SÍNTESE, ESTRUTURA E PROPRIEDADES TÉRMICAS DE CARBONILA DE RÊNIO CONTENDO DERIVADOS HETEROBIMETÁLICOS DE VANÁDIO (III)

SYNTHESIS, STRUCTURE AND THERMAL PROPERTIES OF RHENIUM CARBONYL CONTAINING HETEROBIMETALLIC DERIVATIVES OF VANADIUM (III)

СИНТЕЗ, СТРОЕНИЕ И ТЕРМИЧЕСКИЕ СВОЙСТВА РЕНИЙКАРБОНИЛСОДЕРЖАЩИХ ГЕТЕРОБИМЕТАЛЛИЧЕСКИХ ПРОИЗВОДНЫХ ВАНАДИЯ(III)

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RESUMO

Este artigo descreve os dados sobre a síntese de bisciclopentadienilvanádio (III) do complexo de bistetrahidrofuranato de pentacarbonil-rênio com a reação entre cloreto de dicitlopentadienilvanádio (III) e sódio-hipocloridrato de rênio em tetrahidrofurano (THF). Formada neste caso, o produto alvo foi separado da mistura reacional por extração com hexano quente. Sua capacidade reacionária em relação aos ácidos protônico e aprônico Lewis foi inversa. É revelado que, na interação dos complexos acima mencionados com HCl, existe uma ligação Re-V dividida com formação $(C_5H_5)_2VCl$ e $HRe(CO)_5$; $(C_5H_5)_2VCl$ e $HRe(CO)_4PPh_3$ respectivamente. Na integração com $HgCl_2$ também ocorre uma ligação de V-Re de ruptura e ele se mostra $(C_5H_5)_2VCl$ e $(OC)_5ReHgCl$; $(C_5H_5)_2VCl$ e $PPh_3(OC)_4ReHgCl$. É investigada a interação destes complexos com vários ligantes dentados. Um ligante monodentado trifenilfosfina (PPh_3) substitui um dos grupos carbonila no fragmento $Re(CO)_5$. O ligante bidentado acetilacetona (acac) facilmente expulsa da esfera de coordenação o vanádio mais doente ligante - ciclopentadienil. A composição e estrutura dos complexos foram caracterizados pelos dados de RMN, IR, espectroscopia RPE e análise térmica.

Palavras-chave: Síntese, complexos heterobinucleares, ligação metal-metal de vanádio (III), fragmentos de tetracarbonil rênio.

ABSTRACT

This paper describes the data on synthesis of bis(cyclopentadienyl)vanadium(III) of pentacarbonyl rhenium bistetrahydrofuranate complex with the reaction between dicyclopentadienylvanadium (III) chloride and rhenium sodiumpentacarbonyl in tetrahydrofurane (THF). Formed in this case the target product was separated from reaction mixture by extracting with hot hexane. Their reactionary ability in relation to protonic and aprotic acids Lewis had been investigated. It is revealed, that at interaction of the above mentioned complexes with HCl there is a splitting Re-V bond with formation $(C_5H_5)_2VCl$ and $HRe(CO)_5$; $(C_5H_5)_2VCl$ and $HRe(CO)_4PPh_3$ respectively. At interaction with $HgCl_2$ also occurs having break V-Re bond and it turns out $(C_5H_5)_2VCl$ and $(OC)_5ReHgCl$; $(C_5H_5)_2VCl$ and $PPh_3(OC)_4ReHgCl$. The interaction of these complexes with ligands of various dentate is investigated. A monodentate ligand-triphenyl phosphine (PPh_3) substitutes one of carbonyl-groups in $Re(CO)_5$ – fragment. Bidentate ligand- acetylacetone (acac) easily push out from coordination sphere vanadium more donor ligand – cyclopentadienyl. The composition and structure of the complexes were

characterized by the data of NMR, IR, EPR-spectroscopy and thermal analysis.

