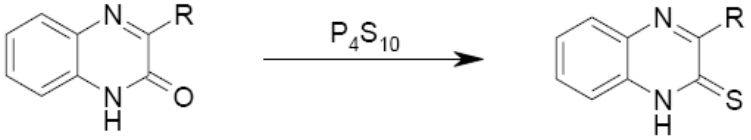


$R_3 = CH_3C_{19}H_{24}N_2O_6$
$R_3 = C_3H_5C_{21}H_{26}N_2O_6$
$R_3 = C_4H_9C_{22}H_{30}N_2O_6$
$R_3 = C_8H_{17}C_{26}H_{38}N_2O_6$
$R_3 = C_{10}H_{21}C_{28}H_{42}N_2O_6$
$R_3 = C_{12}H_{25}C_{30}H_{46}N_2O_6$

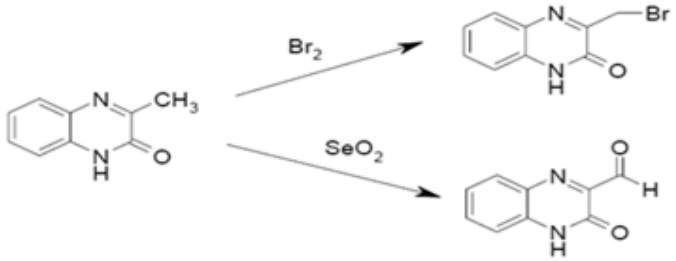
Nucleophilic substitution in position 2: Nucleophilic substitution in position 2 of the 1,2-dihydroquinoxalin-2-one has enabled to isolate the chlorinated products by action of $POCl_3$ or PCl_5 [89].



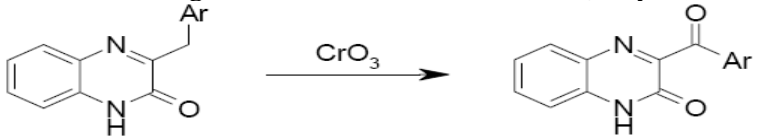
In the case where R = H [90], the chlorination reaction gives the 2,3-dichloroquinoxaline. The reaction of thionation was achieved by the action of phosphorus pentasulfide in pyridine [91, 92].



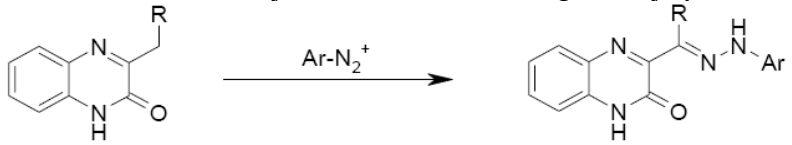
Reactivity of alkyl group in position 3: The alkyl group in position 3 of the quinoxalin-2-one is very reactive to some electrophil agents. Thus, it is easily made the bromination of 3-methylquinoxalin-2-one. The oxidation of quinoxaline 3 by selenium oxide to obtain 3-formyl-quinoxaline [93].



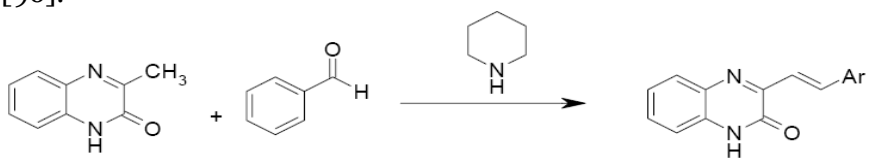
According to an oxidation reaction, the 3-acyl-1,2-dihydroquinoxalin-2-one [94].



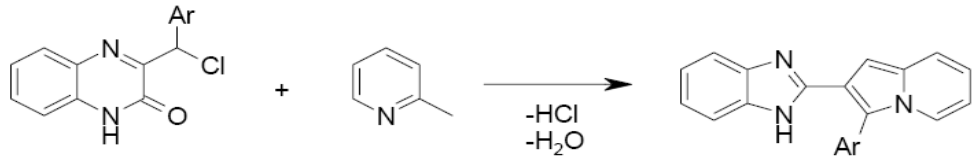
The action of aryldiazonium salt with 3-methylquinoxalin-2-one [95].



The condensation of 3-methylquinoxalin-2-one with aromatic aldehydes gives the compound [96].

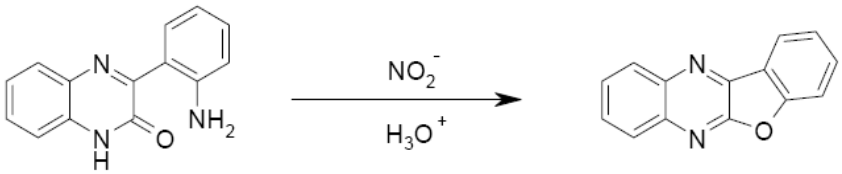


The 2-(indolizin-2-yl) bezimidazole, by condensing 3-(arylchloromethyl-quinoxalin-2-one, with α-picoline [97].

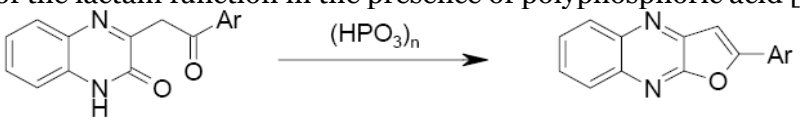


Ar = 4-$NO_2C_6H_4$, Ph, 2,4-$Cl_2C_6H_3$, 3,5-$Cl_2C_6H_3$, CH_2Ph

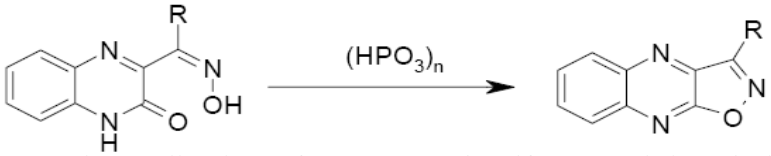
Cyclization reactions involving positions 2 and 3 of the quinoxaline: The cyclization reactions leading to oxygenated heterocyclic systems have been known for a long time and they can give an oxygen and sulfur heterocycles joined to quinoxaline. The Marchlewski and Sosnowski reaction, conducted in the presence of hydrochloric acid, constitutes an oldest example [98].



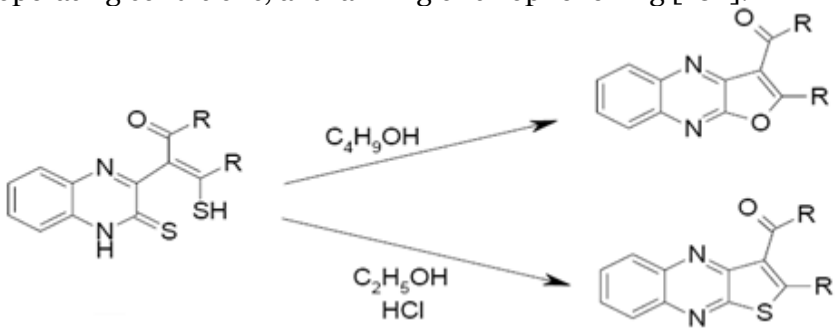
The cyclization of 3-aroylmethyl-1,2-dihydroquinoxalin-2-one, involving the carbonyl group of the lactam function in the presence of polyphosphoric acid [99].



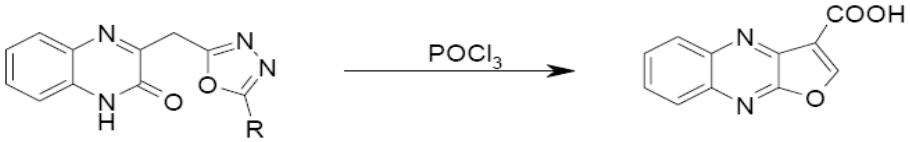
In the same conditions as before, the cyclization of oximes [100,101].



The cyclization of unsaturated sulfur-containing derivatives can provide, according to the operating conditions, a furan ring or thiophene ring [102].

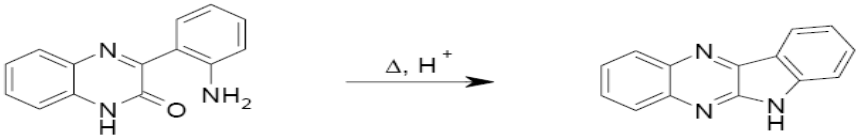


The heating of 3-(1,3,4-oxadiazol-2-yl)-methyl-1,2-dihydroquinoxalin-2-one, in the presence of phosphorus oxychloride allows the preparation of the furoquinoxaline [103].



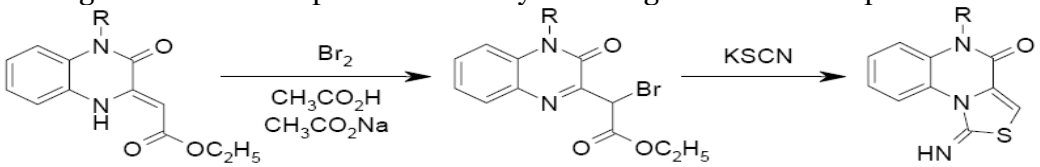
The synthesis of 2-(3-thienyl)-2,3-dihydrofurano[2,3-b] quinoxaline by condensing the 3-methylquinoxaline-2-one with 3-formylthiophene, at 150 °C [104].

