O‘ZBEKISTON MILLIY UNIVERSITETI HUZURIDAGI ILMIY DARAJALAR BERUVCHI DSc.03/30.12.2019.K.01.03 RAQAMLI ILMIY KENGASH ASOSIDAGI BIR MARTALIK ILMIY KENGASH

O‘ZBEKISTON MILLIY UNIVERSITETI

ELIBOYEV ILYOS ASKAROVICH

SIKLODEKSTRIN ASOSIDAGI SUPRAMOLEKULYAR KOMPLEKSLARNING ELEKTROKIMYOVIY VA ADSORBSION XOSSALARI

02.00.04 – Fizik kimyo (kimyo fanlari)
02.00.11 – Kolloid va membrana kimyosi (kimyo fanlari)

KIMYO FANLARI BO‘YICHA FALSAFA DOKTORI (PhD) DISSERTATSIYASI AVTOREFERATI

Toshkent – 2024

UO‘T 541.138.2; 546.185.4; 661.635.68.

Kimyo fanlari bo‘yicha falsafa doktori (PhD) dissertatsiyasi avtoreferati mundarijasi

Оглавление автореферата диссертации доктора философии (PhD) по химическим наукам

Contents of dissertation abstract of doctor of philosophy (PhD) on chemical sciences

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Kimyo fanlari bo‘yicha falsafa doktori (PhD) dissertatsiyasi mavzusi O‘zbekiston Respublikasi Oliy ta’lim, fan va innovatsiyalar vazirligi huzuridagi Oliy attestatsiya komissiyasida B2022.4.PhD/K560 raqam bilan ro‘yxatga olingan.

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KIRISH (falsafa doktori (PhD) dissertatsiyasi annotatsiyasi)

Dissertatsiya mavzusining dolzarbligi va zarurati. Bugungi kunda dunyoda metallarni korroziyadan himoya qiluvchi turli kislotali muhitlarda yuqori samaradorlikka ega hamda import o‘rnini bosuvchi ingibitorlar yaratish muhim ahamiyatga ega. Texnika va sanoat ishlab chiqarish jarayonlarining rivojlanishi natijasida metallarga bo‘lgan talab yildan yilga ortib bormoqda, bu esa, o‘z navbatida, samarali ingibitorlarga bo‘lgan talabning ortishiga olib kelmoqda. Bundan tashqari zaharli va yuqori konsentratsiyalarda qo‘llaniluvchi birikmalardan voz kechgan holda iqtisodiy tomondan qulay bo‘lgan ekologik xavfsiz supramolekulyar kompleks tipidagi ingibitorlar yaratishga alohida e’tibor berilmoqda. Jumladan, metall sirtida mustahkam himoya qavati hosil qiluvchi hamda past konsentratsiyalarda va turli harorat intervalida samaradorlikka ega ingibitorlar yaratish muhim ahamiyat kasb etadi.

Jahonda metallar korroziyasiga qarshi qo‘llaniladigan ingibitorlarga bo‘lgan talabning o‘sib borishi, organik va supramolekulyar birikmalar asosida yangi, universal ingibitorlarni yaratish maqsadga muvofiqligini ko‘rsatadi. Yuqoridagi muammolarni hal qilishda mahalliy xomashyolardan talab etilgan xususiyatlarga ega bo‘lgan ingibitorlarni olish muhim ilmiy ahamiyat kasb etadi. O‘simliklardan ajratib olinadigan organik moddalarni qo‘llagan holda yashil ingibitorlar orqali metallar korroziyasini kamaytirishga alohida e’tibor berilmoqda.

Respublikamizda ilg‘or innovatsion texnologiyalarni ishlab chiqish, shuningdek, sanoatni barqarorlashtirish, jadal rivojlantirishga alohida e’tibor qaratilmoqda. Bu borada amalga oshirilgan chora-tadbirlar doirasida muayyan natijalarga erishilmoqda, ayniqsa, turli agressiv muhitlarda, suvli sovitish yoki isitish tizimlarida, neft va gaz sanoatida metall materiallarni korroziyadan himoya qilishning ilmiy asoslarini yaratishga erishilmoqda. Yangi O‘zbekistonni rivojlantirish strategiyasida “Milliy iqtisodiyotni jadal rivojlantirish va yuqori o‘sish sur’atlarini ta’minlash[1]”ga qaratilgan muhim vazifalar belgilab berilgan. Shu munosabat bilan import o‘rnini bosuvchi, eksportbop, raqobatbardosh, jahon sifat standartlari talablariga mos bo‘lgan, kam konsentratsiyada yuqori samaradorlikka ega, xavfsiz, biologik parchalanuvchi korroziyaga qarshi ingibitorlarni yaratish dolzarb vazifalardan hisoblanadi.

O‘zbekiston Respublikasi Prezidentining 2021-yil 9-iyundagi PF-6244-sonli “Hududlarning sanoat salohiyatini oshirishga doir qo‘shimcha chora-tadbirlar to‘g‘risida”gi hamda 2022-yil 28-yanvardagi PF-60-sonli “2022-2026-yillarda Yangi O‘zbekistonni rivojlantirish strategiyasi to‘g‘risida”gi farmonlarida nazarda tutilgan vazifalarni, 2020-yil 12-avgustdagi PQ-4805-sonli “Kimyo va biologiya yo‘nalishlarida uzluksiz ta’lim sifatini va ilm-fan natijadorligini oshirish chora-tadbirlari to‘g‘risida” va 2017-yil 29-avgustdagi PQ-3264-sonli “Kimyo sanoati tashkilotlarining eksport-import faoliyatini takomillashtirish chora-tadbirlari to‘g‘risida”gi qarorlari hamda mazkur faoliyatga tegishli boshqa me’yoriy-huquqiy

[1] O‘zbekiston Respublikasi Prezidentining 2022-yil 6-iyuldagi PF-165-sonli “2022-2026-yillarda O‘zbekiston Respublikasining innovatsion rivojlanish strategiyasi to‘g‘risida”gi farmoni.

hujjatlarda belgilangan vazifalarni amalga oshirishda ushbu dissertatsiya ishi muayyan darajada xizmat qiladi.

Tadqiqotning respublika fan va texnologiyalari rivojlanishining ustuvor yo‘nalishlariga mosligi. Mazkur tadqiqot respublika fan va texnologiyalar rivojlanishining VII. “Kimyo texnologiyalari va nanotexnologiya” ustuvor yo‘nalishlariga muvofiq bajarilgan.

Muammoning o‘rganilganlik darajasi. Butun dunyoda olimlar tomonidan olib borilayotgan ko‘pgina ilmiy tadqiqot ishlari korroziya ingibitorlarining yangi avlodini ishlab chiqarishga bag‘ishlangan. Adabiyotlar sharhi shuni ko‘rsatadiki, juda ko‘p ishlar (L.Guo, B.Fan, D.K.Verma, A.Dehghani, O.Dagdag, F.Damien, J.Berge, J.Wang, G.T.Burstein va O.R.Mattos) elektrokimyoviy usullar tadqiqotlariga bag‘ishlangan bo‘lib, ularda ingibitorlar sifatida turli xil materiallar qo‘llanilgan. Bugungi kunda korroziya ingibitorlari tadqiqotlarida fizik-kimyoviy, elektrokimyoviy va boshqa turli usullar ishlab chiqilgan, biroq texnologiya rivojlanishi bilan korroziya jarayonida organik birikmalarni ingibitor sifatida ta’sir qilish mexanizmi hamda po‘lat sirtiga ta’sirini o‘rganish bo‘yicha ilmiy tadqiqot ishlariga alohida e’tibor qaratilmoqda.

O‘zbekiston olimlari, jumladan, R.S.Tillayev, Z.A.Tadjixodjayev, F.K.Kurbanov, A.T.Djalilov, A.Ikramov, D.Yusupov, X.I.Akbarov, V.P.Guro, A.J.Xoliqov, X.I.Qodirov, N.B.Eshmamatova, E.T.Berdimurodov va boshqalar metallarni korroziyadan himoyalash muammosini hal qilishda hamda ingibitorlar sifatida ishlatiladigan kimyoviy birikmalarni yangi avlodini sintez qilib olinishida o‘z ilmiy tadqiqotlari bilan katta hissa qo‘shganlar. Lekin po‘lat 20 sirtining siklodekstrin asosidagi supramolekulyar komplekslar bilan ingibirlash mexanizmlari kuchli kislotali muhitlarda o‘rganilmagan.

Dissertatsiya tadqiqotining dissertatsiya bajarilgan oliy ta’lim muassasasining ilmiy tadqiqot ishlari rejalari bilan bog‘liqligi. Dissertatsiya tadqiqoti O‘zbekiston Milliy universitetining ilmiy tadqiqot ishlari rejasiga muvofiq №A-12-46 “Polielektrolitlarning antikorrozion samaradorligini oshirish va uni amaliyotga qo‘llash” (2015-2017-yy.) mavzusidagi amaliy loyiha doirasida olib borilgan.

Tadqiqotning maqsadi siklodekstrin asosidagi supramolekulyar komplekslar sintez qilish hamda ularning kuchli kislotali muhitda po‘lat korroziyasiga qarshi elektrokimyoviy va adsorbsion xossalarini o‘rganishdan iborat.

Tadqiqotning vazifalari:

Beta siklodekstrin asosida supramolekulyar komplekslarni sintez qilish va ularning tuzilishini IQ, ^{1}H YaMR, Raman spektroskopiya, TGA usullari yordamida aniqlash;

gravimetrik usul yordamida siklodekstrin asosidagi ingibitorlarning adsorbsion samaradorligi, himoyalash darajalari, faollanish va termodinamik xossalarini tadqiq qilish;

potensiodinamik qutblanish va elektrokimyoviy qarshilik spektroskopiya usullari yordamida po‘lat 20 namunalari uchun kuchli kislotali muhitlarda ingibitorlarning samaradorligini o‘rganish;

elektron mikroskoplar, kvant-kimyoviy hisoblashlar va Raman spektroskopiyasi yordamida metall sirtdagi strukturaviy o‘zgarishlarga ingibitorlarning ta’sirini o‘rganish;

ingibirlash mexanizmlari, ingibitor va metall yuzasining o‘zora tasirlarini atom darajadagi ko‘rinishlarini zichlik funksional nazariyasi, MK va MD simulyatsiyalari yordmida tadqiq qilish;

ingibitorlarning samaradorligini o‘rganish bo‘yicha laboratoriya sinovlarini o‘tkazish va ularni kon-metallurgiya kombinatlari bilan neft-gaz sanoati korxonalariga tatbiq etish.

Tadqiqotning obyekti sifatida beta siklodekstrin ortofenilendiamin (β-SDoFDA), beta siklodekstrin melamin (β-SDME), beta siklodekstrin 1,5-difenilkarbazid (β-SDDFK), beta siklodekstrin naftilamin-1 (β-SDNA) va beta siklodekstrin atsetanilid (β-SDAS) supramolekulyar komplekslar olingan.

Tadqiqotning predmetiga gravimetrik, elektrokimyoviy, sirt tahlili usullari va kvant kimyoviy hisob-kitoblari bilan metallarni korroziyadan himoyalash hamda ingibirlash mexanizmlarining umumiy qonuniyatlarini tadqiq qilish kiradi.

Tadqiqotning usullari. Dissertatsiya ishida infraqizil spektroskopiya, Raman spektroskopiya, proton yadro magnit-rezonans spektroskopiya, termogravimetrik analiz, gravimetrik, potensiodinamik qutblanish, elektrokimyoviy qarshilik spektroskopiyasi, skanerlovchi elektron mikroskop, energiya-dispersion spektroskopiya, atom kuch mikroskop, zichlik funksional nazariyasi, Monte Karlo va molekulyar dinamik simulyatsiya usullari qo‘llanilgan.

Tadqiqotning ilmiy yangiligi quyidagilardan iborat:

ilk bor β-SDoFDA, β-SDME, β-SDDFK, β-SDNA va β-SDAS supramolekulyar komplekslari po‘lat 20 uchun samarali hamda yangi korroziya ingibitori ekanligi aniqlangan;

sintez qilingan supramolekulyar komplekslarning yuqori ingibitorlik xossalari korrozion tok zichligi ($i_{korr} = 0{,}85$ μA/sm^2) kamayishi, zaryad almashish qarshiligi ($R_{ZAl} = 126{,}4$ Ω /sm^2), himoyalash darajasi ($\eta_{\text{Grav.}} = 96{,}93$) hamda sirtni qoplash darajalari ($\theta_{\text{Grav.}} = 0{,}97$) qiymatlarining ortishi orqali isbotlangan;

Kvant kimyoviy hisoblashlar, metall sirtining AKM va SEM mikrofotografiyalari, EDS hamda Raman spektrlari yordamida supramolekulyar komplekslarning ingibirlash mexanizmlari aniqlangan;

Monte Karlo va molekulyar dinamik simulyatsiyalari orqali ingibitorning neytral hamda protonlangan shakllarini metall sirtiga adsorbsiyalanish pozitsiyalari dalillangan;

ilk bor molekulyar dinamik simulyatsiya yordamida β-SDoFDA supramolekulyar kompleksining Fe sirti bilan ta’sirlashishi nazariy jihatdan hisoblangan va Fe-N bog‘ining uzunligi 8,93 Å, Fe-O bog‘ining uzunligi 6,55 Å ga tengligi aniqlangan.

Tadqiqotning amaliy natijalari quyidagilardan iborat:

tadqiqot obyektlari 100 mg/l konsentratsiyada qo‘llanilganda korroziyadan samarali himoyalashi va metall yuzasiga yaxshi adsorbsiyasi isbotlangan, shu bilan birga β-siklodekstrin asosidagi supramolekulyar komplekslardan foydalanilganda

o‘zaro sinergetik ta’sir natijasida po‘lat 20 tarkibli uskunalarda 97 %gacha himoyalash darajasiga erishilgan;

Navoiy va Olmaliq kon-metallurgiya kombinatlarida β-SDoFDA, β-SDME, β-SDDFK, β-SDNA va β-SDAS supramolekulyar komplekslari suv aylanma tizimlari, sovitish va isitish tizimlarida ishlatiladigan metall konstruksiyalar korroziyasini oldini oluvchi samarali ingibitorlar ekanligi isbotlangan.