Keywords: *Synthesis, heterobinuclear complexes, metal-metal bond of vanadium (III), tetracarbonyl rhenium fragments.*

АННОТАЦИЯ

В статье приводятся данные по синтезу бисциклопентадиенилванадий(III)пентакарбонильного ренийбистетрагидрофуранатного комплекса реакцией между дициклопентадиенилванадий(III) хлоридом и натрийпентакарбонилем рения в тетрагидрофуране(THF). Образующиеся при этом целевые продукты были выделены из реакционной смеси путем экстрагирования горячим гексаном. Изучены их реакции с протонными, апротонными кислотами Льюиса. Обнаружено, что при взаимодействии вышеуказанных комплексов с HCl происходит расщепление V-Re связи с образованием $(C_5H_5)_2VCl$ и $HRe(CO)_5, (C_5H_5)_2VCl$ и $HRe(CO)_4PPh_3$ соответственно. При взаимодействии с $HgCl_2$ также происходит разрыв связи V-Re и получаются $(C_5H_5)_2VCl$ и $(OC)_5ReHgCl$; $(C_5H_5)_2VCl$ и $PPh_3(OC)_4ReHgCl$. Исследовано также взаимодействие этих комплексов с лигандами различной дентатности. Монодентатный лиганд-трифенилфосфин(PPh_3) вытесняет одну из CO-групп в $Re(CO)_5$ -фрагменте. Бидентатный лиганд-ацетилацетон(асас) легко вытесняет из координационной сферы ванадия более донорный лиганд – циклопентадиенил. Состав и строение полученных комплексов охарактеризованы данными ЯМР, ИК, ЭПР-спектроскопией и термическим анализом.

Ключевые слова: *синтез гетеробиядерных с металл-металл связью комплексов ванадия (III)содержащие пентакарбонильные и трифенилфосфинзамещенные тетракарбонилренийевые.*

INTRODUCTION

Recently metal-metal bond heterobimetal derivatives with metal carbonyl fragments of most of transition and rare earth elements have been intensively studied (Trifonov, 2010). It was found out that first, such complexes can be used as catalysts of homogeneous catalysis, secondly, they are primary compounds for creation of new more effective catalytic systems for important industrial chemical processes (Liu *et al.* 2004; Gambarotta, 2003).

Nevertheless, interest in metallocene catalyst systems from the government side still remains low.

In the overwhelming number of publications, dedicated to organo metallocene catalysis of the polymerization of ethylene and higher olefins, systems based on metals of 4,8,9 and 10 groups (Janas, 2010; Gupta *et al.* 2008; Li *et al.* 2008; Agapie, 2011; Collins, 2011; Poddel'sky *et al.* 2009; Lamberti *et al.* 2009; Makio & Fujita, 2005; Park *et al.* 2004; Fujisawa & Nabika, 2013) are considered. Despite the fact that effectiveness of complex compounds of vanadium practically an order of magnitude lower than compounds based on metals of the 4th group uniqueness of polymers gained at such systems makes them indispensable in the production of synthetic rubbers and elastomers. Besides, huge scientific and practical interest

represents the possibility of usage of vanadium compounds in the ultra-high molecular weight polyethylene with a narrow molecular weight distribution synthesis, as well as copolymers of ethylene with higher, cyclic and in some cases also with polar olefins.

Main problem related to usage of catalysts based on vanadium, is that metal in the active center of the catalytic system can change its degree of oxidation in the range from +5 to +2 during polymerization, as a result of which an inevitable change in the composition and structure of the active sites occurs and, as a consequence, the activity of the system decreases sharply, until the polymer formation process is completely terminated. One of the possible ways of solving of this problem – oxidation of the central atom, "resuscitating" active centers by adding the reactivators (promoters). As example, addition of hexachlorocyclopentadiene (Lorber *et al.* 2002) or trichloroacetic acid ethyl ester (Clowes *et al.* 2013) during the formation of inactive catalytic centers of vanadium (+2) allows to achieve increased system activity and stable kinetics of absorption and polymerization of ethylene. This fact indicates the oxidation of vanadium atoms (2+) to higher degrees, the values of which in the active center have hitherto been the subject of discussion.

Big set of experimental data in the field of

metallocene catalytic systems with the participation of various transition metals allows us to assert that in addition to the nature of the metal atom, the nature and geometry of the ligand and the composition of the activator (co-catalyst) play no less a role in the efficiency of the catalytic system.

The target of the present work is the synthesis of new heteronuclear compounds, revealing their structural and catalytic features.