The contiguous quinoxaline nitrogen heterocycles such as indole and pyrazole. To cyclize the 3-(*o*-aminophenyl)-1,2-dihydroquinoxalin-2-one **93** (Scheme 34), with the reflux of acetic acid or hydrochloride acid [105, 106].

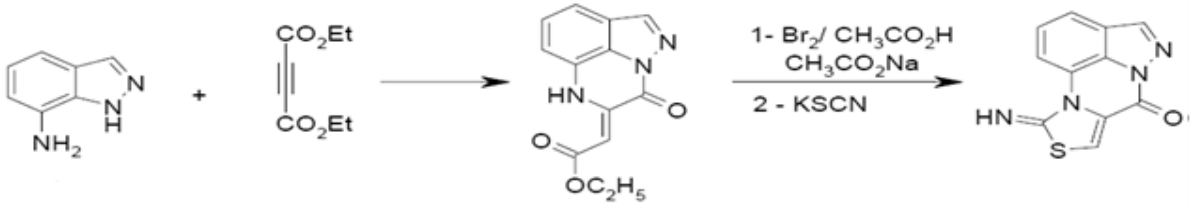


he cyclization of hydrazone to obtain the derivatives of pyrazolo[3,4-b]quinoxalines called « Flavazoles » [107, 108].

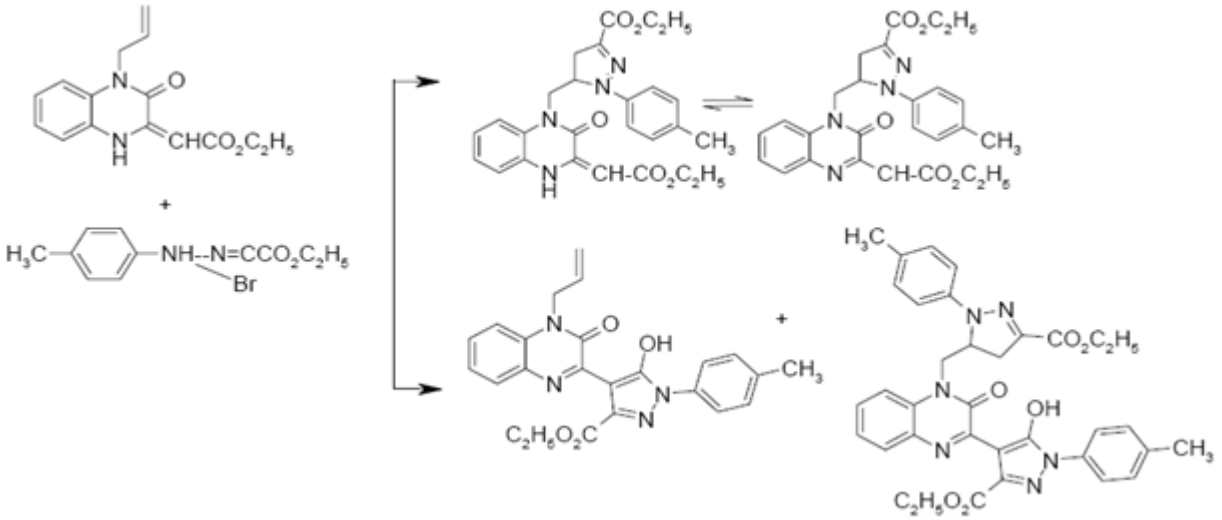
The cyclization occurs in an alkaline solution [109] or at reflux of acetic acid [110]. Several flavazoles were well prepared, when R=aryl or sugar. When R=H, the cyclization could not take place, neither in alkaline, or by heating in acid. A tricyclic system containing the quinoxaline contiguous to the thiazole was obtained by exploiting the presence of β-enaminoester synthon. Thus, the bromination of 3-ethoxycarbonylmethylidene-quinoxalin-2-one by the bromine in acetic acid in the presence of sodium acetate leads to the bromo compound which subsequently undergoes the action of potassium thiocyanate to give the thiazoloquinoxalin-2-one [111].



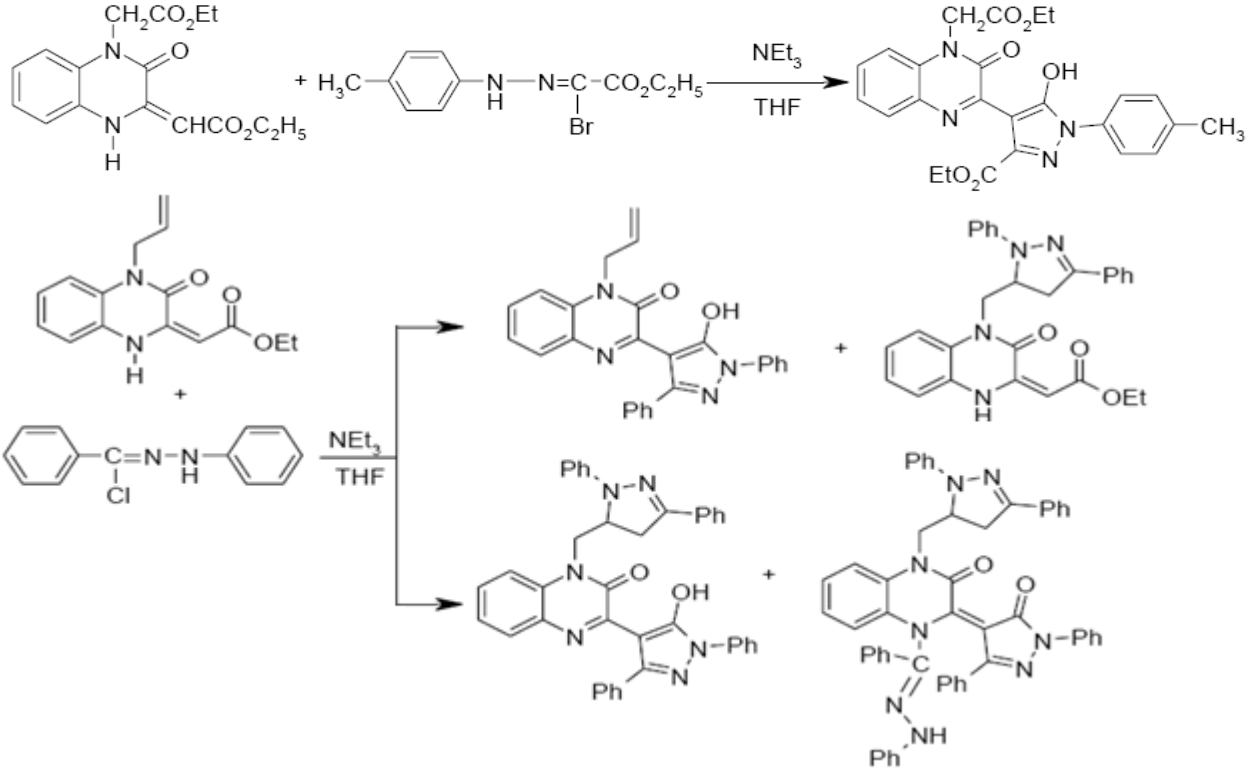
Similar results were observed by condensing the 7-amino-indazole with diethyl acetylenedicarboxylate. The pyrazolo quinoxaline obtained after reaction of bromination followed by action of potassium thiocyanate led to pyrazolothiazolo quinoxaline [112].

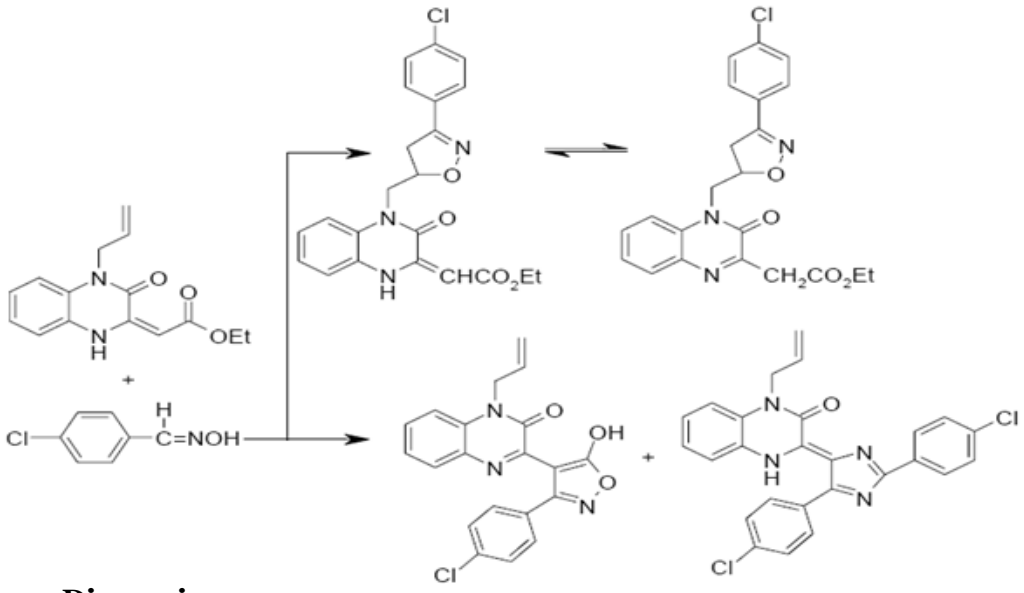


Reaction of 1,3 dipolar cycloaddition on quinoxalinone: The synthesis of heterocyclic systems containing the quinoxaline nucleus linked to various types of pentagonal pyrazole, isoxazole, imidazole and 1,2,3-triazole. The action of diethyl hydrazono-α-bromoglyoxylate on quinoxaline in the presence of triethylamine; the reaction of the 1,3-dipolar cycloaddition leading to a mixture of three products from two competitive reactions, a reaction of 1,3-dipolar cycloaddition involving the double bond of allyl group, leading to the pyrazoline; and a reaction of cyclocondensation involving the enaminoester synthon giving the pyrazole [113-116]. In the same operating conditions as before, the condensation of hydrazonoyle bromide on the 1-ethoxycarbonylmethyl-3-(ethoxycarbonymethylene)-2-oxoquinoxaline, leads exclusively to the 1-(ethoxycarboxymethyl)-5-hydroxypyrazolin-4'-yl)-2-oxoquinoxaline. In the same series of reactions, the treatment of quinoxaline by the α-chloro-phenyl phenylhydrazone for 48 hours leads to a mixture of four products from the reaction of 1,3-dipolar cycloaddition and cyclocondensation, as well as from a reaction of alkylation of the nitrogen atom in position 4 of the quinoxaline ring.