Tadqiqot natijalarining ishonchliligi. Tadqiqot davomidagi barcha natijalar infraqizil spektroskopiya, Raman spektroskopiyasi, proton yadro magnit-rezonans spektroskopiyasi, termogravimetrik analiz, gravimetrik, potensiodinamik qutblanish, elektrokimyoviy qarshilik spektroskopiyasi, skanerlovchi elektron mikroskop, energiya-dispersion spektroskopiya, atom kuch mikroskop, zichlik funksional nazariyasi, Monte Karlo va molekulyar dinamik simulyatsiyalari kabi zamonaviy usullar yordamida isbotlangan, shuningdek, ular asosida yuqori impakt faktorli xorijiy (Scopus bazasidagi) jurnallarda 4 ta maqola chop etilgan.

Tadqiqot natijalarining ilmiy va amaliy ahamiyati.

Tadqiqot natijalarining ilmiy ahamiyati β-SDoFDA, β-SDME, β-SDDFK, β-SDNA va β-SDAS supramolekulyar komplekslarning sintezi hamda 0,5 M HCl eritmasida po‘lat 20 uchun 100 mg/l/0,08 mM da korroziya tezligi ($KT_{Grav.}$= 0,042), himoyalash darajasi ($\eta_{Grav.}$ = 96,7) va sirtni qoplash darajasining ($\theta_{Grav.}$ = 0,97) qiymatlari hamda ingibirlash mexanizmini aniqlashdan iborat.

Tadqiqot natijalarining amaliy ahamiyati siklodekstrin asosidagi olingan supramolekulyar komplekslar suv aylanma tizimlari, sovitish va isitish tizimlarida hamda neft gaz sanoatlaridagi kuchli kislotali agressiv muhitlarda po‘lat 20 namunalarni korroziyadan yuqori darajada himoyalab, metall konstruksiyalarni uzoq muddat samarali ishlashiga xizmat qilishi bilan izohlanadi.

Tadqiqot natijalarining joriy qilinishi. Gravimetrik, elektrokimyoviy, sirt tahlili usullari va kvant kimyoviy hisoblashlar orqali siklodekstrin asosidagi olingan supramolekulyar komplekslarning po‘lat 20 korroziyasini ingibirlash mexanizmlarini kuchli kislotali muhitlarda o‘rganish bo‘yicha olingan ilmiy natijalar asosida:

siklodekstrin asosidagi supramolekulyar komplekslar: β-siklodekstrin ortofenilendiamin, β-siklodekstrin melamin, β-siklodekstrin 1,5-difenilkarbazid, β-siklodekstrin naftilamin-1 va β-siklodekstrin atsetanilidlardan “GISSARNEFTGAZ” O‘zbekiston-Shveysariya qo‘shma korxonasi laboratoriyasida metall konstruksiya hamda qurilmalarida korroziya jarayoniga qarshi ingibitor sifatida sinovdan o‘tkazildi (“GISSARNEFTGAZ” O‘zbekiston-Shveysariya qo‘shma korxonasining 2023-yil 06-noyabrdagi 730-01/11-sonli ma’lumotnomasi). Laboratoriya sinov natijalariga ko‘ra, supramolekulyar komplekslar yuqori harorat va past konsentratsiyalarda yuqori himoyalash darajasiga ega bo‘lgan. Tadqiqot obyektlari sanoatda foydalaniladigan ingibitorlarga qaraganda kuchli kislotali muhitlarda metall konstruksiya va qurilmalarini yemirilishdan yaxshi himoyalagan hamda metall konstruksiya va qurilmalarini korroziyadan himoyalash uchun talab mavjud sohalarda amaliyotga joriy etishga tavsiya qilingan;

siklodekstrin asosidagi olingan supramolekulyar komplekslar Navoiy kon-metallurgiya kombinati aksiyadorlik jamiyati Markaziy ilmiy tadqiqot laboratoriyasida sinovdan o‘tkazilgan (“Navoiy kon-metallurgiya kombinati” AJ ning 2023-yil 13-noyabrdagi 23/01-01-07/575-sonli ma’lumotnomasi). Natijada, tadqiqot obyektlarining sanoatda ishlatiladigan ingibitorlarga nisbatan turli haroratlarda va kislotali muhitlarda metallarni korroziyadan himoyalash imkoniyati yuqoriligi ko‘rsatib berilgan;

siklodekstrin asosidagi olingan supramolekulyar komplekslarning 100 mg/l li eritmalari “Olmaliq kon-metallurgiya kombinati” AJ Rux zavodi sulfat kislotasi sexiga qarashli 1-sonli suv aylanma tizimlarida ishlatiladigan metall konstruksiyalarning korroziyasini oldini oluvchi vosita sifatida sinov tariqasida amaliyotga joriy qilingan (“Olmaliq kon-metallurgiya kombinati” AJ ning 2023-yil 16-noyabrdagi SL-1282-sonli ma’lumotnomasi). Natijada, mazkur birikmalar samarali ingibitorlar sifatida suv aylanma tizimlaridagi metall konstruksiyalarning korroziyasini oldini olish imkonini bergan;

yangi supramolekulyar komplekslarning korroziyadan himoyalash xossalari hamda adsorbsiya mexanizmlari № OT-F7-85-raqamli “Aminometilenfosfat kislotasi asosidagi alifatik va geterotsiklik metallar korroziyasi ingibitorlarining sintezi va fizik-kimyoviy xossalari” mavzusidagi loyihada ingibirlash mexanizmini fizik-kimyoviy tadqiq qilish va elektrokimyoviy xususiyatlarini aniqlash maqsadida foydalanilgan (O‘zbekiston Respublikasi Oliy ta’lim, fan va innovatsiyalar vazirligining 2023-yil 23-avgustdagi 03/10-2023-sonli ma’lumotnomasi). Natijada, neft va gaz sanoatidagi metall materiallarning korroziyasini oldini olishga yordam bergan.

Tadqiqot natijalarining aprobatsiyasi. Mazkur tadqiqot natijalari 8 ta, jumladan, 4 ta xalqaro va 4 ta Respublika ilmiy-amaliy anjumanlarida ma’ruza qilingan hamda muhokamadan o‘tgan.

Tadqiqot natijalarining e’lon qilinganligi. Dissertatsiya mavzusi bo‘yicha 13 ta ilmiy ish chop etilgan, shulardan, O‘zbekiston Respublikasi Oliy attestatsiya komissiyasining falsafa doktori (PhD) dissertatsiyalari asosiy ilmiy natijalarini chop etish tavsiya etilgan ilmiy nashrlarda 1 ta maqola respublika va 4 ta maqola xorijiy (Scopus bazasidagi) jurnallarda nashr etilgan.

Dissertatsiyaning tuzilishi va hajmi. Dissertatsiya kirish, 5 bob, xulosa, foydalanilgan adabiyotlar ro‘yxati va ilovadan iborat. Dissertatsiya hajmi 118 betni tashkil qiladi[2].

DISSERTATSIYANING ASOSIY MAZMUNI

Kirish qismida o‘tkazilgan tadqiqotlarning dolzarbligi va zarurati asoslangan, maqsad va vazifalari keltirilgan, obyekti va predmeti tavsiflangan, tadqiqotning respublika fani va texnologiyasi rivojlanishining ustuvor yo‘nalishlariga mos kelishi ko‘rsatilgan, tadqiqot natijalarining ilmiy yangiligi, ilmiy va amaliy ahamiyati bayon qilingan, olingan natijalarning ilmiy va amaliy ahamiyati, ishonchliligi, ularning amaliyotga tatbiq qilinishi ochib berilgan va chop etilgan ishlar hamda dissertatsiya tuzilishi bo‘yicha ma’lumotlar keltirilgan.

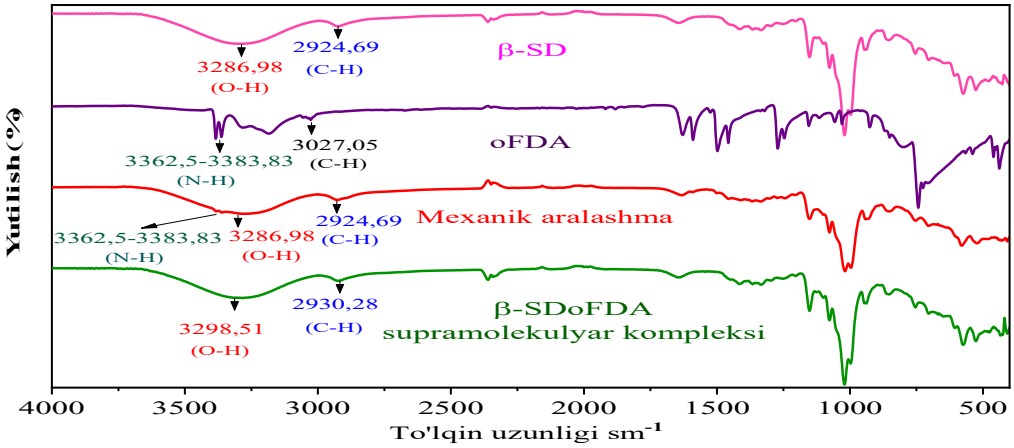
[2]Kimyo fanlari doktori, professor X.I.Akbarovga dissertatsiya ishini bajarishda bergan ilmiy maslahatlari uchun minnatdorlik bildiraman.

Dissertatsiyaning **“Beta siklodekstrin asosidagi yashil korroziya ingibitorlari: So‘ngi ilmiy yutuqlar, innovatsiyalar va imkoniyatlar”** deb nomlangan **birinchi bobi** adabiyotlar sharhiga bag‘ishlangan bo‘lib, unda korroziyaning asosiy xususiyatlari, ta’siri va himoyasi, ekologik toza va samarali korroziya ingibitorlari sifatida beta siklodekstrinning tabiiy polimer bilan modifikatsiyalari, beta siklodekstrin asosidagi supramolekulyar (mezbon-mehmon) komplekslar kislotali agressiv muhitlardagi ingibitorlarning himoyalash mexanizmlari, kislorod va azot saqlovchi siklodekstrin asosidagi supramolekulyar ingibitorlar haqida ma’lumotlar keltirilgan. Hozirgi kunda kislotali muhitdagi korroziyaviy jarayonlarni to‘xtatish bo‘yicha respublikamiz va Chet elda olib borilayotgan ishlar qiyosiy muhokama qilingan. Adabiyotlar tahliliga ko‘ra, siklodekstrin asosidagi supramolekulyar ingibitorlar samaradorligi yuqori bo‘lishi aniqlangan.

Dissertatsiyaning **“Materiallar, siklodekstrin asosidagi supramolekulyar komplekslarning sintezi va tadqiqot usullari”** deb nomlangan **ikkinchi bobida** foydalanilgan po‘lat 20 namunasining tarkibi, tuzilishi, o‘lchamlari va kislotali fon eritmalarning tarkibi keltirilgan. Beta siklodekstrin ortofenilendiamin (β-SDoFDA), beta siklodekstrin melamin (β-SDME), beta siklodekstrin 1,5-difenil karbazid (β-SDDFK), beta siklodekstrin atsetanilid (β-SDAS), beta siklodekstrin naftilamin-1 (β-SDNA) birikmalarining sintez sharoitlari va reaksiya tenglamalari ko‘rsatib o‘tilgan. Infraqizil spektroskopiya, Raman spektroskopiyasi, proton yadro magnit-rezonans spektroskopiyasi, termogravimetrik analiz, potensiodinamik qutblanish, elektrokimyoviy qarshilik spektroskopiyasi, gravimetrik, skanerlovchi elektron mikroskop, energiya-dispersion spektroskopiya, atom kuch mikroskop, zichlik funksional nazariyasi, Monte Karlo va molekulyar dinamik simulyatsiya usullari haqida ma’lumotlar keltirilgan.

Dissertatsiyaning “**Sintez qilingan ingibitorlar tuzilishining tahlili**” deb nomlangan **uchinchi bobida** sintez qilingan supramolekulyar komplekslar tuzilishining IQ-spektroskopiyasi, Raman spektroskopiyasi, ^{1}H YaMR va termogravimetrik analiz usullaridan olingan natijalarning tahlili keltirilgan.

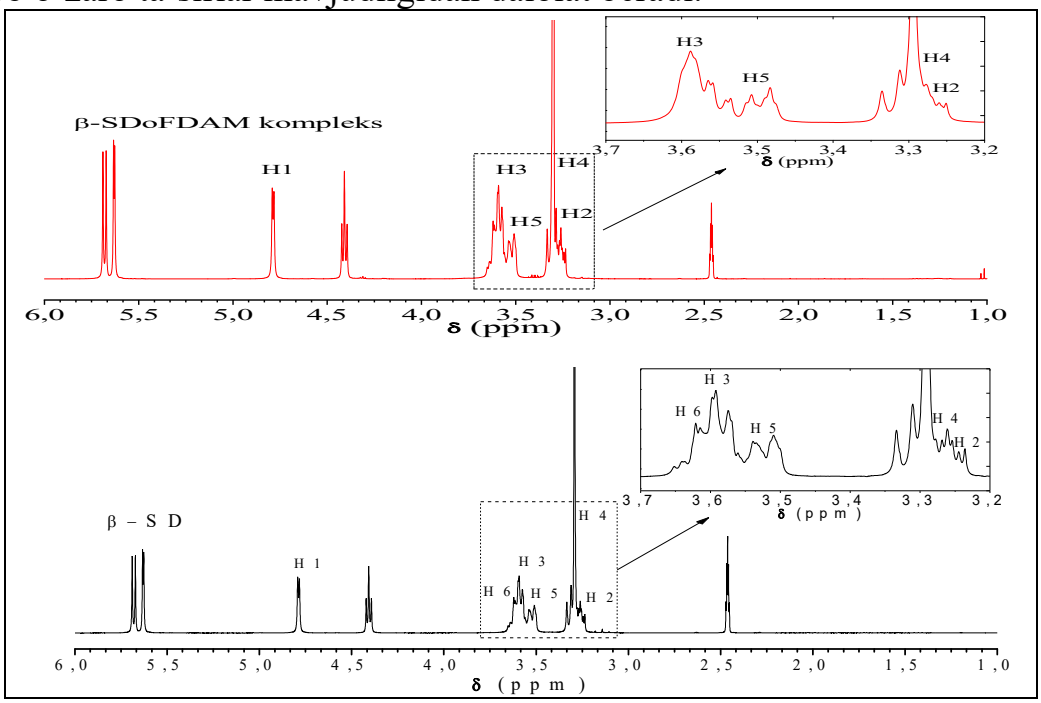
B-SD, oFDA, mexanik aralashma va β-SDoFDA supramolekulyar kompleksini infraqizil spektr tadqiqotlari o‘tkazildi (1-rasmga qarang).