MATERIALS AND METHODS

2.1. Production of biscyclopentadienylvanadium penta carbonyl rhenium complex $(C_5H_5)_2V-Re(CO)_5 \cdot (THF)_2$ vanadium(III) with reaction between bis cyclopentadienylvanadiumhydride tetrahydrofuranate complex $(C_5H_5)_2VH$, rhenium bromium penta carbonyl $(BrRe(CO)_5)$.

Under a helium atmosphere 0, 5 g of $BrRe(CO)_5$ was added into 0.2 g of $(C_5H_5)_2VH$ which was dissolved in 15 ml of chloroform. Reaction mixture was boiled for an hour. The solvent was evaporated from deep red solution. Deep red crystalline residue was washed off with hot hexane and then dried in vacuum. Yield is 0, 44 g (72 %). The substance decomposes at the temperature above $120^\circ C$. Found, %: C 35.20 H 1.85 Re 36, 80. $C_{15}H_{10}VReO_5$. Calculated, %: C 35.49 H 1.90 Re 36,71. IR-spectrum, ν_{CO}, cm^{-1} : in $CHCl_3$ 2065, 2015, 1950, in liquid petrolatum 2058, 2020, 1955.

2.2. Production of bis(cyclopentadienyl) vanadium (III) chloride, $(C_5H_5)_2VCl$

5, 4 g (0.282 mol) of vanadium tetrachloride in 200ml of toluene was placed at $-80^\circ C$ into 2 liter three necked flask provided with mixer, reflux condenser, dropping funnel with discharge for pressure balancing and nitrogen feed pipe. At $-80^\circ C$ the solution obtained by the interaction of 1, 95 g (0,085 mol) of sodium and 8, 5 g (10, 5 ml, 0,13mol) of cyclopentadiene in 100ml of THF was placed into dropping funnel and it was gradually added into mixing solution of VCl_4 . After completing the addition of reagents dark-blue solution was stirred for another 1 hour at room temperature, the solution was removed in vacuum at temperature not more than $60^\circ C$, and dark residue was sublimated in high vacuum. At $100^\circ C$ a small amount of vanadocen was sublimated, then the temperature was increased up to $140-160^\circ C$ and dark-blue needles of

vanadocen chloride are sublimated. Yield is 1,43 g (23, 4%). The complex decomposes, does not melt at temperature higher than $206-207^\circ C$, it is stable in acidic medium, but decomposes under the impact of bases, it is stable in air, easily soluble in water, chloroform and alcohol, ether, benzene, tetrachloride carbon.

By abovementioned method 0.61g of vanadocen chloride (22% output), $(C_5H_5)_2VCl$ with T_{melt} . $203-204^\circ C$ in the form of dark-blue powdery monocrystals were produced from 2, 5 g of vanadium tetrachloride VCl_4 and 0, 86 g/atom sodium and 4, 1g of cyclopentadiene.

2.3. Production of bis cyclopentadienyl vanadium pentacarbonylrhenium complex $(C_5H_5)_2V-Re(CO)_5$ with reaction between biscyclopentadienyl vanadiumchloride complex and rhenium sodium pentacarbonyl

0.22 g of primary biscyclopentadienyl-vanadiumchloride $(C_5H_5)_2VCl$, which was synthesized in accordance with , was dissolved in 15 ml of THF and while mixing 5 g of $NaRe(CO)_5$ was added into 15 ml of solution. Reaction mixture was boiled for 40 min. The solvent was evaporated from pale-yellow solution, yellow crystalline residue was washed off with cold hexane and then dried in vacuum. Yield is 0,48 g (75%). The substance decomposes at the temperature above $50^\circ C$ with isolation of CO. Found, %: C 35.37 H 1.82 V 10, 60. $C_{15}H_{10}VReO_5$. Calculated, %: C 35.49, H 1.90, V 10, 05. IR-spectrum, ν_{CO}, cm^{-1} : in THF 2065, 2015, 1950, in liquid petrolatum 2053, 2020, 1995.