The action of chlorobenzaldoxime of compound, showing a similar behavior towards the dipolarophile sites, leading to a mixture of three products.





Discussion

The quinoxalines are a class of heterocyclic compounds with different applications in various fields, whether pharmacology, agricultural chemistry or chemical industry where various patents were field. Thus, several new synthetic methods have been described in literature. We will show, in this development, the synthesis, reactivity and the biological properties of heterocyclic systems derived from quinoxaline. Quinoxaline also called benzopyrazine is a heterocyclic compound containing a ring complex made up of benzene ring and a pyrazine ring has been considered as a wonder nucleus which posses almost all types of biological activities. This diversity in the biological response profile has attracted the attention of many researchers to explore this skeleton to its multiple potential against several activities [17-125]. Quinoxaline showed considerable interest from both academic and industrial Perceptive. Among the various classes of the nitrogen containing heterocyclic compounds quinoxaline is a vital component of various pharmacologically active compounds. Although rarely described in nature synthetic quinoxaline ring is a part of some antibiotics which are known to inhibit the growth of Gram Positive bacteria and are also active against various transplantable tumors. Quinoxaline is commonly called as *1,4-diazanaphthalene* or *benzopyrine*. Most of the present diseases are due to the invasion by the pathogenic organisms like bacteria, fungal, virus, ricketsia. To treat these diseases many potent nd broad spectrum antibiotics were discovered such as ampicillin, amoxicillin, carbenicillin, oflaxacin, tetracyclines, and ciproflaxcine etc. Even though antibiotics are life saving drugs in therapeutics but they are potentially harmful [126-130]. These effects include allergic and anaphylactic reaction, superinfection, development of resistance, destruction of normal non-pathogenic bacterial flora and selective toxicity like aplastic anemia, kidney damage etc. A considerable amount of research activity is directed towards a potent, more specific and less toxic antibiotics. Substituted quinoxaline have received considerable attention during last two decades as they are endowed with variety of biological activities and have wide range of therapeutic properties. The quinoxaline derivative possesses different pharmacological activities. We thought to synthesize novel substituted quinoxaline moiety. Quinoxaline derivatives are widely distributed in nature and they have been shown to have very interesting biological activities like, anti-bacterial, anti-fungal, anti-inflammatory and analgesic activity. Hence in present study we plan to synthesize novel substituted quinoxaline derivatives.

Conclusion

The quinoxaline has diverse biological potential, and the easy synthetic routes for synthesis have been attention of the researchers. Also the research on antitubercular activity has given positive results. By the present scenario and due to their wide range of applications, these compounds have received a great deal of attention in connection with their synthesis and it can be concluded that quinoxaline have a great potential. Quinoxaline molecules are responsible for

diverse biological activity, but it is interesting to note that this moiety when substituted with other moieties showed a broad spectrum activities. The quinoxaline can be a rich source for exploitation. Therefore in search of new molecules it may be worthwhile to explore the possibility in this area by fusing different moieties and increase the potency.

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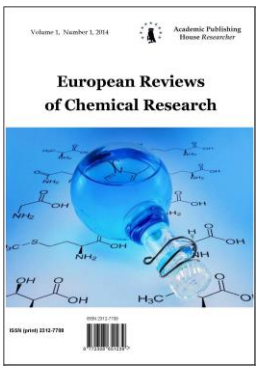

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Viscosity Properties of an Aqueous Suspension $Pd(NO_3)_2$-Al_2O_3-La_2O_3-HAc-H_2O for Afterburning Catalysts

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Abstract

The boundary conditions of formation of hydroxides are determined by calculation of ion equilibrium with use of thermodynamic constants of metals For system "$Pd(NO_3)_2$ – Al_2O_3 – La_2O_3 – HAc – H_2O". Possibility of decrease in dynamic viscosity of the "$Pd(NO_3)_2$ – Al_2O_3 – La_2O_3 – HAc – H_2O", suspension having pH = 3 at addition of 1% of an aqueous solution is experimentally shown cation-active surfactant at 1.74 time: with 850.62 to 488.95 mPa·s. The morphology of particles of suspension before and after the addition in it surfactant cation-active Praestol 655 FC is investigated.

Keywords: afterburning catalysts, ion equilibrium, viscosity, palladium (II) nitrate, suspensions, ion equilibrium, surface-active substances, surfactant, lanthanum oxide.

Introduction

Combustion gases of cars are the main source of pollution of the air atmosphere of the cities. The exhaust gases of vehicles using gasoline, in contrast to vehicles that using on diesel fuel, contain lead compounds. At combustion of fuel in the car engine, products of combustion form the "specific poisonous cocktail" including products of imperfect combustion such as white damp, nitrous oxide, aldehydes, ketones, unsaturated hydrocarbons, and also peroxidates, dioxide of sulfur, compound of lead, soot and many other. Special catalysts of afterburning are used to cleaning and neutralization of combustion gases of petrol engines [1]. Currently, the biggest distribution among them was received by catalysts on the basis of compositions of the platinum metals deposited on porous oxide of aluminum [2, 3]. Palladium treat oxidizing catalyst, it promotes the oxidation of unburned hydrocarbons into water vapor, carbon monoxide into carbon dioxide. Due to its high catalytic ability are considered most effective. The oxides of rare earth elements included in composition of the catalyst interact with platinum metals, and prevent the sintering of the active component at the long-time heating.

The disadvantage of a palladium catalyst based on $Pd(NO_3)_2$ – Al_2O_3 – La_2O_3 – HAc – H_2O system used for a complete series of a number of domestic cars is the complexity of its preparation.

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In the result of arising in disperse system the interaction of aluminum oxide phase, containing oxides of rare earth elements, with a solution of palladium salt there is an increase in viscosity of suspension. This complicates its putting of impregnating method on a ceramic block of afterburner catalyst, influences its oxygen capacity, reduces overall performance. The actual task optimizes the rheological properties of an aqueous suspension "$Pd(NO_3)_2 – Al_2O_3 – La_2O_3 – HAc – H_2O$", is used for the manufacture of catalysts for afterburning of exhaust gases.

For decrease in viscosity of suspensions usually use change of pH and temperature, ultrasonic processing, change of suspension preparation technology. One of the paths reducing viscosity of suspension is the additive in system of surface-active substances. The mechanism of surfactant action in this case is up to the end not clear, however the application results of different types surfactant for increase in oxygen capacity of afterburner catalyst are given in works [4, 5].

The aim of the present work was research of rheological properties of an aqueous suspension $Pd(NO_3)_2 – Al_2O_3 – La_2O_3 – HAc – H_2O$ putting on the ceramic block of afterburner catalyst at addition in its surfactant, change of multiplicity of dilution and change pH.

Experimental part

The basic composition of an aqueous suspension for afterburner catalyst of exhaust gases was reasonable by the main requirements present to them in scientific and technical literature for ensuring effective work [1-9]. The oxidizing component for post-combustion exhaust gases has been selected palladium. The carrier of an oxidizing component used aluminum oxide (II) with the addition 4 % rare earth metal (lanthanum oxide (II)). As the reactionary environment for oxidation of some organic substances ethane acid (acetic acid) was used. Synthesis of suspension was carried out with a preliminary grinding of the powdery oxides of aluminum and lanthanum to the sizes in the limit 6.5-9.5 microns.

Experiments on measurement of dynamic viscosity of suspension were made by method of capillary viscosimetry, which is rely on Poiseuille's law, at 298 K. For this purpose in work Ostvald's viscometer and Brukfild's viscometer were used.

For an estimate of the sizes and research of suspension particles morphology the analyzer of the sizes of particles of HORIBA LB-550 was used and the scanning electronic microscope in the scanning mode JEOL JXA-8500F (Japan) with the probe microanalyzer at the accelerating voltage of the electron beam tension from 10 to 30 kV was used.

Results and discussion

One of the main tasks, from the point of view of the organization of process, is the possibility of forecasting the boundary conditions for obtaining of possible connections. For optimization of suspension composition the areas concentration and pH formations of basic hydroxides of $Pd(OH)_2$, $Al(OH)_3$, $La(OH)_3$ metals in an system $Pd(NO_3)_2 – Al(NO_3)_3 – La(NO_3)_3 – HAc – H_2O$ by the technique described in [10, 11] calculation thermodynamic was carried out.