1-rasm. B-SD, oFDA, mexanik aralashma va β-SDoFDA supramolekulyar kompleksining IQ-spektrlari.

Hosil bo‘lgan supramolekulyar kompleks IQ-spektri dastlabki moddalarning IQ-spektrlari bilan solishtirilganda turli darajada o‘zgarishlarni mavjudligi aniqlandi. Masalan, O-H bog‘ining valent tebranishlarining yutilish sohasi 3286,98 sm^{-1} dan 3298,51 sm^{-1} ga C-H bog‘ining valent tebranishlarining yutilish sohasi 2924,69 sm^{-1} dan 2930,28 sm^{-1} ga o‘zgardi. Bundan oFDA β-SD bo‘shlig‘idagi O-H tebranishini kuchaytirgan. Bu supramolekulyar kompleksda gidrofob va Van der Vaals ta’sirlashish mavjud ekanligidan dalolat beradi.

β-SD va β-SDoFDA kompleksining ^{1}H YaMR spektrlari ko‘rsatilgan; turli protonlarning tegishli kimyoviy siljishlari (2-rasmga qarang) o‘rganildi. B-SD ning gidrofob bo‘shliqdagi H3 va H5 atomlari holatining o‘zgarishi oFDA molekulalari β-SD bo‘shlig‘iga kiritilganligining dalili hisoblanadi. Shu bilan birga, oFDA molekulalari kiritilgandan keyin H4 δ qiymati biroz kamaydi. Yuqorida qayd etilgan siljishlardan quyidagi ikkita xulosani berishi mumkin: birinchi navbatda, oFDA ning elektrodonor guruhi ($-NH_2$) vodorodi signallari, H4 va H6 egallagan tomondan cho‘ziladi hamda himoya effektining kuchayishiga olib keladi. Xususan, β-SD bo‘shlig‘ida joylashgan H3 va H5 protonlarining kimyoviy siljishlari ($-C_6H_4-$) fenilen halqasi bilan β-SD gidrofob ichki bo‘shlig‘i o‘rtasidagi Van der Vaals hamda gidrofob o‘zaro ta’sirlar mavjudligidan dalolat beradi.



2-rasm. β-SD va β-SDoFDA supramolekulyar kompleksining ^{1} H YaMR spektrlari.

Dissertatsiyaning “**Olingan ingibitorlarni metallar korroziyasiga qarshi samaradorligini tadqiq qilish**” deb nomlangan **to‘rtinchi bobida** supramolekulyar komplekslarning ingibitorlik xossalarini tadqiq qilish bo‘yicha olingan amaliy va nazariy ma’lumotlarning tahlili keltirilgan.

Korroziya va ingibirlash jarayonida sistemaning termodinamik kattaliklarini o‘zgarishini aniqlash. Xlorid ionlari tutgan ingibitorsiz fon eritma uchun E_f= 8,7192 kJ/molni (1-jadvalga qarang), 100 mg/l/0,08 mM konsentratsiyada ingibitor kiritilgan 0,5 M HCl sistemalari uchun E_f =57,72 kJ/molni tashkil qilgan. Ingibirlangan muhitdagi E_f ning qiymati ingibirlanmagan eritmaga qaraganda yuqori

bo‘lgan. Buni ingibitor metall sirtida kimyoviy adsorbsiya tufayli korroziya jarayonlari uchun energetik to‘siqlarni hosil qilishi bilan izohlash mumkin. Ingibirlangan 0,5 M HCl eritmalarida ΔH_f qiymatlari korroziya jarayoni endotermik ekanligini tasdiqlaydi. Ingibitor kiritilishi korroziya jarayonini borishi uchun zarur energiyani oshiradi, natijada, korroziya jarayoni ketishi qiyinlashadi.

1-jadval

Faollanish jarayoni uchun termodinamik kattaliklar qiymatlari (β-SDoFDA)

Termodinamik kattaliklar	Fon eritma	25 mg/l/ 0,02 mM	50 mg/l/ 0,04 mM	75 mg/l/ 0,06 mM	100 mg/l/ 0,08 mM
E_f, kJ/mol	8,72	19,14	24,25	34,55	57,72
ΔH_f, kJ/mol	6,08	16,5	21,61	31,91	55,08
ΔS_f kJ/mol T	-379,55	-360,12	-345,3	-314,85	-245,71
E_f-ΔH_f kJ/mol	2,64	2,64	2,64	2,64	2,64

ΔS_f qiymati 0,5 M HCl li fon eritmada (-379,55 kJ/mol T) va 100 mg/l/0,04 mM da (-245,71 kJ/mol T) eritmasida ingibitor kiritilgan eritma uchun aniqlandi. ΔS_f ning qiymatlari faollashtirilgan ingibitor-metall kompleksining barqarorligini va uning assotsiatsiyasini tasdiqlaydi.

Ingibirlash jarayonining kinetik-adsorbsion ko‘rsatkichlarini aniqlash. 2-jadvalda keltirilganidek, K_{ads} 303K da 170,06 M^{-1}, 313K da 205,76 M^{-1}, 323K da 256,41 M^{-1} va 333K da 259,74 M^{-1} ga teng bo‘lgan, K_{ads} ning bu yuqori qiymatlari β-SDoFDA ingibitori 0,5 M HCl eritmasida po‘lat 20 sirtida yuqori adsorbsiya tezligiga ega ekanligini tasdiqlaydi. ΔG^{o}_{ads} ning past qiymatlari β-SDoFDA ingibitori po‘lat 20 sirtiga osongina adsorbsiyalanishini va metall sirtini agressiv Cl^- ionlari hujumidan samarali himoya qilishini tasdiqlaydi. Aniqlangan ΔG^{o}_{ads} qiymatlari β-SDoFDA ingibitorini po‘lat 20 sirtida adsorbsiyasi aralash turdagi adsorbsiya ekanligini ko‘rsatadi. Bu esa shuni anglatadiki, ingibitor metall sirtida adsorbsiyalanishi kimyoviy va fizikaviy adsorbsiya mexanizmlari asosida boradi. Ingibitor molekulasidagi geteroatomlar p-elektron juftlarini metall sirtida temirning bo‘sh bo‘lgan d-orbitallari bilan almashish orqali kimyoviy adsorbsiyanish yuzaga keladi. Ingibitor molekulasidagi musbat zaryadlangan hududlari metall sirtida manfiy zaryadlangan joylari bilan o‘zaro ta’sir qiladi va bu jarayon fizikaviy adsorbsiya deb ataladi.

2-jadval

Adsorbsiya jarayonining termodinamik kattaliklarining qiymatlari (β-SDoFDA)

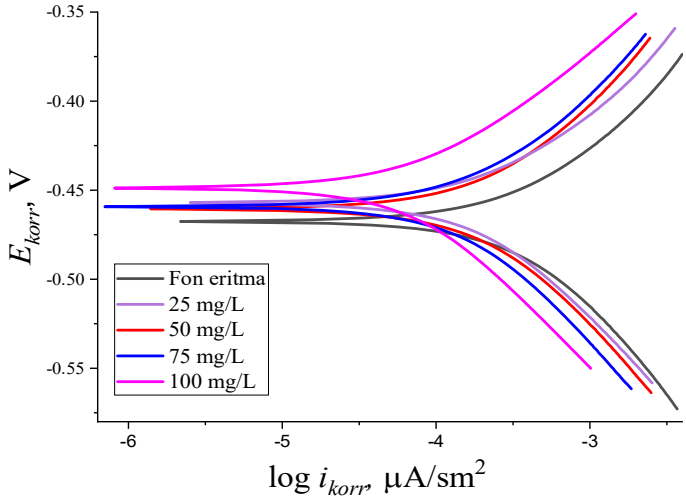
Harorat, K	K_{ads}, M^{-1}	ΔG^{o}_{ads}, kJ/mol	ΔH^{o}_{ads}, kJ/mol	ΔS^{o}_{ads}, J/mol K
303	170,06	-23,06	12,42	117,37
313	205,76	-24,32		
323	256,41	-25,69		
333	259,74	-26,52		

ΔH^{o}_{ads} qiymati 12,42 kJ/mol ekanligi 0,5 M HCl tarkibidagi po‘lat 20 ga β-SDoFDA ning adsorbsiyasi endotermikligini ko‘rsatdi. Shuningdek, ΔS^{o}_{ads} qiymati 117,3 J/mol K ga teng bo‘ladi. Bu adsorbsion qavatning 0,5 M HCl eritmasida barqaror bo‘lishini ko‘rsatadi. Ushbu barqaror adsorbsion qavat ingibitor

tomonidan metall sirtida oldindan adsorbsiyalangan Cl^- va suv molekulalarini almashtirish orqali hosil bo‘ladi.

Elektrokimyoviy usullar yordamida olingan natijalar va ularning tahlili. Katodda vodorod ajralishi va anodda metallning erishi natijasida kationlarga ajralishi kabi korroziya jarayonlariga ingibitorning ta’siri potensiodinamik qutblanish usuli yordamida o‘rganildi (3-rasm va 3-jadvalga qarang). Olingan natijalardan quyidagi xulosalarga kelindi:

(I) Tafel egrilari himoyalanmagan sistemalarda yuqori korrozion tok zichligi (i_{korr}) bo‘lgan hududlarga siljiganini ko‘rish mumkin. Ingibirlanish natijasida himoya qavat hosil bo‘lishi bilan Tafel egrilari qutblanish qarshiligining keskin oshishi natijasida i_{korr} kamayishi tomonga siljigan. Konsentratsiya oshishi bilan Tafel egrilari siljishi yanada oshib ketgan. i_{korr} ning kamayishi metallning yuzasida hosil bo‘lgan himoya qatlamlarining mustahkam ekanligini ko‘rsatadi. Bu himoya qatlami metall yuzasini korrozion muhitdan himoya qiladi. Natijada, metall korroziyasini oldini oladi.



3-rasm. Po‘lat 20 dan tayyorlangan ishchi elektrodning 0,5 M HCl eritmasida.

β-SDoFDA ingibitori bo‘lgan va bo‘lmagan eritmalar uchun Tafel egrilari (II) himoyalangan hamda himoyalanmagan sistemalar uchun korroziya potensiallari (E_{korr}) o‘rtasidagi farq 40 mV dan past bo‘lib, bundan β-SDoFDA ning metall yuzasida aralash turdagi adsorbsiya bo‘lishini ko‘rsatadi.

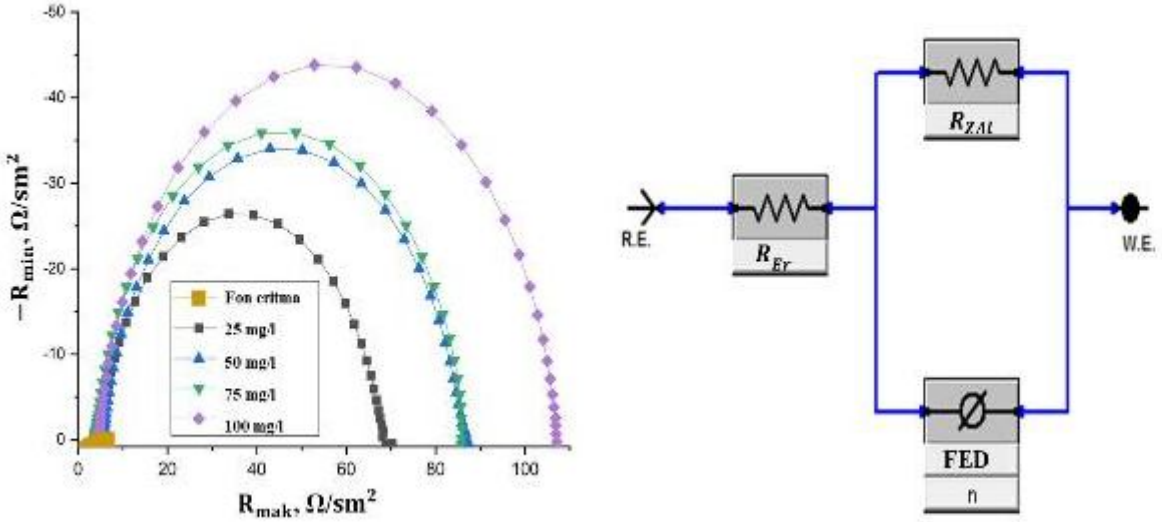
3-jadval

0,5 M xlorid kislotadagi (Po‘lat 20 dan tayyorlangan ishchi elektrod) β-SDoFDA ingibitori bo‘lgan va bo‘lmagan eritmalar uchun elektrokimyoviy parametrlarining hisoblangan qiymatlari

Parametr	C_{ing}, mg/l				
	Fon	25	50	75	100
i_{korr}, µA/sm^2	12,85	1,87	1,65	1,03	0,85
E_{korr}, mV	-479	-456	-459	-461	-452
β_a, mV	275,6	251,9	234,1	201,5	185,6
$-\beta_k$, mV	230,9	221,7	201,5	184,1	152,6
η_{PDQ}, %	-	85,44	87,15	91,98	93,38

(III) himoyalanmagan sistema uchun i_{korr} qiymatlari 12,85 μA/sm^2 bo‘lib, bu qiymat korroziya juda shiddatli borayotganligini ko‘rsatadi. β-SDoFDA qo‘shilishi bilan 0,85 μA/sm^2 gacha kamaydi. Yuqoridagi qiymatlardan foydalanib korroziyadan himoyalash samaradorligi 93,38 % ekanligi topildi.
(IV) Tafel qutblanish egrilari (β_k, β_a) β-SDoFDA ingibitori qo‘shilishi bilan chapga va o‘nga siljishini ko‘rsatdi, bu qutblanish jarayonlari himoya qavat hosil bo‘lishi bilan korroziyaning kamayganligini ko‘rsatadi.
(V) Ingibirlanmagan metall yuzasi yuqori qutblanishga ega eritmada korroziya yuqori tezlikda boradi. Buning sababi, metall sirtining past qutblanish qarshiligiga egaligidir. β-SDoFDA ingibitori qo‘shilgan eritma bilan solishtirganda, himoya qatlamlari hosil bo‘lganligi tufayli qutblanish qarshiligi keskin oshib ketadi.