2.4. Production of bis(cyclopentadienyl)vanadium triphenylphosphinetetra carbonyl rhenium complex $(C_5H_5)_2V-Re(CO)_4PPh_3$

0.22 g of $(C_5H_5)_2VCl$ and 0,5 g of $NaRe(CO)_5$ were mixed in 10 ml of THF and then two equivalents of PPh_3 were added into the reaction mixture. The mixture was boiled for an hour till full exchange of Co to PPh_3 (control – IR-spectrum). The solvent was evaporated on rotary evaporator, dark-yellow residue was washed off with mixture of benzene:hexane 1:1(3x10 ml) to remove excess PPh_3 and dried under vacuum. Yield is 0.71 g (65%). The substance decomposes at temperature higher than $190^\circ C$. Found, %: C 51, 70, H 3, 45, P 4, 11. $C_{32}H_{25}VRePO_4$. Calculated, %: C 51, 81, H 3, 37, P 4, 18. IR-spectrum, ν_{CO}, cm^{-1} : in THF 1972, 1925, 1710, in liquid petrolatum 1980, 1935, 1860, 1715, 1735

2.5. Production of bisacetylacetonatevanadium pentacarbonyl rhenium complex (acac)₂V-Re(CO)₅

Initial biscyclopentadienylvanadiumpentacarbonyl rhenium complex was obtained in compliance with 1. 0.2 g of acetylacetone (acac) CH₃COCH₂COCH₃ was added into 1 mol of (C₅H₅)₂V-Re(CO)₅ in 15 ml of THF. Reaction mixture was boiled for 5 hours. During this time solution dyes dark-yellow with blue shade. Solvent was evaporated, but dark-crystalline residue was washed off with hexane and dried in vacuum. Yield of (CH₃COCHCOCH₃)₂ V-Re(CO)₅ is 0, 38 9 (81%), it decomposes at temperature above 128 °C. Found, %: C 31, 31, H 2, 72, V 8, 90. C₃₂H₃₁VRePO₈. Calculated, %: C 31, 20, H 2, 80, V 8, 83. IR-spectrum, ν_{CO}, cm⁻¹: in THF 2100, 1955, 1880, 1775, in liquid petrolatum 2068, 2060, 2020, 1958. IR-spectrum, ν_{acac}, cm⁻¹ 1618, 1545, 1415, 1455, 1345, 1220.

2.6. Interaction of (C₅H₅)₂V-Re(CO)₅ with protonic (HCl) and a protonic (HgCl₂) acids Lewis.

Reaction with HCl. Initial (C₅H₅)₂V-Re(CO)₅ rhenium complex was obtained in compliance with 1. 1 ml HCl was added into 1 mol of (C₅H₅)₂V-Re(CO)₅ in 15 ml of THF. After mixing, the color of the solution varied from yellow to pale yellow. Several ml H₂O were added to it and extracted 10 ml three times with benzene. The extracts were combined, washed three times with water and dried over MgSO₄. After the removal of benzene, the residue contained Re(CO)₁₀ (T_{melt.} 185-186 °C) and (C₅H₅)₂VCl. (T_{melt.} 203-204 °C).

The reaction with HgCl₂ was obtained by abovementioned method. To 1 mmol of (C₅H₅)₂V-Re(CO)₅ was added 1 mmol of HgCl₂. As a result, (C₅H₅)₂VCl and (OC)₅ReHgCl (T_{melt.} 168-169 °C) were obtained in quantitative yield.

RESULTS AND DISCUSSION:

First attempts of producing heterobinuclear vanadium carbonyl complexes with bond of V-M were made in the work (Nesmeyanova & Kocheshkova, 1974) for carbonyls of cobalt, manganese and rhenium. As authors of this work emphasize due to thermal instability of a bond V-M(CO)_mL, separation of the complexes from reaction medium and characterization of them failed. IR-spectra of tetrahydrofurane solutions of these complexes pointed to the direct interaction of fragments

M(CO)_mL with vanadium atom.

Bis(cyclopentadienyl)vanadium chloride (C₅H₅)₂VCl was obtained using the method (2) with the reaction between vanadium chloride, VCl₃ with sodium cyclopentadiene C₅H₅Na in compliance with ratio of reagents 1:2.

Specific characteristics of (C₅H₅)₂VCl is that it can connect halogenides, alkoxyhalogenides and monoalkylhalogenides and form donor-acceptor complexes which decompose under the impact of strongly solvate solvent THF.

From the other side, vanadocenchloride is easily reduced till compounds of tri- and divalent vanadium, however the bond between vanadium and both cyclopentadienyl ligands is preserved. In literature only some reactions are known where chlorine atoms in (C₅H₅)₂VCl may be replaced to other organic ligands (Redshaw, 2011). On a sample of bimetallic derivative of rhenium carbonyl we observed that introduction of V and Re atoms into coordination medium as both mono- and multi-site organic ligands stabilizes not only metal-metal (V-Re) bond, but also metal-ligand bonds (V-L and Re-L).