For this purpose, the analysis of the ionic balance by a technique [12] which are established in the investigated multicomponent system was carried out. At calculation of formation in solution of known multinuclear complexes of $Me_p(OH)_n$ metals was also took into account.

In the first approximation, the formation boundary conditions in system the phases hydroxides $Pd(OH)_2$, $Al(OH)_3$, La(OH) meet equality of ionic product $IP_{Me(OH)n}$ to solubility product of the meet hydroxide of metal $SP_{Me(OH)n}$, being at this temperature a constant (1):

$$IP_{Me(OH)n} = SP_{Me(OH)n} \quad (1)$$

For begin of solid phase formation process the equality has to be carried out

$$SP_{Me(OH)n} = [Me^{n+}]_н[OH^-]_н^n = (\alpha_{Men+} \cdot C_i) \cdot [OH^-]^n, \quad (2)$$

where α_{Men+} is the a share of the metal uncomplexed ions capable to enter chemical reaction, and C_i is the initial concentration of salt of metal in solution.

According to [11] design formula allowing to calculate value of minimum necessary concentration of salt of metal in a logarithmic form has an appearance (3):

$$pC_i = pSP_{Me(OH)n} - p\alpha_{Men+} - npK_{H2O} + npH^+, \quad (3)$$

where K_{H2O} is the a water ionization constant.

The equation (3) enough fully describes difficult heterogeneous process of metal hydroxide formation. Definition pC_i was carried out with use of thermodynamic constants (K_{H2O}, $SP_{Me(OH)n}$) [13-15].

Results of calculation at a temperature of 298 K in coordinates $pC_i = f(pH)$ are presented graphically in Fig. 1. The obtained data were used for a select pH suspensions from the viewpoint of completeness of sedimentation and stability of palladium s, aluminum and lanthanum hydroxide. Optimum pH should be considered higher than 5.0.

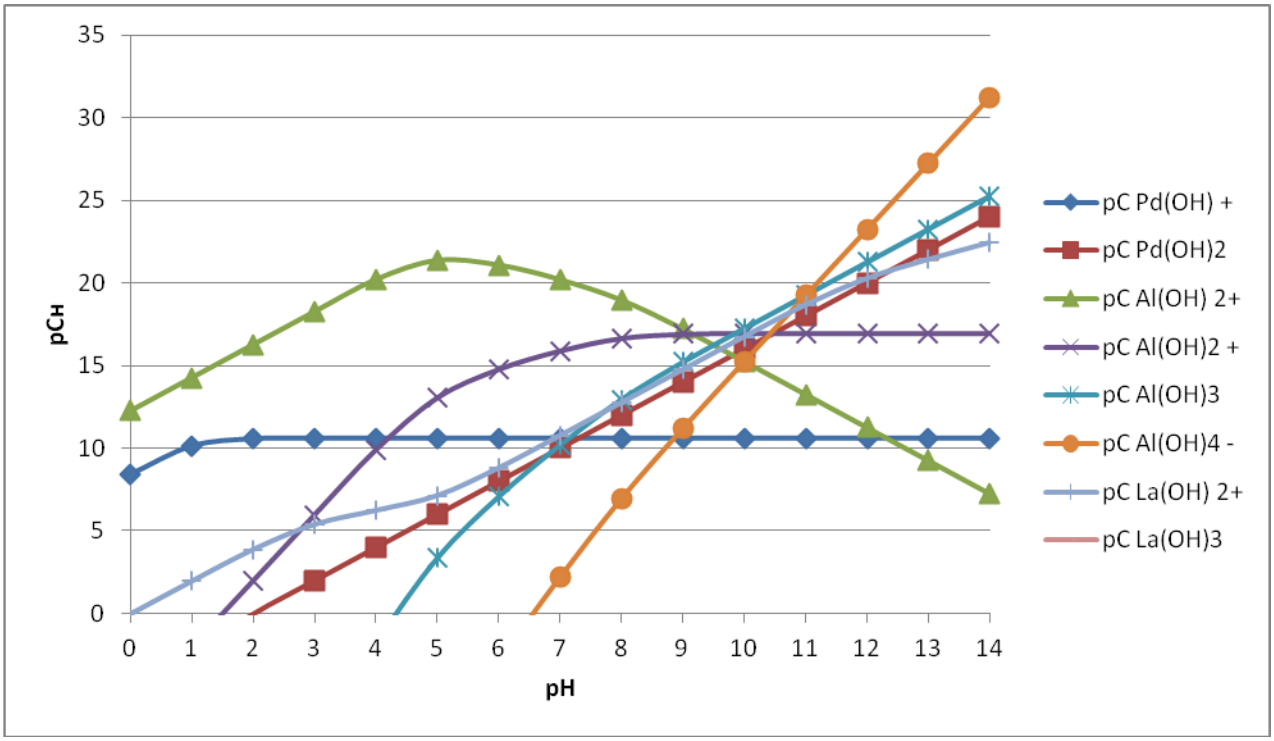


Fig. 1. The boundary conditions the formation of metal hydroxides and hydroxy complexes of palladium, aluminum, lanthanum, in the "$Pd(NO_3)_2$ – $Al(NO_3)_3$ – $La(NO_3)_3$ – HAc – H_2O" at 298 K

Disperse hydroxide systems are structured and for an explanation of the mechanism of their formation it is possible to use some consistent patterns inherent in halkogenidny systems, established in work [16, 17]. As representations of authors in "reactionary mixes with their inherent high satiation on the besieged solid phase at the expense of the cooperative and fluctuation phenomena the molecular complexes, associates, clusters, submicronic formation, having the colloidal nature or being products of structuring colloidal particles can be formed". The presence of charged groups in the molecules causes special hydrodynamic characteristics of polyampholytes solutions. Their behavior substantially depends on the value pH and the ionic force of the environment. By increasing in pH of the environment viscosity of suspension, as a rule, increases as associates increase in volume owing to straightening of formation polymeric.

Analysis of the literature [18-21] showed that the behavior and properties of viscous fluids is significantly affected by their composition, including existence of surface-active substances of various type.

The results of the particles sizes measurement in suspension and an assessment of their quantitative distribution showed that addition in suspension of 1 % of water solution Praestol 655 FC surfactant in the ratio 1:10 sharply reduces dispersion of particles by the sizes, at the same time increasing variations of the particles average size (Fig. 2).

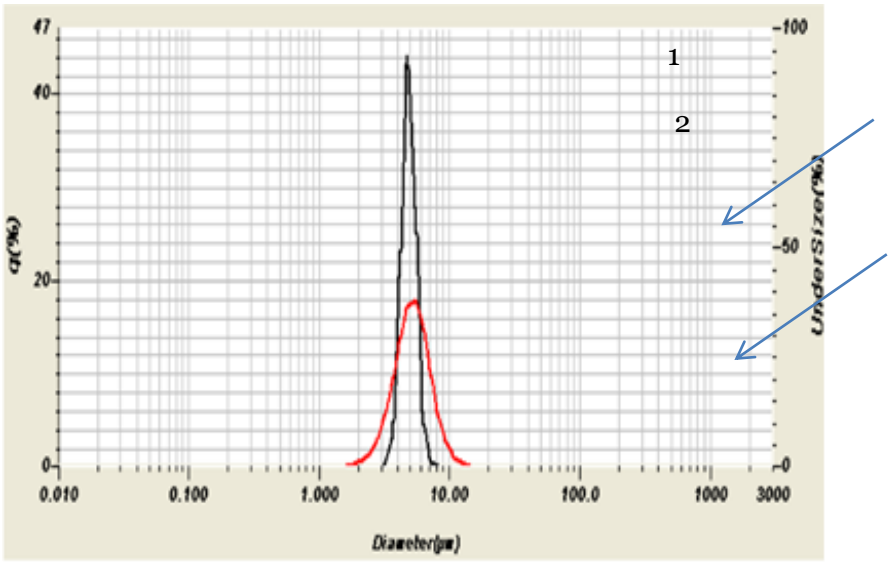
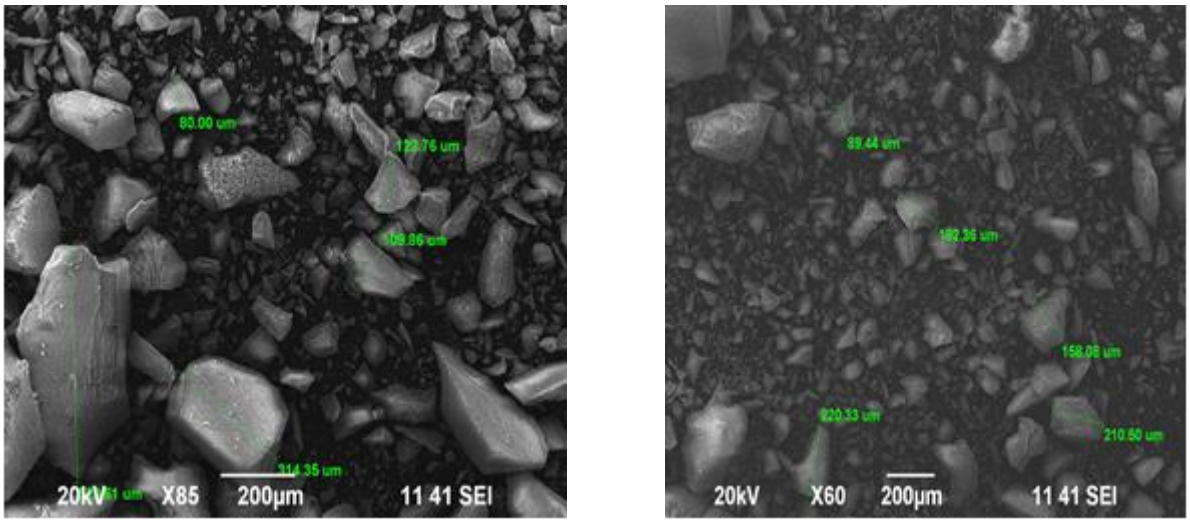


Fig. 2. Comparative characteristics of particles distribution by the suspension sizes $Pd(NO_3)_2$ – Al_2O_3 – La_2O_3 – HAc – H_2O at its dilution by 1:10 water (1) and 1 % water solution Praestol 655 FC (2) surfactant at pH = 3

The particles microimages of the studied suspension to absence surfactant and after its introduction in the form of 1 % of water solution are presented for comparison in Fig. 3.