Elektrokimyoviy qarshilik spektroskopiyasi (EQS) usuli yordamida olingan natijalar va ularning tahlili. EQS analizi yordamida Naykvist egrilari, Body va faza burchak egrilari olindi (4-, 5-rasmlarga qarang). Bu egrilar metall yuzasidagi korroziyalanish va ingibirlanish jarayonlarining elektrokimyoviy kinetik parametrlarini qanday o‘zgarishini ko‘rsatadi.

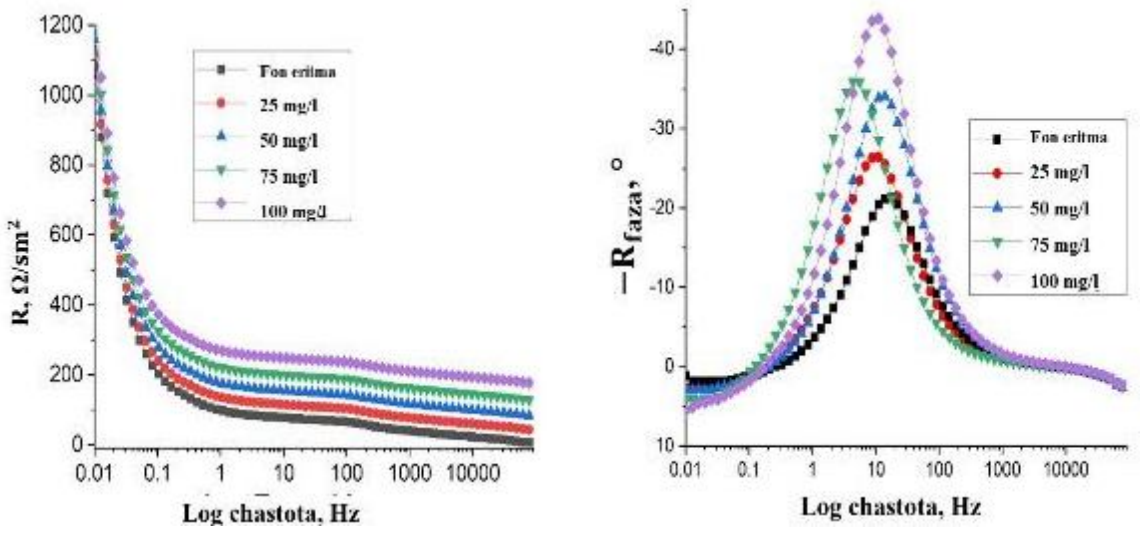


a **b**

4-rasm. 0,5 M xlorid kislotada (Po‘lat 20 dan tayyorlangan ishchi elektrod) β-SDoFDA ingibitori bo‘lgan va bo‘lmagan eritmalar uchun Naykvist egrilari (a) hamda ekvivalent tok modeli (b).

Katod va anod o‘rtasidagi elektrokimyoviy reaksiyalar, zaryadlarning tashib o‘tilishi, korroziyalanish va ingibirlanish jarayonlarining ba’zi elektrokimyoviy parametrlari topiladi. Naykvist egrilaridan olingan xulosalar shuni ko‘rsatadiki, β-SDoFDA konsentratsiyasining oshishi bilan katod va anod hududlari o‘rtasida zaryad almashinuviga keskin kamayadi. Naykvist egrilarining o‘lchami β-SDoFDA qo‘shilishi bilan keskin oshdi, bu ingibirlash jarayonida zaryad o‘tkazish tezligining pasayishini ko‘rsatadi. Olingan Naykvist egrilarida, qutblanish chizmalari himoyalanmagan sistemada yuqori sohalarda joylashganligi aniqlandi. Bu ko‘rsatkich ingibirlangan muhitda past sohalarga o‘zgargan. Z_{mod} o‘zgartirishlar himoyalangan va himoyalanmagan sistemalar o‘rtasida keskin farq qiladi (5a-rasmga qarang). Korrozion sistemaga β-SDoFDA qo‘shilishi Z_{mod} ning qiymati yuqori sohalarda namoyon bo‘ldi, ingibitor bo‘lmaganda esa Z_{mod} quyi sohalarda

namoyon bo‘ldi. Bu natijalar β-SDoFDA ning yaxshi ingibirlash xossalariga egaligini ko‘rsatadi.



a **b**

5-rasm. 0,5 M xlorid kislotada (Po‘lat 20 dan tayyorlangan ishchi elektrod) β-SDoFDA ingibitori bo‘lgan va bo‘lmagan eritmalar uchun Body (a) hamda faza burchak (b) egrilari.

Elektrokimyoviy natijalarga ko‘ra (4-jadvalga qarang) β-SDoFDA ingibitori katod va anod o‘rtasida zaryad almashish jarayonlariga juda keskin ta’sir qiladi. Natijada, metall yuzasida himoya qatlami hosil bo‘ladi. Buning sababi, organik molekulaning tarkibidagi amino va gidroksil guruhlari bilan metall sirti ta’sirlashishidan bog‘lar hosil bo‘lgan. Bu hosil bo‘lgan bog‘lanishlar natijasida metall yuzasi ingibirlanadi.

4-jadval

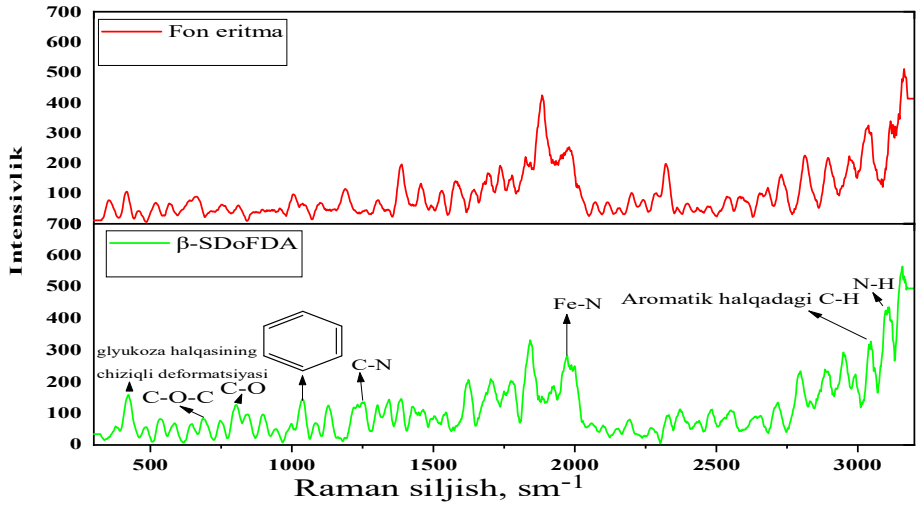
B-SDoFDA ingibitori bo‘lgan va bo‘lmagan eritmalar uchun EQS parametrlari

C_{ing}, mg/l	R_{Er}, Ω /sm^2	Y_0 × 10^{-3}	n	R_{ZAl}, Ω /sm^2	η_{EQS}, %	C_{QQQ}, μF/sm^2	Xatolik ×10^{-6}
Fon	0,38	51,32	0,8632	5,17	-	265,61	54,31
25	1,51	3,41	0,9247	47,85	89,1	156,14	41,25
50	1,76	2,31	0,9314	75,64	93,16	110,32	36,25
75	2,34	1,15	0,9531	93,21	94,45	88,32	21,25
100	3,14	0,87	0,9861	126,41	95,91	45,12	20,36

Himoyalanmagan sistemalarning zaryad almashish qarshiligi juda kichkina 5,17 Ω /sm^2 ingibitor kiritilishi bilan bu qiymatlar 126,64 Ω /sm^2 ga teng bo‘lgan buning sababi konsentratsiya oshishi bilan bog‘liq. n qiymatlari bu metall sirtini o‘rtacha silliqlik morfologiyasini ko‘rsatadi. Ingibirlanmagan metall sirti uchun *n=0,8632* ga teng bo‘lib, ingibirlanganda esa bu qiymatlar *n=0,9861* gacha oshadi. *n* qiymati birga yaqin bo‘lib, bu ingibitor kiritilishi bilan metallning sirtidagi yoriqlar yopilib metall sirti silliqlanishiga erishilgan. Fon eritma uchun tuzlar, gidroksidlar va korroziya mahsulotlarining ko‘p to‘planishi tufayli qo‘sh qavatli qoplama sig‘imi (C_{QQQ}) qiymati 265,61 μF/sm^2 bo‘ldi. Metall sirtida himoya qatlamining shakllanishi korroziya mahsulotlarning kamayishiga olib keldi. Korroziya

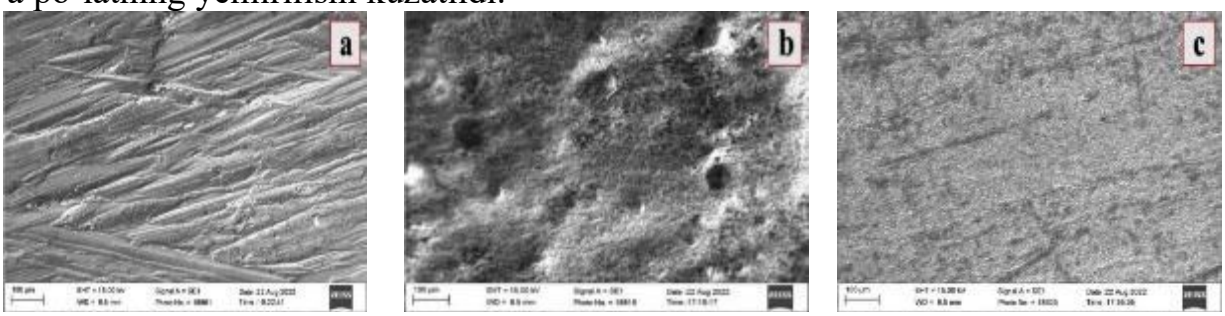
mahsulotlari kamayishi bilan C_{QQQ} ning qiymati sezilarli darajada kamayib 45,12 μF/sm^2 bo‘lib qolgan. C_{QQQ} ning pasayishi himoya qoplamining ingichkaligi oshishiga (d) va eritmaning o‘tkazuvchanligining pasayishiga ta’sir qilgan (ε –ingibitor bo‘lgan va ε^0– bo‘lmagan muhitning o‘tkazuvchanligi).

Po‘lat 20 Metall sirtiga ingibitorlarning qoplanishi natijasida vujudga kelgan funksional guruhlarning spektral o‘zgarishlari Raman spektroskopiyasi orqali o‘rganildi. 6-rasmda β-SDoFDA eritmasidagi metall sirtning va fon eritmadagi metall sirtining Raman sochilish ko‘rsatilgan. Olingan natijalardan ma’lum bo‘ldiki:
(I) oFDA aromatik halqasining C-H va aminoguruhlarning (N-H) bog‘lari uchun Raman signallari mos ravishda 3106 sm^{-1} va 3046 sm^{-1} sohalarda paydo bo‘lgan;
(II) Fe-N signallari 1979 sm^{-1} sohada topilgan; oFDA ning C-N bog‘ signallari 1251 sm^{-1} sohada kuzatilgan;
(III) β-SD ning glyukoza halqasi chiziqli deformatsiyasi uchun 422 sm^{-1}, C-O-C guruh uchun 470 sm^{-1} va C-O bog‘lanishlari 897 sm^{-1} sohalarga mosligi aniqlandi;
Olingan tafsilotlar β-SDoFDA ning metall sirtida adsorbsiyalanganligini ko‘rsatadi.



6-rasm. Ingibirlanmagan va β-SDoFDA supramolekulyar kompleksi bilan ingibirlangan metall sirtini Raman spektrlari.

Skanerlovchi elektron mikroskop yordamida olingan tasvirlar va ularning tahlili (7-rasmga qarang). Skanerlovchi elektron mikroskop yordamida ingibitorsiz muhitda po‘latning korroziyalanishi natijasida hosil bo‘lgan korroziya mahsulotlari va po‘latning yemirilishi kuzatildi.