It was established that during exchange reaction of VCl₃ with NaRe(CO)₅ the mixture of mono- Cl₂VRe(CO)₅, di- ClV[Re(CO)₅]₂ and tri- V[Re(CO)₅]₃ substituted thermally instable di-, tri- and tri-nuclear rhenium carbonyl complexes of vanadium is formed. In VCl₃ replacement of two chlorine ions to cyclopentadienyl anions and further reaction of (C₅H₅)₂VCl (I) with Na+Re(CO)₅, allowed producing a thermally stable binuclear complex (C₅H₅)₂V-Re(CO)₅ II, which contains metal-metal bond (V-Re). From the other side bis(cyclopentadienyl)vanadium chloride is easily reduced till the compound of tri- and divalent vanadium, however the bond of vanadium with both – cyclopentadienyl rings is preserved (Eq.1).

Some thermal and structural features of complex II were studied. It was also found that break of σ-bond V-Re goes under the impact of chlorine hydride with formation of relevant hydrocarbons which are used to identify radicals related with vanadium.

The ability of complex I to hydrolyze under the action of various proton (HCl) and aprotic (HgCl₂) Lewis acids, as well as to the exchange of ligands in the coordination sphere of V and Re atoms with the V-Re bond.

It was found that, when HCl was passed through a tetrahydrofuran solution of complex I, V-Re bond was cleaved for several minutes, which resulted in the formation of $(C_5H_5)_2VCl$ and $HRe(CO)_5$. The presence of the latter in the reaction solution is confirmed by IR spectroscopy data (band at 1250 cm^{-1} , referring to Re-H oscillations).

The interaction of I with $HgCl_2$ leads to the breakdown of the V-Re bond with the formation of $(C_5H_5)_2VCl$ and $(OC)_5ReHgCl$, which were isolated and identified using IR and NMR spectroscopy methods and comparing the obtained data with the literature data (Magomedov *et al.* 1988).

When a monodentate ligand-triphenylphosphine (PPh_3) interacts with I, one of the CO groups in the $Re(CO)_5$ fragment is exchanged and a compound of the formula $(C_5H_5)_2V-Re(CO)_4PPh_3$ is obtained. The bidentate ligand-acetylaceto (acac) readily displaces the more donor ligand-cyclopentadienyl from the coordination sphere of vanadium. This can be explained by the influence of the V-Re bond on the lability of the V- C_5H_5 bond, and also by the oxophilicity of the vanadium atom.

Absorption bands in the range of ν_{CO} $2000-2100\text{ cm}^{-1}$ in IR-spectra which is typical for analogous binuclear compounds and absence of bands in the region below $\nu_{CO} 1850\text{ cm}^{-1}$ which is usually observed in bridged carbonylate complexes, serves as a confirmation of metal-metal bond. Metal-metal bond in complex II is solid enough which allows isolating it from reaction mixture. It should be noted that absorption bands of carbonyl groups ν_{CO} in $Na+Re(CO)_5$ are observed in the range of 1860 and 1908 cm^{-1} , but in $(C_5H_5)_2V-Re(CO)_5$ analogous bands are in ν_{CO} 2065 , 2015 , 1960 cm^{-1} .

Next results were received while heat treatment of complex II in the open air.

It was found out that at a low operating temperature of the investigated complex at first by the results of spectral method of IR, one of the terminal CO groups by easily emigrating to Re-V metal bonding forms CO mucus with the ν_{CO} 1760 cm^{-1} bridge (Eq.2).

Which is during subsequent heat treatment easily leans towards decarbonization turns into double bounded $(C_5H_5)_2V=Re(CO)_4$ metal carbonyl complex with new assembly.

This expected experimental result can be confirmed by an absorption band located in the KP spectrum.

As a result of subsequent long-term heating of $(C_5H_5)_2V=Re(CO)_4$ complex in DMSO, a transformation into a new 7-coordinated thermally stable complex consisting vanadium is observed.

The result of this combination is that it has a structure with (Eq. 3).