It is clearly visible that the suspension containing surfactant has considerably the smaller average particles size that probably is connected with its adsorption action which is slowing down integration of particles.



a) *b)*

Fig. 3. Electronic and microscopic images of the suspension particles $Pd(NO_3)_2$ – Al_2O_3 – La_2O_3 – HAc – H_2O to (a) and after an additive in it 1% of water solution Praestol 655 FC surfactant in the ratio 1:10 (b)

In the real work influence on properties of suspension viscous an additive perspective cation-active Praestol 655 FC surfactant was investigated. For comparison purposes efficiency of addition surfactant in system dependence of change of dynamic viscosity of suspension on dilution by its water was also received. Below in fig. 4 the results of dilution influence on dynamic suspension viscosity of dilution by water (1) and one-percentage water solution surfactant (2) are given below.

As appears from Fig. 4 the increase dilution frequency rate of 1 % water solution Praestol 655 FC surfactant to level 1.12 leads to bigger decrease in dynamic viscosity of suspension, than dilution

by its water. The same time the maximum distinctions in viscosity reaching 1.74 times are observed at frequency rate of dilution 1.10. At the dilution more than 1.12 situation changes on the return and dilution by water becomes more preferable. When putting suspension on the ceramic block strong dilution is undesirable as reduces the oxygen capacity of the catalyst. Therefore, the recommended dilution level providing considerable advantage of 1 % of water solution Praestol 655 FC surfactant should be considered dilution level 1.10.

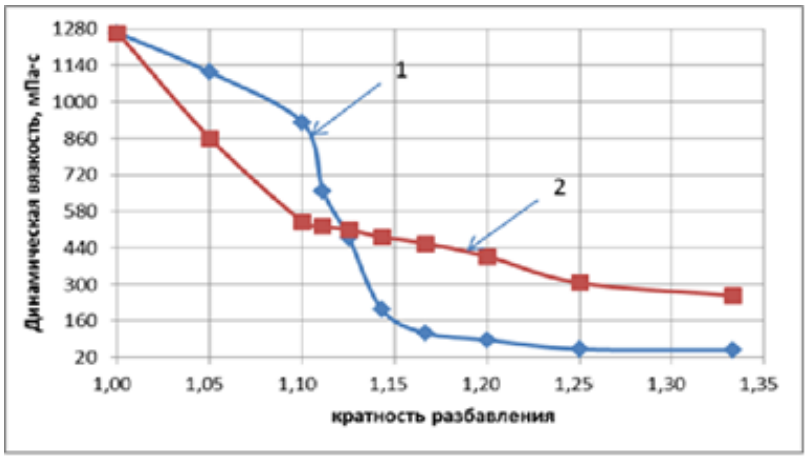


Fig. 4. The change of dynamic viscosity of suspension $Pd(NO_3)_2 – Al_2O_3 – La_2O_3 – HAc – H_2O$ at a temperature of 298 To from frequency rate of its dilution by water (1) and 1 % water solution Praestol 655 FC (2) surfactant

The dependence of the dynamic viscosity of the studied suspension at various pH values ranging from 3 to 5 in cases of dilution it 1 % aqueous surfactant Praestol 655 BC (2) at 1.10 multiplicity of dilution shows on Fig. 5.

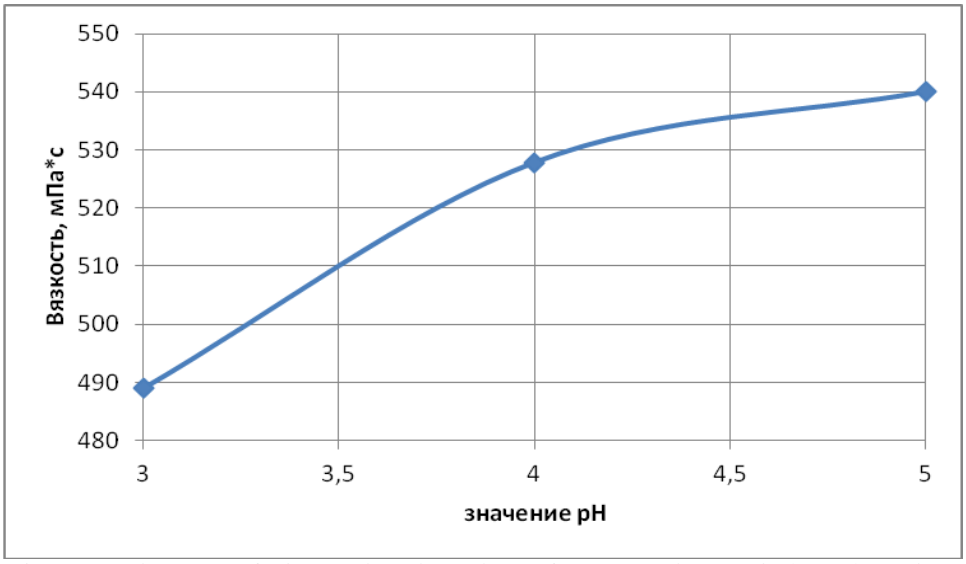


Fig. 5. Change of dynamic viscosity of suspension Pd (NO3)2-Al2O3-La2O3-HAc-H2O at a temperature of 298 To from value pH at frequency rate of its dilution by 1.10 water (1) and 1 % water solution Praestol 655 FC (2) surfactant

Dependencies in fig. 5 show a decrease in the viscosity of the suspension from 540.06 to 488.95 MPa c for an acidic working environment (pH = 3). Increasing in dynamic viscosity of suspension with pH increases is connected with the formation of particles, more resistant to destruction.

Conclusion

By calculation of ionic balances in the "nitrate of palladium (II)-oxide of aluminum (II)-oxide of lanthanum (II)" system boundary conditions and the concentration fields of education of hydroxides of metals are defined.

In the course of experimental studies foundthat suspension $Pd(NO_3)_2$ – Al_2O_3 – La_2O_3 – HAc – H_2O dilution of 1 % water solution cation-active Praestol 655 FC surfactant in the ratio 1:10 reduces its dynamic viscosity 1.74 times stronger in comparison with similar dilution by water.

It is shown that the most preferable range for receiving this suspension is the sour pH area.

By electronic and microscopic researches and measurements of the sizes of suspension particles it is revealed that dilution of its 1 % water solution Praestol 655 FC surfactant reduces the average size of particles and their dispersion by the sizes.

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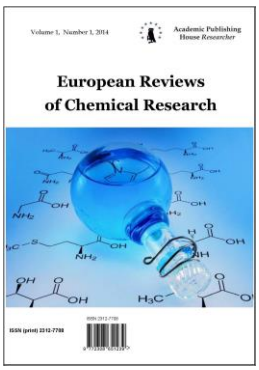

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Ligand Background of the Reaction Mixture as a Factor of the CdS – PbS thin Films Formation by Chemical Bath Deposition

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Abstract

The concentration planes of lead and cadmium sulphide formation in "Cd^{2+} – Pb^{2+} – L – OH^- – N_2H_4CS"systems (where L – $C_6H_5O_7^{3-}$, $H_2NCH_2CH_2NH_2$, $C_6H_5O_7^{3-}$ + $H_2NCH_2CH_2NH_2$) were calculated by analyzing of the ion equilibrium. Scaning electron microscopy and energy dispersive analysis results showed the effect of the nature and strength of the complexing agents on composition and morphology of synthesized nanocrystalline CdS – PbS films.

Keywords: ionic equilibrium, ligands, hydrochemical deposition, thin films, lead sulfide, cadmium sulfide, substitutional solid solutions.

Introduction

At present, more and more attention to the issues of detecting infrared radiation is given to heterostructures. The use of these materials allows for a more meaningful results compared with the photodetectors based on silicon and germanium. The use of functional-elements on the basis of substitutional solid solutions is also very attractive in this respect. Changing the content of the replacement component we can regulate their properties over a wide range and the range depends on differences of the basic compounds characteristics. In particular, change of cadmium content in composition of the $Cd_xPb_{1-x}S$ solid solution allows widely varying characteristics of the semiconductor material from the narrow-band galena PbS (ΔE_g = 0.41eV) to wide- band CdS (ΔEg = 2.4 eV). This ensures effective solution of various problems in optoelectronics, such as the manufacture of environmental monitoring instrumentation, optical sensors of temperature control, fast-acting photodetector e.t.c.