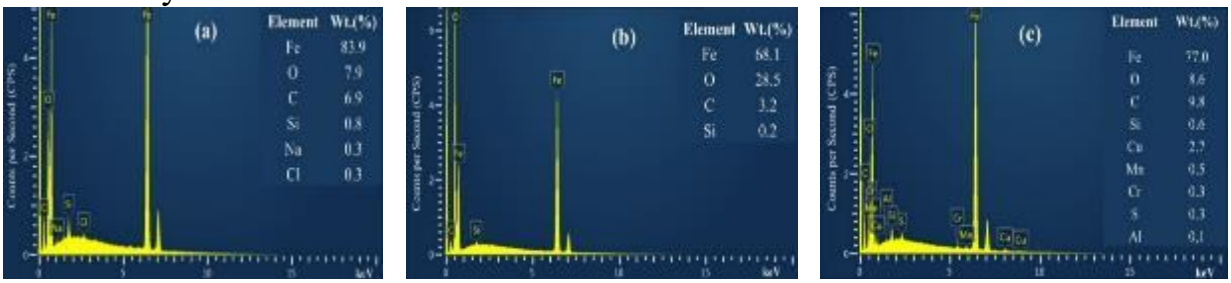


7-rasm. Skanerlovchi elektron mikroskop yordamida olingan po‘lat sirtining dastlabki (a-100 μm), ingibitorsiz sharoitda korroziyalangan (b-100 μm), β-SDoFDA ingibitori yordamida ingibirlangan (c-100 μm) ko‘rinishi.

Fon eritmaga β-SDoFDA ingibitori kiritilganda po‘lat sirtiga kimyoviy va fizikaviy adsorbsiyalanishi natijasida kompleks birikmalar hosil bo‘lishi aniqlandi.

Ingibirlangan po‘latning sirtida komplekslarning hosil bo‘lishi korroziyalanuvchi sirtning keskin kamayishiga va muhitning turli ta’sirlariga nisbatan barqarorligining ortishiga sabab bo‘ladi.

Energiya-dispersion spektroskopiya natijalari va ularning tahlili. Ingibitorsiz muhitdagi metall sirtining EDS tahliliga ko‘ra O ning miqdori ancha yuqori (28,5 %) va Fe miqdori ancha past (68,1 %) bo‘lib, bu po‘lat 20 ning sirti jiddiy oksidlanganligini ko‘rsatadi (8-rasmga qarang). β-SDoFDA ingibitorini korroziya eritmasiga qo‘shgandan so‘ng, Fe tarkibi sezilarli darajada oshdi (77 %) va O konsentratsiyasi ancha pasaydi (8,6 %). Bu metall sirtining deyarli oksidlanmaganligini, ya’ni korroziyaga uchramaganligini ko‘rsatdi. Kislorod atomlarining mavjudligi, bu po‘lat 20 plastinkasi sirtiga β-SDoFDA ning adsorbsiyasi tufayli yuzaga keldi. Bundan tashqari, po‘lat 20 tarkibida C (9,8 %) keskin o‘sish kuzatildi, bu β-SDoFDA ning po‘lat 20 sirtida adsorbsiyalanganligini ham isbotlaydi.



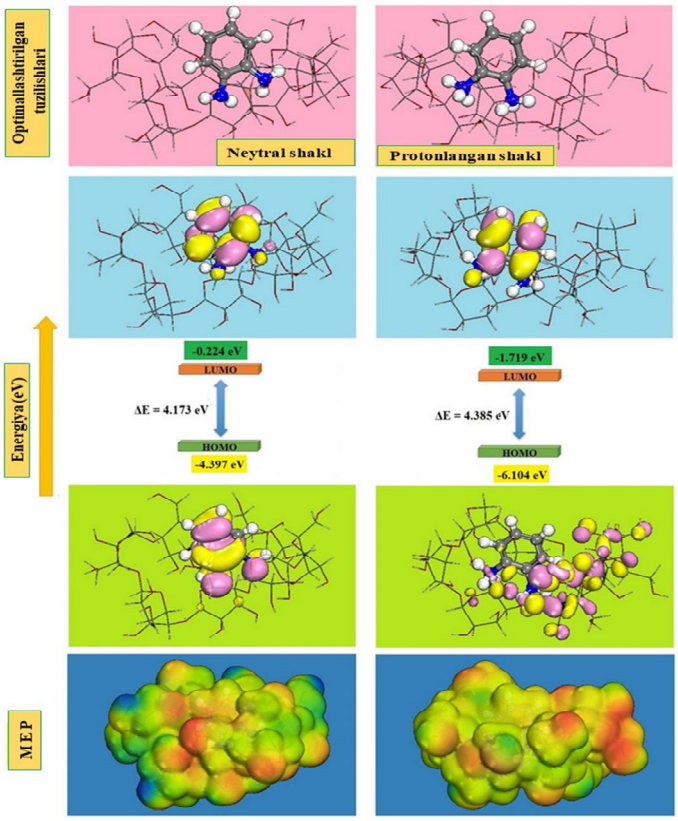
8-rasm. Metall sirtining dastlabki (a), korroziyalangan (b) va β-SDoFDA bilan ingibirlangan(c) plastinkalarning EDS natijalari.

Dissertatsiyaning “**Ingibirlash jarayonini kvant kimyoviy tahlili**” deb nomlangan **beshinchi bobida** sintez qilingan supramolekulyar komplekslarning ingibirlash jarayonini kvant kimyoviy tahlil qilish bo‘yicha olingan ma’lumotlar keltirilgan.

Zichlik funksional nazariyasi (ZFN) tahlillari β-SDoFDA ning neytral va protonlangan shakllarida amalga oshirildi. Ushbu usulda olingan natijalar asosida, korroziya ingibitorlarining himoyalash xossalari ularning tuzilishiga va fizik-kimyoviy xossalariga bog‘liqligi aniqlandi. β-SDoFDA ingibitorining neytral va protonlangan shakllarining optimallashtirilgan tuzilishlari, LUMO, HOMO va molekulyar elektrostatik potensial (MEP) tuzilishlari topildi (9-rasmga qarang). β-SDoFDA ning optimallashtirilgan tuzilishlari, ingibitorning yuqori qutblanish indeksiga ega ekanligini ko‘rsatdi. Bu xossa, β-SDoFDA yuqori ingibirlash xususiyatiga ega ekanligini ko‘rsatadi. β-SD bo‘shlig‘idagi oFDA ning optimallashtirgan neytral yoki protonlangan shakllari, sterik parametrlar, funksional guruhlarning joylashuvlari va aromatik halqalar hamda geteroatomlarning tabiati ingibirlash xossalariga ta’sir qiladi.

β-SDoFDA ingibitorining neytral va protonlangan supramolekulyar kompleksning nazariy fizik-kimyoviy xossalari aniqlandi (5-jadvalga qarang). Olingan natijalar asosida, quyidagi xulosalar topildi:

(I) β-SDoFDA ning protonlangan shakli yuqori elektromanfiy molekula ekanligi aniqlandi. Korroziyadan himoya qilish mexanizmida protonlangan molekulalar metall sirti bilan o‘zaro ta’sirlashadi.



9-rasm. β-SDoFDA ingibitorining neytral va protonlangan shakllarining optimallashtirilgan tuzilishlari, LUMO va HOMO sohalari, molekulyar elektrostatik potensial (MEP).

(II) β-SDoFDA ning kimyoviy qattiqlik va yumshoqlik xususiyatlari protonlanish jarayonlari bilan o‘zgaradi. Chunki aminoguruhlarning protonlanishi β-SDoFDA kimyoviy qattiqligi va yumshoqligiga ta’sir qiladi. Bu o‘zgarishlar β-SDoFDA ning ingibirlash xossalariga ta’sir qiladi.

5-jadval

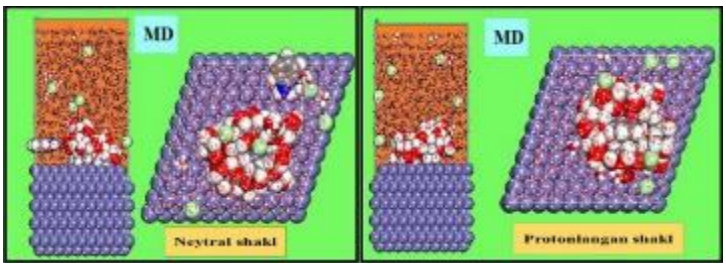
Neytral va protonlangan β-SDoFDA supramolekulyar kompleksning nazariy topilgan fizik-kimyoviy xossalari

Fizik-kimyoviy xossalari	Neytral shakl	Protonlangan shakl
I (eV), Molekulyar ionlanish potensiali	4,397	6,104
A (eV) Elektron yaqinligi	0,224	1,719
χ (eV) Elektron manfiyligi	2,310	3,911
η (eV) Kimyoviy qattiqlik	2,086	2,192
σ (eV) Kimyoviy yumshoqlik	0,479	0,456
ΔN Elektron almashish miqdori	0,321	0,336
ΔE Elektron fraksiya miqdori	-0,521	-0,548

(III) ΔN va ΔE ning qiymatlari protonlangan shaklda yuqori ekanligi aniqlandi. Bu xossa β-SDoFDA ning korroziyaga qarshi xossaga ekanligini tasdiqlaydi.

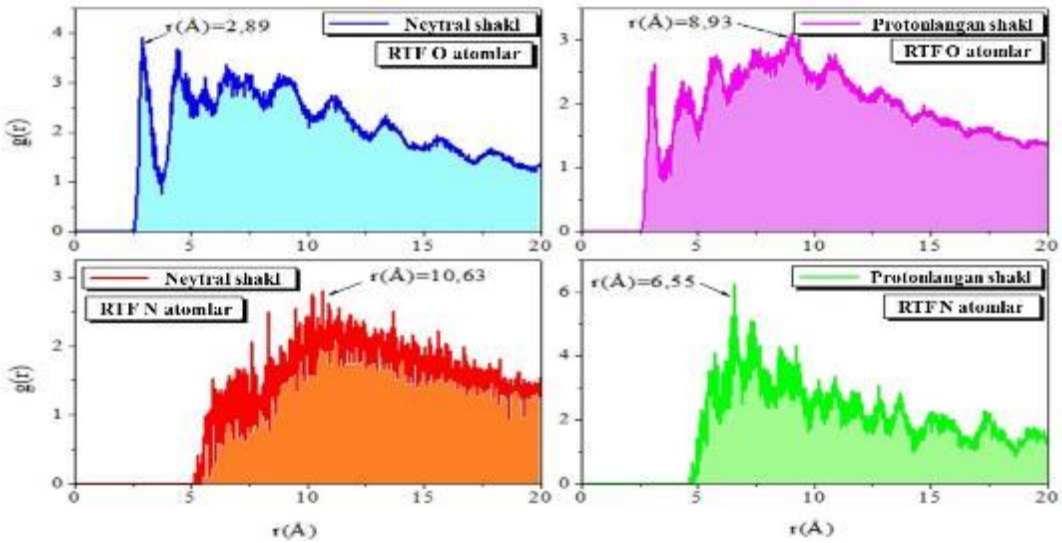
Molekulyar dinamik simulyatsiyasi. MD simulyatsiya natijasida β-SDoFDA ingibitorining neytral va protonlangan shakllarini Fe (110) sirtida adsorbsion konfiguratsiyalari topildi (10-rasmga qarang). Olingan natijalar shuni ko‘rsatdiki, mehmon molekulasining aminoguruhlari va β-SD ning gidroksil funksional

guruhlari po‘lat 20 sirtiga adsorbsiyalanishini taminlaydigan asosiy markazlar hisoblanadi. β-SDoFDA ingibitorining neytral va protonlangan shakllari metall sirtiga parallel adsorbsiyalanishi ko‘rsatdi. Metall sirtiga xlorid ionlari va suv molekulalarining ta’sirini hosil bo‘lgan himoya qatlam keskin kamaytirishi natijasida korroziyani kamayishiga erishilgan. Tanlangan ingibitor metall sirtida hosil qilgan barqaror mustahkam qavat evaziga boshqa agressiv ionlari va metall sirti o‘rtasida himoya to‘siq hosil qiladi. Natijada, metallning eritma bilan ta’sirlanishi kamayib ketadi. β-SDoFDA ingibitorining neytral va protonlangan shakllarining MD simulyatsiya qilish jarayonini harorat o‘zgarishiga bog‘liqligi aniqlandi.



10-rasm. β-SDoFDA ingibitorining neytral va protonlangan shaklarini Fe (110) sirtida adsorbsiyasini MD simulyatsiyasi orqali topilgan natijalari.

Olingan natijalardan ma’lum bo‘ldiki, tanlangan supramolekulyar sistemalarning MD simulyatsiyasi harorat o‘zgarishiga nisbatan chidamliligi aniqlandi. Harorat o‘zgarishi bilan deyarli metall yuzasida ingibitorning adsorbsiyasi o‘zgarmaganligi dalillandi. MD simulyatsiyasi natijalarida radial tarqalish funksiyasi (RTF) tahlili amalga oshirildi natijada Fe (110) sirtida Fe-N va Fe-O bog‘lanish qiymatlari nazariy jihatdan hisoblab chiqildi (11-rasmga qarang).



11-rasm. MD simulyatsiyasi orqali olingan Fe(110) sirtida β-SDoFDA ingibitorining neytral va protonlangan supramolekulyar kompleksning N hamda O atomlarining RTF qiymatlari.

MD simulyatsiyasi usuli orqali olingan β-SDoFDA ingibitorning neytral va protonlangan supramolekulyar kompleksning Fe(110) sirtida adsorbsiyalanishi natijasida Fe-O va Fe-N bog‘larining hosil bo‘lishi RTF usuli yordamida topildi. Olingan natijalardan ma’lum bo‘ldiki, neytral shaklda Fe-O uchun bog‘lanish

uzunligi 2,89 Å va Fe-N uchun 10,63 Å. Protonlangan shaklda esa Fe-O uchun bog‘lanish uzunligi 8,93 Å va Fe – N uchun 6,55 Å ekanligi aniqlandi. Ushbu hodisa O va N atomlarining metall sirti bilan yaxshi o‘zaro ta’sirlanishi natijasida kuchli kimyoviy bog‘lar hosil qilishini tasdiqlaydi.