Differences in chemical shifts are observed in NMR¹N spectra of rhenium carbonyl complexes of vanadium. In primary $(C_5H_5)_2VCl$ protons of both cyclopentadienyl rings are equivalent and observed in $\delta_{C_5H_5}=5.5\text{ ppm}$, but in $(C_5H_5)_2V-Re(CO)_5$ this signal splits into two $\delta_{C_5H_5}=5.17$; 5.35 ppm , which points to symmetric position of C_5H_5 ligands in vanadium atom.

The same location of C_5H_5 -ligands in vanadium atoms is observed even in phosphine substituted rhenium carbonyl complexes of vanadium $(C_5H_5)_2V-Re(CO)_4PPh_3$; $\delta_{C_5H_5}=5.06$; 5.22 ppm , where up field shift of protons from C_5H_5 ligand is related to weakening of acceptor capacity of $Re(CO)_4PPh_3$ fragment (Fig.1).

From the other hand according to NMR¹N-spectra atom using the reaction (3) during the exchange of C_5H_5 ligand to acac in coordination medium of vanadium we observed cleavage of both CH_3 ($\delta_{CH_3}=1.96\text{ ppm}$), and CH -groups ($\delta_{CH_3}=0.96\text{ ppm}$) in acac in trans-location of these ligands.

Fig.2 shows ESP spectrum of the complex $(C_5H_5)_2V-Re(CO)_4PPh_3$. Unlike the complex $(C_5H_5)_2V-Re(CO)_5$ in $(C_5H_5)_2V-Re(CO)_4PPh_3$ we observed anisotropic signal at $g=1$, 978 with width of value of an effective magnetic moment $\mu_{eff}=1.89\text{ M.B.}$, which confirms paramagnetic properties of the complex (Rakitin, 1993). IR-spectra of vanadium acetylacetonate complexes of rhenium carbonyl $(C_5H_5)_2V-Re(CO)_4PPh_3$, show the shift of absorption bands ν_{CO} to higher frequency region of $1950-2100\text{ cm}^{-1}$.

However, thermally more stable binuclear complex (III) where decomposition temperature of this complex varies in the range of $180-200^\circ\text{C}$, is formed using the reaction (2) between $(C_5H_5)_2VCl$ and triphenylphosphine substituted derivative of rhenium carbonyl.

It was found that the change of one of the carbonyl groups to more donor

triphenylphosphine group in rhenium carbonyl complexes of vanadium has a stabilizing effect on V-Re bond (Eq. 4) of vanadium $\text{Re}(\text{CO})_5$ fragments of heterobinuclear metal complex.

By the reaction (Eq. 5, Eq. 6) bidentate ligand – acetylacetone (acac) easily displaces more donor ligand-cyclopentadiene from coordination medium of vanadium (IV).

This can be explained by the impact of V-Re bond on instability of V-C₅H₅ bond, as well as oxophilicity of vanadium atom.

CONCLUSIONS:

Synthesis of previously unknown vanadium (III) contained heteronuclear rhenium carbonyl tetrahydrofuranate complexes first implemented. Factors, affecting on the character of interaction of the rhenium carbonyl fragment with vanadium (III) atoms were established. It was found that the rhenium carbonyl fragment $\text{Re}(\text{CO})_m\text{L}$, with these metals forms or complexes with metal-metal connection, or complexes where their interactions are implemented through oxygen of carbonyl group. Based on ESP and EPR data it was found that during interaction of rhenium carbonyl complexes of vanadium with bidentate ligand-acetylacetone, complexation with charge transfer happens, decomposition of which in the presence of oxygen leads to oxidation of ligand and recovery of vanadium. It was established that tetrahydrofuranate complexes of vanadium react with the L-H acids of Luisin the same manner, leading to the corresponding mononuclear L_mM complexes.

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Figure 1. NMR¹ spectra of $(C_5H_5)_2V-Re(CO)_4PPh_3$, $(C_5H_5)_2V-Re(CO)_5$ in $CDCl_3$ without internal standard. Chemical shift was measured from up field shift of protons C_4H_8O (1.752 ppm)

Figure 2. ESR spectra of radicals in $(C_5H_5)_2V-Re(CO)_4PPh_3$

(Eq. 1)

(Eq. 2)

(Eq.3)

(Eq. 4)

(Eq. 5)

(Eq. 6)