However, according to the equilibrium phase diagram [1, 2] sulphides of lead and cadmium don't form a continuous series of solid solutions and their mutual solubility is decreaseswith the temperature: solubility limit of cadmium sulfide into lead sulfide reaches 38 mol. % at 1325 K and it does not exceed $9 \cdot 10^{-3}$ mol. % at 523 K. Probably the prevalence of high temperature methods of

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preparing solid solutions in the system CdS – PbS [3, 4], requiring complex and expensive technological equipment due to this.

The use of chemical bath deposition method which is related to methods of "light chemistry" (at temperatures below 373 K) for preparing of solid solution allows to expand the range of mutual solubility of the sulfides to form a supersaturated metastable solid solutions and reduce the costs associated with the technical process equipment [5] by the features of colloid-chemical process step [6, 7]. Experimental confirmation of this can be found in Kitaev's and his disciples' works [8-12]. They obtained homogeneous thin films $Cd_xPb_{1-x}S$ with a maximum of replacementshare 16.1 mol. % by chemical bath deposition from the reaction mixture containing metal salts, thiourea as halkogeneizator and ligands complexing cadmium and lead ions (sodium citrate and ammonia) [10-12].

It was found [10] that the content of cadmium sulfide in $Cd_xPb_{1-x}S$ solid solution is actually a function of the ratio of lead and cadmium ions concentration in the reaction mixture, i.e. the ratio of rates of the CdS and PbS sulphides formation. Among factors that affect at the rate of synthesis process, a special role in the reaction bath is for ligand background: through the use of the ligands of different strength and nature it can regulate the amount of free metal ions in the solution.

This work is dedicated to the thermodynamic evaluation of the possibility of forming $Cd_xPb_{1-x}S$ films by chemical bath deposition using a same ligands for both metal (citrate ions $C_6H_5O_7^{3-}$, ethylenediamine$H_2NCH_2CH_2NH_2$) and different ligands, in particular, mixtures of ethylenediamine with citrate ions ($C_6H_5O_7^{3-}$ + $H_2NCH_2CH_2NH_2$) and moreover the study of the effect of the ligand background on the films morphology and composition.

Experimental

Deposition of films in a system CdS – PbS carried out at a temperature of 358 K for 120 minutes on a degreased sitall substrate ST-50. The reaction mixture contained metal salts $Pb(C_2H_3O_2)_2$ (0.04 – 0.068 M) and $CdCl_2$ (0.05M), thioureaCSN_2H_4 (0.6 M) as a source of S^{2-} ions, and various ligands for metal ions. As ligands depending on the system used: sodium citrate $Na_3C_6H_5O_7$, ethylenediamine$H_2NCH_2CH_2NH_2$and a mixture of ethylenediamine with citrate ion ($H_2NCH_2CH_2NH_2$ + $C_6H_5O_7^{3-}$).

The film thickness was determined by interference microscopy on the microinterferometer Linnik MII-4M.

Study of the surface morphology and elemental composition of the films was performed by scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (the EDX) using the Scanning Electron Mucroscope JEOL JSM-5900LV.

Results and discussions

Obtaining of metal sulfides thin films by chemical bath deposition is a complex multi-step process, which is based on the reaction of interaction of the metal ion complexed with sulfide ion, which is formed as a result of thiourea hydrolytic decay [5]. Since S^{2-} ion can potentially be distributed between the two metal ions at the co-precipitation CdS and PbSsulfeeds, the formation of substitutional solid solution phase in the reaction system takes place in two competing reactions deposition of individual CdS and PbS sulfides to forming a common crystal lattice:

$$(1-x)Pb^{2+} + xCd^{2+} + CSN_2H_4 + 2OH^- = Cd_xPb_{1-x}S + H_2CN_2 + 2H_2O \qquad (1)$$

The proportion of the active uncomplexed metal ions that can enter into a chemical reaction with sulfur ions, can be estimated using the expression:

$$\alpha_{Me^{2+}} = \frac{[Me^{2+}]}{C_{Me}} = \frac{1}{1 + \frac{[L]}{k_1} + \frac{[L]^2}{k_{1,2}} + \cdots + \frac{[L]^n}{k_{1,2\ldots n}}}, \qquad (2)$$

where $[Me^{2+}]$ – concentration of free metal ions; C_{Me}- analytical total concentration of metal ions in the solution; L – ligand concentration; k_1, $k_{1,2}$, $k_{1,2,..n}$ – instability constants of different metal complex forms.

To determine complex forms prevailing in the solution that exert a decisive influence on the process in each of the systems analysis of the ion equilibrium was held in Cd^{2+} –L – H_2O» and «Pb^{2+} – L – H_2O» systems was carried out. Contributions of each of the metal ions to the total concentration in the solution can be calculated similarly (2), by substituting in the numerator of

the expression the respective concentration of the complex instead of free cadmium ion concentration.

At choosing synthesis parameters an important factor is apriori estimation of the forming solid solution possibility under certain conditions that can help to reduce an amount of experimental research. That's why in this work thermodynamic calculation of the concentration areas and the pH range of the existence of metal sulfides and impurity phases – hydroxides and cyanamide that were considered due to most of them provide a high level of supersaturation on them in solution because of having a low solubility [5].

The minimum of necessary metal salts concentration was calculated using expression [5]:

$$pC_H = pSP_{MeS} - p\alpha_{Me^{2+}} - \left(pk_{H_2S} - 2pH + 0.5pK_c + p[N_2H_4CS]_H + +0.5p\frac{\beta_C}{\beta_S}\right) - \frac{0.86\cdot\sigma\cdot V_M}{R\cdot T\cdot r_{cr}}, \quad (3)$$

where $C_н$ – the minimum of required for the the solid phase formation concentration of metal salt; SP_{MeS} – product of metal sulfide solubility (pSP_{CdS} = 26.10; pSP_{PbS}= 27.8); k_{H_2S} – constant of hydrogen sulphide ionization, that is product of thiourea degradation pk_{H_2S}= 19.88; K_C – constant of hydrolytic thiourea degradation pK_c= 22.48; $[N_2H_4CS]_H$ – the initial concentration of thiourea; Δ_{cr} – the critical value of supersaturation; σ – specific surface energy of metal sulfide; V_M – molar volume of the synthesized phases; rкр – the radius of the critical size embryo; R – universal gas constant; T – temperature of the process. Values β_S and β_C are equal $\beta_S = [H_3O^+]^2 + k_{HS^-}[H_3O^+] + k_{H_2S}$ and $\beta_C = [H_3O^+]^2 + k_{HCN_2^-}[H_3O^+] + k_{H_2CN_2}$ [7], where k_{HS^-} (1.0·10–7) and $k_{HCN_2^-}$ (4.7·10–11) – constants of hydrogen sulfide and cyanamide ionization at the first stage; $k_{H_2CN_2}$ (3.0·10–22) - constant of cyanamide ionization.

The minimum initial metal salt concentration $pC_н$ that provide formation of phases – $Cd(OH)_2$ and $Pb(OH)_2$ was determined by equation [5]:

$$pC_H = pSP_{Me(OH)_2} - p\alpha_{Me^{2+}} - 2pK_W + 2pH_H, \quad (4)$$

where $pSP_{Cd(OH)_2}$ = 13.66 [13]; $pSP_{Pb(OH)_2}$ = 15.5 [13]; pK_W=14 [13].

For the calculation of conditions of metal cyanamide formation was used equation [7]:

$$pC_H = pSP_{MeCN_2} - p\alpha_{Me^{2+}} - \left(pk^{1,2}_{H_2CN_2} - 2pH_H + 0.5pK_C + 0.5p[N_2H_4CS]_H + +0.5p\frac{\beta_S}{\beta_Ц}\right), \quad (5)$$

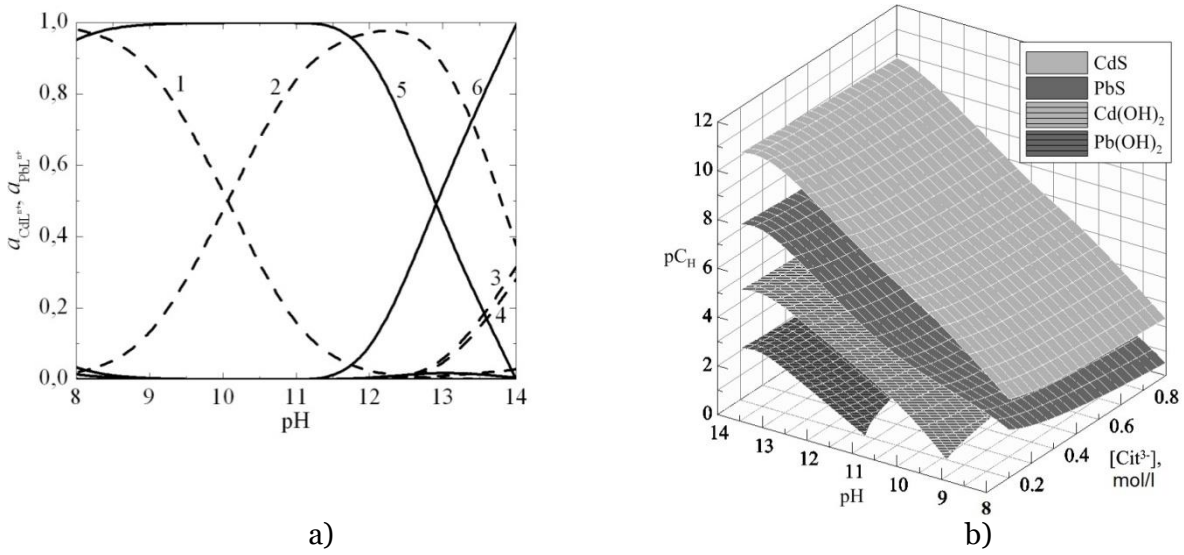
where pSP_{CdCN_2} =14.1 [14]; pSP_{PbCN_2} =15.8 [14]; $pk^{1,2}_{H_2CN_2}$ =21.52 [13].