XULOSALAR

1. Beta siklodekstrin asosida kompleks tipidagi yangi β-SDoFDA, β-SDME, β-SDDFK, β-SDNA va β-SDAS supramolekulyar ingibitorlar sintez qilindi. β-SD aminlar bilan mezbon-mehmon turdagi komplekslar hosil qilishi va ularning tuzilishi IQ, ^{1}H YaMR, Raman spektroskopiya va TGA usullari yordamida isbotlandi.

2. Gravimetrik usul yordamida 0,5 M HCl li muhitda ingibitorlar samaradorligi turli konsentratsiya va haroratlarda o‘rganildi. 100 mg/l konsentratsiyali β-SDoFDA bilan ingibirlash jarayonning E_f (57,72 kJ/mol) va ΔH_f (55,08 kJ/mol) qiymatlari po‘lat 20 korroziyasi uchun yuqori energetik to‘siq yaratishi, shuningdek, adsorbsiya jarayoninig termodinamik funksiyalari (ΔG^{o}_{ads}=-26,52 kJ/mol) qiymatlaridan esa jarayonda bir vaqtning o‘zida fizikaviy va kimyoviy adsorbsiya borishi aniqlandi.

3. Potensiodinamik qutblanish va elektrokimyoviy qarshilik spektroskopiya usullari yordamida supramolekulyar komplekslar katod (β_a=185,6 mV) hamda anod ($-\beta_k$=152,6 mV) jarayonlariga ta’sir qilishi aniqlandi. Bu ta’sirlar ingibitorlarning metall yuzasida himoya qavati hosil qilishini, shuningdek, metall yuzasi va muhit zarrachalari o‘rtasidagi aloqani maksimal darajada kamayishini isbotladi.

4. Ingibirlanmagan va ingibirlangan muhitlarda po‘lat 20 ning sirt morfologiyasi SEM, EDS, AKM va Raman spektroskopiya yordamida tahlil qilindi. Ingibitorlar metall yuzasida yupqa himoya qavati hosil qilishi va bu qavat po‘lat 20 yuzasini suv hamda boshqa agressiv ionlaridan yuqori darajada himoyalashi aniqlandi.

5. Zichlik funksional nazariyasi yordamida supramolekulyar komplekslarning protonlangan shakllari yaxshi ingibirlash xossasiga ega ekanligini isbotladi. Molekulyar dinamik simulyatsiya yordamida bog‘ uzunliklari (β–SDoFDA ingibitorida Fe-O 8,93 Å va Fe-N 6,55 Å) aniqlandi.

6. O‘rganilgan ingibitorlar “Navoiy kon-metallurgiya kombinati” AJ da, “Olmaliq kon-metallurgiya kombinati” AJ da va “GISSARNEFTGAZ” O‘zbekiston-Shveysariya qo‘shma korxonasida yopiq aylanma metall konstruksiyalari hamda qurilmalarida korroziya jarayoniga qarshi ingibitor sifatida sinovdan o‘tkazildi va joriy etishga tavsiya qilindi.

THE ONE-TIME SCIENTIFIC COUNCIL BASED ON THE SCIENTIFIC COUNCIL ON AWARD OF SCIENTIFIC DEGREES DSc.03/30.12.2019.K.01.03 AT THE NATIONAL UNIVERSITY OF UZBEKISTAN

NATIONAL UNIVERSITY OF UZBEKISTAN

ELIBOEV ILYOS ASKAROVICH

ELECTROCHEMICAL AND ADSORPTION PROPERTIES OF SUPRAMOLECULAR COMPLEXES BASED ON CYCLODEXTRIN

02.00.04. – Physical chemistry
02.00.11 – Colloid and membrane chemistry

DISSERTATION ABSTRACT OF THE DOCTOR OF PHILOSOPHY (PhD) IN CHEMICAL SCIENCES

Tashkent – 2024

The title of the doctor of philosophy (PhD) has been registered by the Supreme Attestation Commission at the Ministry of Higher education, science and innovations of the Republic of Uzbekistan with registration number B2022.4.PhD/K560.

The dissertation has been carried out at the National University of Uzbekistan

The abstract of dissertation in three languages (Uzbek, English and Russian (resume)) is available online of Scientific council (www.ik-kimyo.nuuz.uz) and on the website of "ZiyoNET" information-educational portal (www.ziyonet.uz).

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Leading organization:	**Institute of General and Inorganic Chemistry**

The defense of the dissertation will take place on "06" 04 2024 in "11^{00}" at the meeting of Scientific Council DSc.03/30.12.2019.K.01.03 at National University of Uzbekistan (Address: 100174, Tashkent, University street. 4. Ph.: (99871) 227-12-24; fax: (99824) 246-02-24; e-mail ilmiy_kengash@nuu.uz).

The dissertation has been registred at the Informational Resource Centre of National University of Uzbekistan under № 20 (Address: 100174, Tashkent, University street 4. Ph.: (99871) 227-12-24), fax: (99824) 246-02-24; e-mail: nauka@nuu.uz).

The abstract of the dissertation has been distributed on "12" 03 2024 year
Protocol at the register № 16 dated "11" 03 2024 year

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INTRODUCTION (abstract of PhD dissertation)

The relevance and importance of the dissertation title. Today, the importance of having high efficiency in various acidic environments to protect metals from corrosion is recognized globally, alongside the development of import-substituting inhibitors. Technical and industrial advancements have led to an increasing demand for metals, which, in turn, fuels the need for effective corrosion inhibitors. Special emphasis is being placed on creating environmentally friendly, economically viable supramolecular complex-type inhibitors, moving away from toxic, high-concentration compounds. Crucial to this effort is the development of inhibitors that form a solid protective layer on metal surfaces, effective in low concentrations and across various temperature ranges.

The rising global demand for metal corrosion inhibitors highlights the advisability of developing new, universal inhibitors based on organic and supramolecular compounds. Addressing these challenges involves producing inhibitors with specific properties from local raw materials, a significant scientific endeavour. Emphasis is also on reducing metal corrosion through green inhibitors derived from organic plant-based substances.

In our republic, there is a strong focus on advancing innovative technologies and fostering the swift and stable growth of the industry. As part of these efforts, notable progress is being made in various aggressive environments, including water cooling/heating systems and the oil and gas industry, establishing scientific foundations for protecting metal materials from corrosion. The new development strategy for Uzbekistan sets out key objectives for the rapid growth of the national economy and achieving high growth rates[3]. In this context, creating import substitutes that are competitive, compliant with global quality standards, efficient in low concentrations, safe, and biodegradable is a pressing task.

The decrees issued by the President of the Republic of Uzbekistan, including № PF-6244 of June 9, 2021, on enhancing industrial potential in regions, №. 60 of January 28, 2022, on the New Uzbekistan development strategy for 2022-2026, PQ-4805 of August 12, 2020, on improving the quality of continuing education and science productivity in chemistry and biology, and PQ-3264 of August 29, 2017, on improving export-import activities in the chemical industry, as well as the outcomes of this dissertation, will contribute significantly to the implementation of these initiatives.

The conformity of research with priority directions of development of science and technologies of the Republic. This work is related to the development of science and technology of the Republic, specifically under the VII plan. It is being carried out in accordance with the priorities of “Chemical Technology and Nanotechnology”.

The degree of study of the problem. Most of the research conducted by scientists worldwide is focused on the development of a new generation of corrosion inhibitors. A literature review reveals that extensive work has been dedicated to electrochemical methods involving various materials as inhibitors (Guo et al., Fan

[3] Decree of the President of the Republic of Uzbekistan “On the innovative development strategy of the Republic of Uzbekistan in 2022-2026” PF-165 on July 6, 2022.

et al., Verma et al., Dehghani et al., Dagdag et al., Damien et al., Berge et al., Wang et al., Burstein et al., and Mattos et al.). Currently, a wide range of physical, chemical, electrochemical, and other methods have been developed for researching corrosion inhibitors. However, with the advancement of technology, particular attention is being given to scientific investigations into the mechanisms of organic compounds as inhibitors in the corrosion process and their impact on the surface of steel.

Scientists from Uzbekistan, including Tillayev, Tadjikhodjayev, Kurbanov, Djalilov, Ikramov, Yusupov, Akbarov, Guro, Kholikov, Kadyrov, Eshmamatova, Berdimurodov, and others, have made significant contributions to addressing the challenge of protecting metals from corrosion and synthesizing novel chemical compounds for use as inhibitors. However, the mechanisms by which cyclodextrin-based supramolecular complexes interact with the surface of Steel 20 in strongly acidic environments have not been studied.

The connection of investigation with plans of science-investigated works of the science-investigate institution where dissertation was carried out. The research dissertation with the reference number A-12-46 titled “Improving the Effectiveness of Anticorrosion Polyelectrolytes and Its Application in Practice” was conducted as part of a hands-on project in accordance with the research work plan of the National University of Uzbekistan (2015-2017). The objective of the study was to enhance the efficiency of polyelectrolytes as anticorrosion agents and explore their practical applications.

The purpose of the study is to synthesis of cyclodextrin-based supramolecular complexes and investigate their corrosion inhibition properties for steel in aggressive acidic solutions with the electrochemical and adsorption properties.

The tasks of the research work are:

synthesis of cyclodextrin-based supramolecular complexes and confirm their structure based on IR, 1H NMR, Raman spectroscopy and TGA methods.

investigate the adsorption efficiency, protection levels, activation, and thermodynamic properties of the cyclodextrin-based inhibitors using the gravimetric method.

examine the effectiveness of the inhibitors in strongly acidic environments for Steel 20 samples through the utilization of potentiodynamic polarization and electrochemical resistance spectroscopy methods.

study the effects of the inhibitors on structural changes on metal surfaces by employing electron microscopes, quantum-chemical computations, and Raman spectroscopy.

investigate the corrosion inhibition mechanism, interactions between the metal surface and inhibitors by DFT, MC and MD simulations methods.

conduct laboratory tests to evaluate the effectiveness of the newly developed inhibitors and facilitate their implementation in the oil and gas industry, particularly within mining and metallurgical operations.

The objects of the research work is that beta-cyclodextrin orthophenylenediamine (β-CDoPhDA), beta-cyclodextrin melamine (β-CDME),

beta-cyclodextrin supramolecular complexes of 1,5-diphenylcarbazide (β-CDDPhC), beta-cyclodextrin naphthylamine-1 (β-CDNA), and beta-cyclodextrin acetanilide (β-CDAA) have been successfully synthesized and obtained for the purpose of this study.

The subject of investigation encompasses the investigation of general mechanisms governing the corrosion protection and reduction of metal thinning.

The methods of research. The dissertation work employed a wide range of analytical techniques and methodologies, including infrared spectroscopy, Raman spectroscopy, proton nuclear magnetic resonance spectroscopy, thermogravimetric analysis, gravimetric analysis, potentiodynamic polarization, electrochemical resistance spectroscopy, scanning electron microscopy, energy-dispersion spectroscopy, atomic force microscopy, density functional theory, Monte Carlo simulations, and molecular dynamics simulations.

The scientific novelty of the study consists of:

In the initial phase of the study, supramolecular complexes, namely β-CDoPhDA, β-CDME, β-CDDPhC, β-CDNA, and β-CDAA, were discovered to exhibit significant effectiveness as corrosion inhibitors for Steel 20, presenting novel approaches to corrosion protection.

The synthesized supramolecular complexes demonstrated remarkable properties, including a reduction in corrosion current density (i_{corr}= 0.85 μA/cm^2), enhanced charge-sharing resistance (R_{ct} = 126.4 Ω/cm^2), high levels of protection ($\eta_{Grav.}$= 96.93), and improvements in surface coating ($\theta_{Grav.}$ = 0.97), as indicated by increasing values.

The mechanisms underlying the thinning effects of the supramolecular complexes were identified through quantum chemical computations, as well as through the analysis of atomic force microscopy (AFM) and scanning electron microscope (SEM) microphotographs of metal surfaces, energy-dispersion spectroscopy (EDS), and Raman spectra.

By conducting Monte Carlo simulations, the adsorption positions of the neutral and protonated forms of the inhibitor onto the metal surface were determined.

Significantly, for the first time, the theoretical calculation of the interaction between the supramolecular complex and the Fe surface in β–CDoPhDA was accomplished using molecular dynamics (MD) simulation. The bond length between Fe and N was measured as 8.93 Å, while the bond length between Fe and O was determined to be 6.55 Å.

The practical results of the study include:

The research objects have demonstrated significant effectiveness in protecting against corrosion when applied at a concentration of 100 mg/l. Furthermore, these objects have exhibited excellent adsorption capabilities on metal surfaces. Notably, the utilization of β-cyclodextrin-based supramolecular complexes has resulted in a remarkable cross-synergistic action, resulting in up to 97% protection for Steel 20-composition equipment.

In practical applications, such as in the Navoi and Olmalik mining metallurgical combines, β-CDoPhDA, β-CDME, β-CDDPhC, β-CDNA, and β-CDAA supramolecular complexes have proven to be effective corrosion inhibitors

for metal structures used in water circulation systems, as well as cooling and heating systems.

The reliability of obtained results. All the findings obtained throughout the course of the study were validated using state-of-the-art techniques including infrared spectroscopy, Raman spectroscopy, proton nuclear magnetic resonance spectroscopy, thermogravimetric analysis, gravimetric analysis, potentiodynamic polarization, electrochemical resistance spectroscopy, scanning electron microscopy, energy-dispersion spectroscopy, atomic force microscopy, density functional theory, Monte Carlo simulations, and molecular dynamics simulations. Additionally, the results were disseminated through the publication of four research papers in high-impact factor foreign journals listed in the Scopus database.

The scientifically and practical value of results of the research.

The research results hold scientific significance due to several key findings. Firstly, the synthesis of β-CDME, β-CDDPhC, β-CDNA, and β-CDAA supramolecular complexes in β–CD of is noteworthy. Additionally, the corrosion rate of Steel 20 in a 0.5 M HCl solution, at a concentration of 100 mg/l/0.08 mM, was determined to be $CR_{Grav.}$=0.042. Moreover, the study yielded important values for the protection level ($\eta_{Grav.}$=96.7) and surface coverage level ($\theta_{Grav.}$=0.97), along with the identification of the thinning mechanism.

The practical significance of these research findings lies in the application of cyclodextrin-based derived supramolecular complexes. These complexes play a crucial role in protecting metal structures in water circulation systems, cooling and heating systems, and even in highly acidic and aggressive environments prevalent in the oil and gas industries. Notably, the supramolecular complexes effectively safeguard Steel 20 samples from corrosion, ensuring their long-term structural integrity and optimal performance.

Implementation of the research results. Based on the scientific results obtained from the study on the corrosion thinning mechanisms of cyclodextrin-based derived supramolecular complexes in strongly acidic environments using gravimetric, electrochemical, surface analysis methods, and quantum chemical computations:

Cyclodextrin-based supramolecular complexes, including β-cyclodextrin orthophenylenediamine, β-cyclodextrin melamine, β-cyclodextrin 1,5-diphenylcarbazide, β-cyclodextrin naphthylamine-1, and β-cyclodextrin "GISSARNEFTGAZ" from acetanilides, were tested as anti-corrosion inhibitors in metal structures and devices at the Joint Venture Laboratory of Uzbekistan-Switzerland (Reference № 730-01/11 of the joint venture of Uzbekistan-Switzerland "GISSARNEFTGAZ" dated November 06, 2023). Laboratory testing revealed that these supramolecular complexes provide a high degree of protection and surface coating at high temperatures and low concentrations. They exhibit superior corrosion protection performance compared to industry-standard inhibitors in strongly acidic environments. Therefore, they are recommended for practical implementation in areas where metal structures require protection.

The tested supramolecular complexes based on cyclodextrin were also evaluated at the Central Research Laboratory of Navoi Mining and Metallurgical

Combine Joint Stock Company ("Navoi Mining and Metallurgical Combine" of JSC dated November 13, 2023, reference № 23/01-01-07/575). The results demonstrated that these research materials offer higher corrosion protection for metals at various temperatures and acidic environments compared to industry-standard inhibitors.

Furthermore, on a trial basis, 100 mg/l solutions of cyclodextrin-based derived supramolecular complexes were implemented as corrosion-preventing agents for metal structures used in water circulation systems, cooling, and heating systems of sulfuric acid workshop № 1 at the "Mining-Metallurgical Combine" AJ zinc plant (Reference №. 1282 of "Mining-Metallurgical Combine" AJ dated November 16, 2023). The effectiveness of these compounds as inhibitors in preventing corrosion of metal structures in water circulation systems, cooling, and heating systems was positively assessed.

Additionally, the project on the topic "synthesis and physico-chemical properties of aliphatic and heterocyclic metal corrosion inhibitors based on Aminomethylenphosphatic acid" (№. 7-F7-85) examined the corrosion protection properties of new supramolecular complexes and their adsorption mechanisms (No. 03/10-2023) under the Ministry of Higher Education, Science, and Innovation of the Republic of Uzbekistan dated August 23, 2023. The results enabled the use of selected inhibitors in the oil and gas industry for protecting metal materials from corrosion.

Approbation of the research results. The results of this study were reported and discussed at 8 Scientific and practical conferences, including 4 international and 4 Republican.

The publication of results of investigation. On the topic of the dissertation, 5 scientific works were published, among which 1 article was published in Republican and 4 articles in foreign (Scopus-based) journals in scientific publications, where it was recommended to publish the main scientific results of the doctor of Philosophy (PhD) dissertations of the Higher Attestation Commission of the Republic of Uzbekistan.

The structure and volume of dissertation. The dissertation consists of an introduction, 5 chapters, a conclusion, A list of used literature and an appendix. The volume of the dissertation is 118 pages[4].

MAIN CONTENT OF DISSERTATION

In the introduction, the relevance and necessity of the conducted studies are established, the goals and objectives are presented, and the subject and object of the research are described. It is emphasized that the study aligns with the priorities of the development of Republican Science and Technology. Additionally, the scientific novelty and practical significance of the research results are highlighted.

The first chapter of the dissertation, titled **"Green corrosion inhibitors based on beta cyclodextrin: recent scientific advances, innovations, and opportunities"** focuses on the literature review. It discusses the main properties, effects, and corrosion protection provided by beta cyclodextrin modifications with natural polymers as environmentally friendly and effective corrosion inhibitors. The

[4] The author expresses sincere gratitude to Doctor of Chemical Sciences, Professor Akbarov Kh.I. for scientific advice during the dissertation work.

chapter also provides information on supramolecular (host-guest) complexes based on beta cyclodextrin and their mechanisms, including oxygen and nitrogen-retaining cyclodextrin-based supramolecular inhibitors. A comparative discussion on the ongoing work in our republic and foreign researchers regarding the prevention of corrosive processes in an acidic environment is included. Based on the literature analysis, cyclodextrin-based supramolecular inhibitors are found to exhibit high efficiency.

The second chapter of the dissertation, titled **"Materials, synthesis, and research methods of cyclodextrin-based supramolecular complexes"** presents the composition, structure, dimensions, and composition of the Steel 20 sample used in the materials section. The reaction equations and synthesis conditions for beta cyclodextrin orthophenylenediamine (β–CDoPhDA), beta cyclodextrin melamine (β–CDME), beta cyclodextrin 1,5-diphenyl carbazide (β–CDDPhC), beta cyclodextrin acetanilide (β–CDAA), and beta cyclodextrin naphthylamine-1 (β–CDNA) compounds are provided. The chapter further includes data from various analytical techniques such as infrared spectroscopy, Raman spectroscopy, proton nuclear magnetic resonance spectroscopy, gravimetric analysis, potentiodynamic polarization, electrochemical resistance spectroscopy, scanning electron microscopy, energy-dispersion spectroscopy, atomic force microscopy, density functional theory, Monte Carlo simulations, and molecular dynamic simulations.

The third chapter of the dissertation, titled **"Analysis of the structure of synthesized inhibitors"** focuses on the IQ spectroscopy analysis of the synthesized supramolecular complexes and presents data from ^{1}H NMR and infrared spectrum studies of the β–CD and β–CDoPhDA supramolecular complexes (see Figure 1).

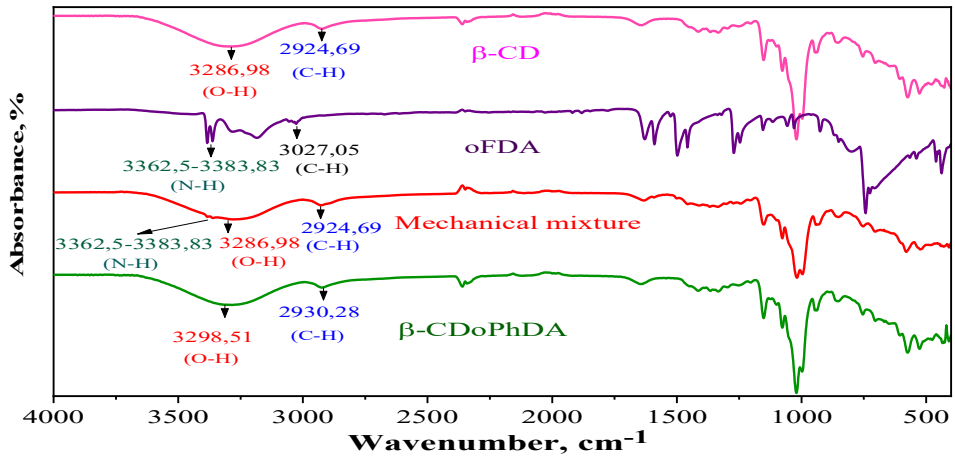


Figure 1. IR spectra of supramolecular complex in β–CD, oPhDA, mechanical admixture, and β–CDoPhDA.

The resulting IR spectrum of the supramolecular complex exhibited varying degrees of variation compared to the IR spectra of the original substances. For example, the absorption range of valence oscillations of the O-H group shifted from 3286.98 cm^{-1} to 3298.51 cm^{-1}, and the absorption range of valence oscillations of the C-H group shifted from 2924.69 cm^{-1} to 2930.28 cm^{-1}. These shifts indicate that oPhDA is incorporated into the β–CD space, amplifying the O-H oscillation. This observation suggests the presence of hydrophobic and Van der Waals interactions within the supramolecular complex.

The results and analysis of the ^{1}H NMR spectra of the supramolecular complexes in β–CD and β–CDoPhDA are presented. The ^{1}H NMR spectra of the complex in β–CD and β–CDoPhDA are shown, and the corresponding chemical shifts of different protons are provided (see Figure 2). The change in the state of the H3 and H5 atoms within the hydrophobic space of β–CD serves as evidence that oPhDA molecules are introduced into the β–CD space. Additionally, the value of H4 "δ" slightly decreased after the introduction of oPhDA molecules. Based on the observed shifts, two conclusions can be drawn. First, the hydrogen signals of the electronegative group (-NH_2) of oPhDA, stretching from the side occupied by H4 and H6, contribute to an increased protective effect. Secondly, the chemical shifts of protons H3 and H5, located in the β–CD cavity, are influenced by Van der Waals and hydrophobic interactions between the phenylene ring and the hydrophobic inner cavity of β–CD.

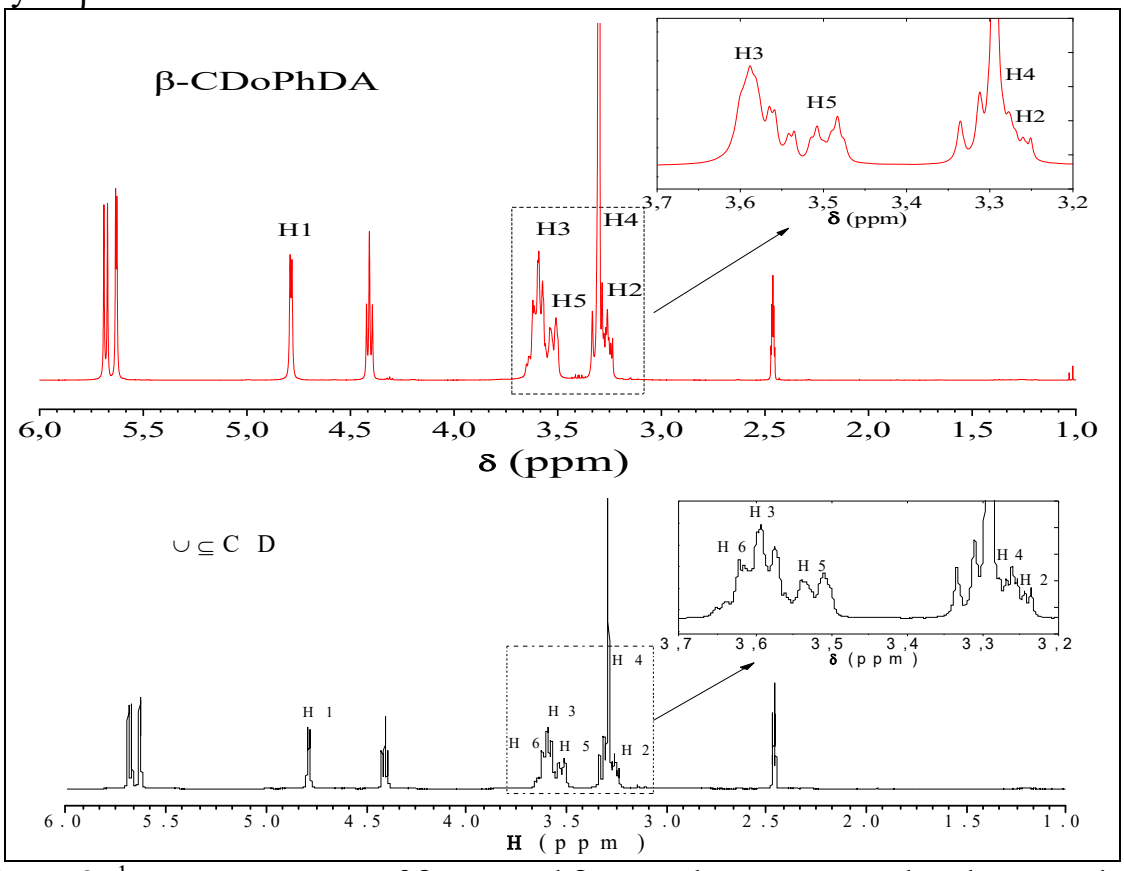


Figure 2. ^{1}H NMR spectra of β-CD and β-CDoPhDA supramolecular complex.

The **fourth chapter of the dissertation**, titled "**Research on the effectiveness of obtained inhibitors against metal corrosion**" presents an analysis of the practical and theoretical data obtained to study the corrosion inhibitory properties of the supramolecular complexes.

The chapter begins by discussing the determination of changes in the thermodynamic sizes of the system during corrosion and thinning processes. For an aggressive acid solution containing chloride ions, the value of E_a is calculated to be 8.7192 kJ/mol (see Table 1).

In 0.5 M HCl systems, the value of E_a is found to be 57.72 kJ/mol at 100 mg/l/0.08 mM. This indicates that in a thinned environment, E_a is higher compared to an unthinned solution. The increased E_a value is attributed to the inhibitor's ability

to create energy barriers for corrosion processes through chemical adsorption on the metal surface. In thinned 0.5 M HCl solutions, the values of ΔH_a confirm that the corrosion process is endothermic. The introduction of the inhibitor raises the energy required for the corrosion process to occur, making the corrosion process more challenging to proceed.

The value of ΔS_a is determined in a 0.5 M HCl background solution (-379.55 kJ/mol t) and in a solution of 100 mg/l/0.08 mM (-245.71 kJ/mol t) for the injected inhibitor solution. The ΔS_a values confirm the stability of the activated inhibitor-metal complex and its association.

Table 1.

Values in thermodynamic functions of activation for uninhibited and inhibited systems (β-CDoPhDA).