Thermodynamic evaluation of the $Cd_xPb_{1-x}S$ solid solution formation conditions at co-precipitation of CdS and PbS sulfides was carried out by a joint solution of equations (3) for lead and cadmium.

In this paper discusses three reaction systems that contain in various set of ligands which are complexed cadmium and lead ions: sodium citrate $Na_3C_6H_5O_7$, ethylenediamine $H_2NCH_2CH_2NH_2$ and a mixture of ethylenediamine with citrate ion ($H_2NCH_2CH_2NH_2 + C_6H_5O_7^{3-}$).

According to the results of ionic equilibria analysis, the influence of hydroxide ions is relatively small until pH = 13 in all systems, which is difficult to achieve under the above conditions (Fig. 1-3). When we used citrate ions as a ligand, in almost entire range of pH as lead and cadmium are in solid bound complexes $Pb(OH)Cit^{2-}$ (pk = 13.7) and $Cd(OH)Cit^{2-}$ (pk = 9.3) (Figure 1a). Indicator of cadmium complex instability constant is significantly lower whereby primarily cadmium sulfide solid phase is formed in a solution (Figure 1b) that can prevent the formation of substitutional solid solution instead of the mixture of the CdS and PbS individual phases.

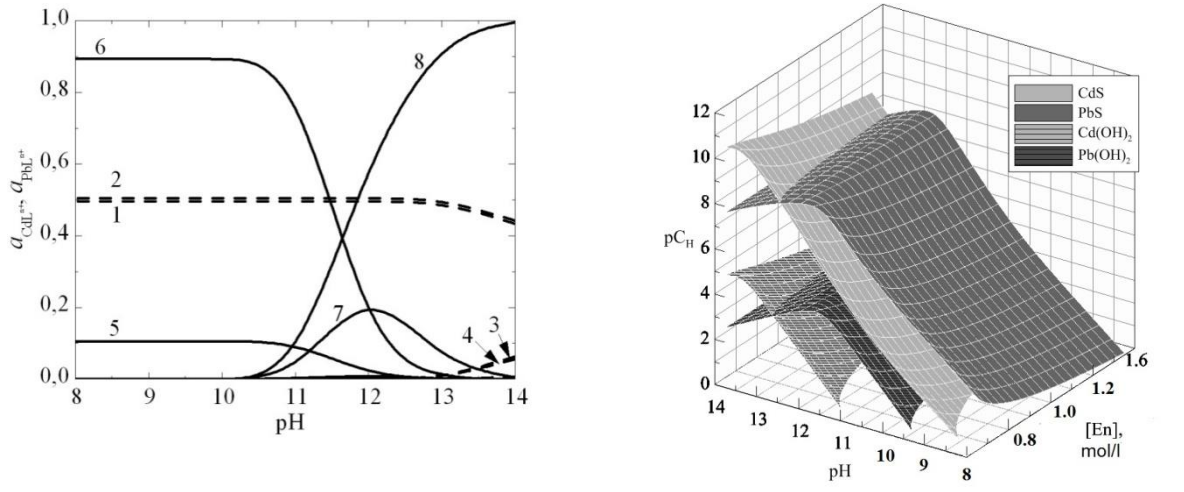
To solve the problem of solid solution forming it can be the use of an additional ligand for cadmium for which strength complexes with cadmium is better than for complexes with lead. It is known quite a number of works devoted to the preparation of a solid solution $Cd_xPb_{1-x}S$ by chemical bath deposition, where sodium citrate was used as ligands for lead, and ammonia was used as ligands for cadmium [8-10]. In [15] as an alternative to ammonia it is proposed to use ethylenediamine that is less volatile and has ionization constant close to that of ammonia.



a) b)

Figure 1. Ionic equilibria in system "Cd^{2+} – Pb^{2+} – Cit^{3-} – H_2O" (a): 1 – $CdCit^{3-}$, 2 – $Cd(OH)Cit^{2-}$, 3 – $Cd(OH)^{3-}$, 4 – $Cd(OH)_4^{2-}$, 5 – $Pb(OH)Cit^{2-}$, 6 – $Pb(OH)_4^{2-}$; the boundary conditions of CdS, PbS, $Cd(OH)_2$, $Pb(OH)_2$ formation in system "Cd^{2+} – Pb^{2+} – Cit^{3-} – N_2H_4CS" taking into account the factor of the crystallization (b). The calculation was performed with $[CS(NH_2)_2]$ = 0.6 mol/l.

According to the ionic equilibrium analysis in the system, where the complexing agent for metals is only ethylenediamine and major complex compounds that prevent rapid precipitation of metal sulfides in the work range of pH = 11-12 [7] for cadmium is $Cd(En)_2^{2+}$ (pk = 10.22) и $Cd(En)_3^{2+}$ (pk = 12.29); for lead $Pb(En)_2^{2+}$ (pk = 8.45) (Figure 2a). There is the opposite situation – the cadmium ions complexed stronger than Pb2+ and firstly solids PbS is formed at pH <12.5. At high pH (greater than 13) stable complex $Pb(OH)_4^{2-}$ becomes dominant for the lead. Thus there is the intersection zone of concentration planes of PbS and CdS formation, i.e. at this value of pH (~ 12.5) formation of solid individual sulphide phases occur simultaneously and hence likely formation of a substitution solid solution.

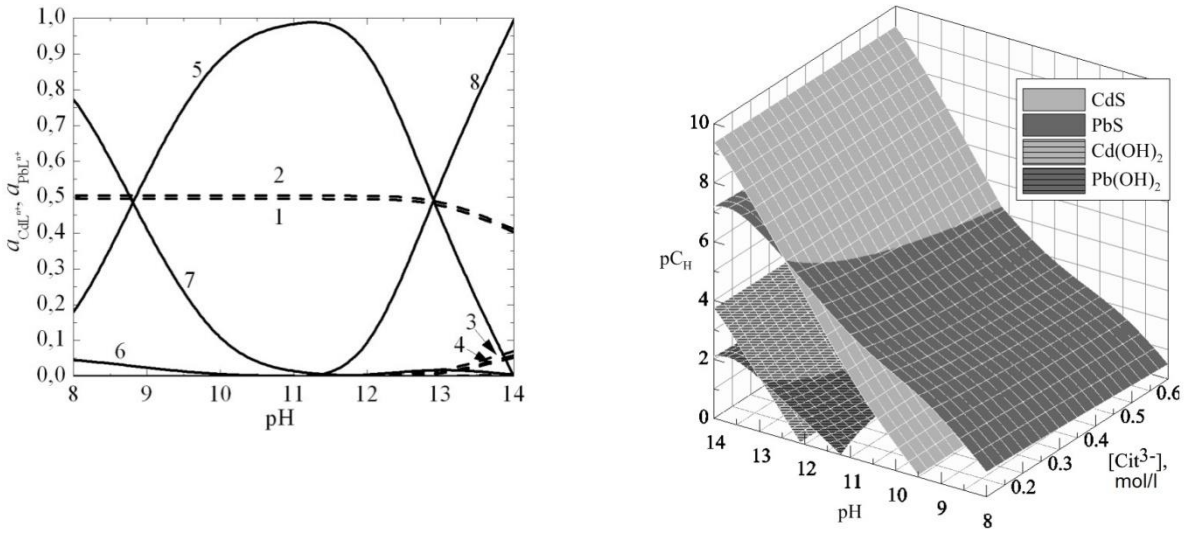


a) b)

Figure 2. Ionic equilibria in system "Cd^{2+} – Pb^{2+} – En – H_2O" (a): 1 – $CdEn_2^{2+}$, 2 – $CdEn_3^{2+}$, 3 – $Cd(OH)_3^-$, 4 – $Cd(OH)_4^{2-}$, 5 – $PbEn^{2+}$, 6 – $PbEn_2^{2+}$, 7 – $Pb(OH)_3^-$, 8 – $Pb(OH)_4^{2-}$; the boundary conditions of CdS, PbS, $Cd(OH)_2$, $Pb(OH)_2$ formation in system "Cd^{2+} – Pb^{2+} – En – N_2H_4CS" taking into account the factor of the crystallization (b). The calculation was performed with $[CS(NH_2)_2]$ = 0.6 mol/l.

Using specific ligands for each of the metals: citrate ions to lead and ethylenediamine to cadmium (Figure 3) allows to move the intersection of concentration planes in a pH range from 11.5 to 12.5 (Figure 3b). This is due to the fact that the ions Cd^{2+} are bound in ethylenediamine complexes $CdEn_2^{2+}$ (pk = 9.98) and $CdEn_3^{2+}$(pk = 10.21), which are similar in strength to connecting lead complex $Pb(OH)Cit^{2-}$ (pk = 13.7) (Figure 3a).

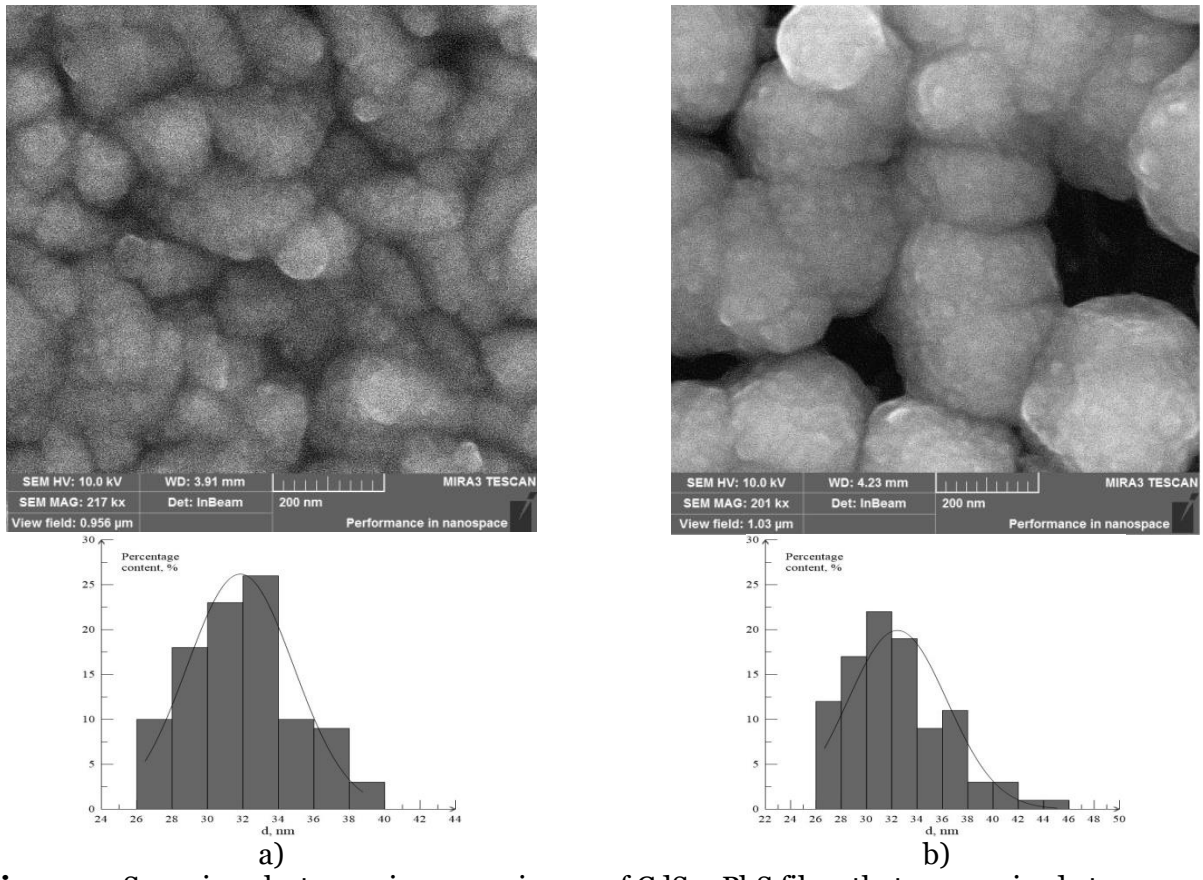
As a result, according to preliminary calculations, citrate – ethylenediamine system is the most promising for the production of solid solutions in the system CdS – PbS from a thermodynamic point of view.



a) b)

Figure 3. Ionic equilibria in system "Cd^{2+} – Pb^{2+} – Cit^{3-} – En – H_2O" (a): 1 – $CdEn_2^{2+}$, 2 – $CdEn_3^{2+}$, 3 – $Cd(OH)_3^-$, 4 – $Cd(OH)_4^{2-}$, 5 – $Pb(OH)Cit^{2-}$, 6 – $PbEn^{2+}$, 7 – $PbEn_2^{2+}$, 8 – $Pb(OH)_4^{2-}$; the boundary conditions of CdS, PbS, $Cd(OH)_2$, $Pb(OH)_2$ formation in system "Cd^{2+} – Pb^{2+} – Cit^{3-} – En – N_2H_2CS" taking into account the factor of the crystallization (b). The calculation was performed with $[CS(NH_2)_2]$ = 0.6 mol/l.

It is worth noting that the preliminary calculations of ionic equilibrium in the system "Cd^{2+} – Pb^{2+} – L – N_2H_4CS" (L – $C_6H_5O_7^{3-}$, $H_2NCH_2CH_2NH_2$, $C_6H_5O_7^{3-}$+$H_2NCH_2CH_2NH_2$) only indicate the principle possibility of the process chemical bath deposition of lead and cadmium sulfide solid phases, without considering the ways in which they flow. Therefore, in order to prove the correctness of the thermodynamic evaluation and to determine the actual effect of the ligands nature on the formation of a semiconductor CdS – PbS there was carried out the synthesis of CdS–PbS thin film sample from etilendiamine andethylenediamine–citrate. The temperature of synthesis of all systems was 353 K. As a result, the thin films with thickness of about 100 nm evenly covering the substrate were prepared, its surface microimage are shown in Figure 4.



a) b)

Figure 4. Scanning electron microscopy image of CdS – PbS films that are received at 353 K for 120 minutes by chemical bath deposition of ethylenediamine (a) and citrate – ethylenediamine (b) system at increase of × 200 000 and its particle size distribution diagrams

Studies of the films microstructure by scanning electron microscopy and the elemental analysis results indicate about the formation of compounds that contains Cd, Pb, S as major components. Relative sulfur content in all samples was 50 ± 5 at. %. The determination of oxide phases in samples by the elemental analysis was not accurately because of the fact that the total amount of oxygen is submitted by the substrate material due to the small thickness of the films. In this regard, the presence of oxygen in the films are not taken into account.

Samples obtained from the reaction systems containing a different set of ligands are differ from each other both in the composition (Table 1) and layer morphology (Figure 4). The films of ethylenediamine system are characterized by the most uniform surface, that consist of spherical particles of about 25–35 nm united in globules of 180-200 nm densely covering the surface of the substrate. This indicates that in this system both metals are bound in complexes stronger and influence of ligand on the proportion of free ions Cd^{2+} and Pb^{2+} is approximately the same. This is confirmed by the composition film samples: ratio of this metals is close to one (28.8 at. % lead and 20.7 at.% of cadmium).

The cadmium content in the films made from the citrate-ethylenediamine system greatly exceeds the lead content (see Table 1), based on what it can be assume that $Pb(OH)Cit^{2-}$ complexes that are characterized by high constant of ionization ($pk(Pb(OH)Cit^{2-})$ = 13.7), reduce the proportion of free ions of lead, cadmium in turn is connected to ethylenediamine complexes. The particles that form the surface of CdS film in citrate – ethylenediamine system which have the same size are combined into larger agglomerate of ~ 350 nm compared with the previous system and its amount is significantly lower, whereby they are less tightly adjacent to each other (Figure 5b.)

Table 1. The elemental composition of the CdS - PbS films, obtained by Chemical bath deposition in systems with different ligand background

	Contentofelementsat. %		
Ligands	Pb	Cd	S
$H_2NCH_2CH_2NH_2$	28.8	20.7	50.5
$C_6H_5O_7^{3-}$+ $H_2NCH_2CH_2NH_2$	5.8	39.5	44.65

The reasons of differences in the morphology of films in systems with different ligand background are ambiguous because of chemical bath deposition is a complex process and the ligand molecules may influence on the formation of films, both at the stage of nucleation due to the strength of the resulting metal complex forms, and at the stage of film growth due to different spatial structures ligand molecules [19].

Conclusions

In this work the analysis of ionic equilibrium in reaction systems «Cd^{2+} – L – $CS(NH_2)_2$» and «Pb^{2+} – L – $CS(NH_2)_2$», where L – $C_6H_5O_7^{3-}$, $H_2NCH_2CH_2NH_2$, ($C_6H_5O_7^{3-}$+$H_2NCH_2CH_2NH_2$)) was carried out. The ranges of pH and minimum concentrations of metal salts that are necessary for the formation of solid phases of lead and cadmium sulfide, as well as impurity related compounds – metals hydroxides and cyanamides were identified. The thermodynamic probability of solid solutions CdS – PbS formation in these systems were shown.

Thin film samples with good adhesion to the substrate from ethylenediamine, ethylenediamine, ethylenediamine-citrate and triethanolamine systems were prepared by chemical bath deposition, its thickness was about 100 nm.

The studies of scanning electron microscopy of the films CdS – PbS shows nanocrystal character of their surface.

The results of EDX-analysis of the film showed that the composition of the samples depends essentially on the ligand background that is produced in the reaction mixture. Thus, the ratio of metals in the ethylenediamine system is close to one, whereas in the films of the citrate-ethylenediamine systems cadmium content is much more as compared with lead.

Acknowledgements

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