Thermodynamic functions	Blank	25 mg/l/ 0.02 mM	50 mg/l/ 0.04 mM	75 mg/l/ 0.06 mM	100 mg/l/ 0.08 mM
E_a, kJ/mol	8.72	19.14	24.25	34.55	57.72
ΔH_a, kJ/mol	6.08	16.5	21.61	31.91	55.08
ΔS_a, kJ/mol×T	-379.55	-360.12	-345.3	-314.85	-245.71
$E_a - \Delta H_a$, kJ/mol	2.64	2.64	2.64	2.64	2.64

The determination of kinetic adsorption indicators for the thinning process is discussed in this section. According to the data presented in Table 2, the K_{ads} values are found to be 170.06 M^{-1} at 303 K, 205.76 M^{-1} at 313 K, 256.41 M^{-1} at 323 K, and 259.74 M^{-1} at 333 K. These high K_{ads} values confirm that in β–CDoPhDA, the inhibitor exhibits a high adsorption rate on the Steel 20 surface in a 0.5 M HCl solution. The low values of ΔG^o_{ads} confirm that in β–CDoPhDA, the inhibitor readily adsorbs onto the Steel 20 surface and effectively protects the metal surface from attack by aggressive Cl^- ions. The observed ΔG^o_{ads} values indicate that the adsorption of the inhibitor on the Steel 20 surface in β–CDoPhDA follows a mixed type adsorption mechanism. This means that the adsorption occurs based on both chemical and physical adsorption mechanisms. Chemical adsorption takes place through the exchange of heteroatoms *p*-electron pairs on the inhibitor molecule with the iron's free d-orbitals on the metal surface. Additionally, the positively charged regions of the inhibitor molecule interact with the negatively charged areas on the metal surface, which is known as physical adsorption.

Table 2.

Values in adsorption thermodynamic functions of β-CDoPhDA.

Temperature, K	K_{ads}, M^{-1}	ΔG^o_{ads}, kJ/mol	ΔH^o_{ads}, kJ/mol	ΔS^o_{ads}, J/mol K
303	170.06	-23.06	12.42	117.37
313	205.76	-24.32		
323	256.41	-25.68		
333	259.74	-26.52		

The ΔH^o_{ads} value, which is determined to be 12.42 kJ/mol for Steel 20 in a 0.5 M HCl solution, indicates that the adsorption of β–CDoPhDA is endothermic. Additionally, the ΔS^o_{ads} value is calculated to be 117.3 J/mol K, suggesting that the adsorption process is stable in the presence of the 0.5 M HCl solution. This stable

adsorption occurs as the inhibitor replaces pre-adsorbed Cl^- and water molecules on the metal surface, forming a protective adsorption layer.

Electrochemical methods were employed to investigate the effects of the inhibitor on corrosion processes, such as hydrogen evolution at the cathode and metal dissolution into cations at the anode. The potentiodynamic polarization method was utilized for this purpose, as shown in Figure 3 and Table 3. Based on the results obtained, the following conclusions can be drawn:

(I) Tafel curves for unprotected systems exhibit regions with high corrosion current density (i_{corr}). However, the formation of a protective layer due to the presence of the inhibitor leads to a shift in the Tafel curvature towards a reduction in i_{corr} and a sharp increase in polarization resistance. With increasing inhibitor concentration, this shift becomes more prominent. The decrease in i_{corr} indicates the formation of strong protective layers on the metal surface, effectively shielding it from corrosive environments and preventing metal corrosion.

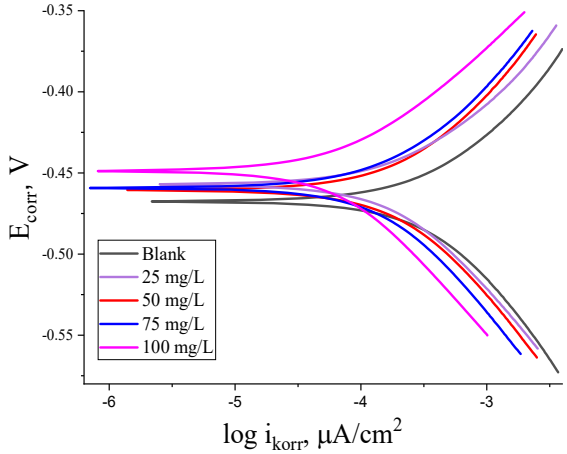


Figure 3. In a 0.5 M HCl solution of a working electrode made of Steel 20 Tafel curves for solutions with and without inhibitors in β–CDoPhDA

(II) In both protected and unprotected systems, the difference between corrosion potentials (E_{corr}) is below 40 mV, indicating mixed-type adsorption of β–CDoPhDA on the metal surface.

3-jadval

Calculated values of electrochemical parameters for solutions with and without inhibitors in β–CDoPhDA in 0.5 M hydrochloric acid (working electrode made of Steel 20).

Parameters	C_{inh}, mg/l				
	Blank	25	50	75	100
i_{corr}, μA/cm^2	12.85	1.87	1.65	1.03	0.85
E_{corr}, mV	-479	-456	-459	-461	-452
β_a, mV	275.6	251.9	234.1	201.5	185.6
$-\beta_c$, mV	230.9	221.7	201.5	184.1	152.6
η_{PDP}, %	-	85.44	87.15	91.98	93.38

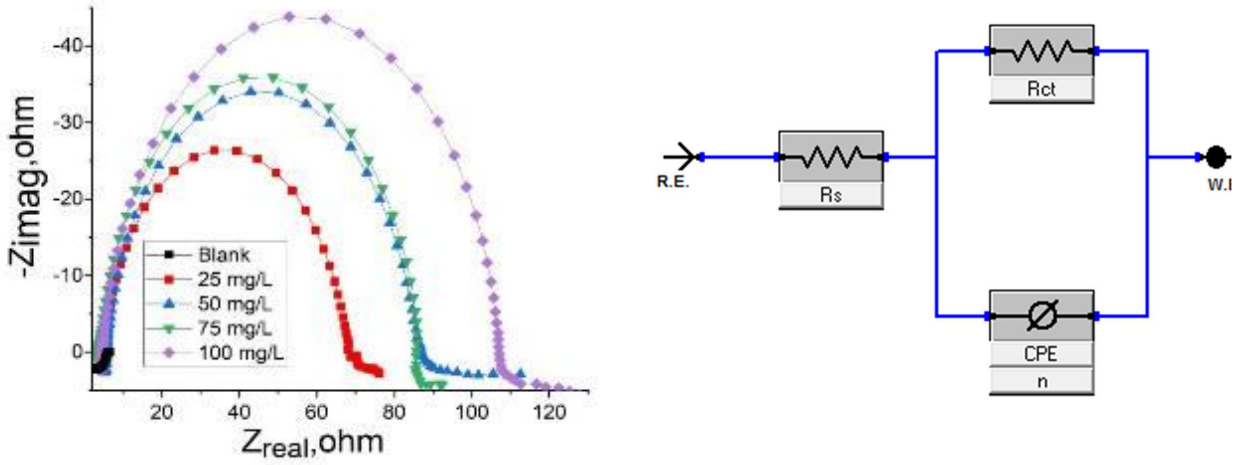
(III) In an unprotected system, the i_{corr} value is measured to be 12.85 μA/cm², indicating a high corrosion rate. However, with the addition of

β–CDoPhDA, the i_{corr} value decreases significantly to 0.85 μA/cm². This reduction in i_{corr} demonstrates the effectiveness of β–CDoPhDA in inhibiting corrosion. The corrosion protection efficiency is determined to be 93.38%. This indicates that the addition of β–CDoPhDA provides a high level of protection against corrosion, resulting in a significant reduction in the corrosion rate.

(IV) Tafel showed that polarization curves $(-\beta_c, \beta_a)$ shift left and ten with the addition of an inhibitor in β–CDoPhDA, which indicates that polarization processes reduced corrosion with the formation of a protective layer.

(V) corrosion in a solution with high polarization of the non-ingested metal surface goes at high speed. This is because the metal surface has low polarization resistance. in β–CDoPhDA, polarization resistance is dramatically increased due to the formation of protective layers compared to the solution with the addition of inhibitors.

Results obtained using the electrochemical resistance spectroscopy (EIS) method and their analysis. Using EIS analysis, Nyquist curves, Body and phase curves were obtained (see Figures 4, 5). These curves show how the processes of corrosion and thinning on the metal surface change the electrochemical kinetic parameters.

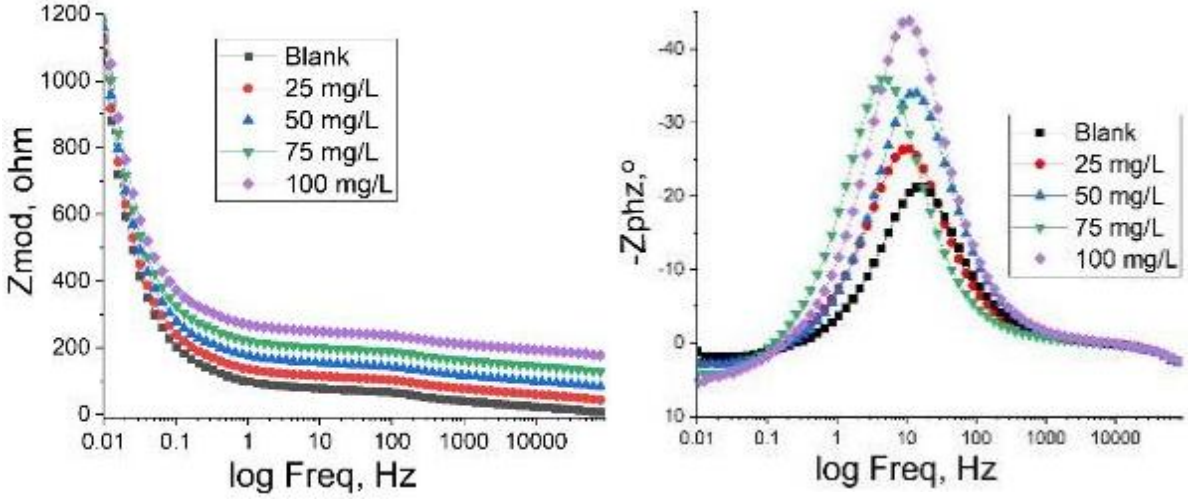


a **b**

Figure 4. 0.5 M in hydrochloric acid (working electrode made of Steel 20) for solutions with and without an inhibitor in β–CDoPhDA, the Nyquist plots (a) and the equivalent current Model (b).

Various electrochemical parameters related to electrochemical reactions, charge transport, corrosion, and thinning processes between the cathode and the anode were determined. Conclusions drawn from Nyquist eigenvalues suggest that an increase in concentration of β–CDoPhDA leads to a significant reduction in charge exchange between the cathode and anode regions. Furthermore, the Nyquist eigenvalues exhibited a substantial increase with the addition of β–CDoPhDA, indicating a decrease in the rate of charge transfer during the thinning process. The resulting Nyquist eigenvalues showed that the polarization plots were predominantly located in higher regions in an unprotected system, but this trend shifted to lower regions in a thinned environment. The Z_{mod} modifications exhibited remarkable

differences between protected and unprotected systems, as depicted in Figure 5a. The inclusion of β-CDoPhDAM in the corrosive system resulted in higher Z_{mod} values, while in the absence of an inhibitor, Z_{mod} values were observed in lower domains. These findings suggest that β-CDoPhDA possesses favorable thinning properties.



a **b**

Figure 5. 0.5 M in hydrochloric acid (working electrode made of Steel 20) Body (A) and phase angle (b) curves for solutions with and without inhibitors in β-CDoPhDA.

The electrochemical results are presented in Table 4, highlighting the significant impact of the inhibitor in β-CDoPhDA on charge-sharing processes between the cathode and the anode. This effect leads to the formation of a protective layer on the metal surface. The formation of bonds between the metal surface and the amino and hydroxyl groups present in the organic molecule contributes to this protective layer. Consequently, the interaction between the inhibitor and the metal surface may result in thinning of the metal surface due to the formation of these bonds.

Table 4

EIS parameters for solutions with and without inhibitors in β-CDoPhDA.

C_{inh}, mg/l	R_s, ohm/cm^2	$Y_0 \times 10^{-3}$, S-s^n/cm^2	n	R_{ct}, ohm/cm^2	η_{EIS}, %	C_{dl}, μF/cm^2	The goodness of Fit ×10^{-6}
Blank	0.38	51.32	0.8632	5.17	-	265.61	54.31
25	1.51	3.41	0.9247	47.85	89.1	156.14	41.25
50	1.76	2.31	0.9314	75.64	93.16	110.32	36.25
75	2.34	1.15	0.9531	93.21	94.45	88.32	21.25
100	3.14	0.87	0.9861	126.41	95.91	45.12	20.36

With the introduction of a very small amount of inhibitor, the charge-sharing resistance of unprotected systems decreases to 5.17 Ω/cm². However, with an increase in inhibitor concentration, this value increases to 126.64 Ω/cm². The n - values indicate the average surface smoothness of the metal. For an uncoated metal surface, n = 0.8632, but when the inhibitor is present, these values increase to n = 0.9861. The value of n is close to one, indicating that the cracks on the metal

surface are sealed and the surface becomes smoother. Due to the accumulation of salts, hydroxides, and corrosion products in the background solution, the double-layer capacitance (C_{dl}) is measured to be 265.61 µF/cm². However, the formation of a protective layer on the metal surface reduces the amount of corrosion products, resulting in a significant decrease in the value of (C_{dl}) to 45.12 µF/cm². This decrease in (C_{dl}) is associated with an increase in the thinness of the protective coating (d) and a decrease in the solution's permeability (ε-inhibitor) compared to the permeability of the medium (ε^0).

Raman spectroscopy was performed on the surface of Steel 20 to study the spectral variations of functional groups. The Raman scattering of the metal surface in the presence of β–CDoPhDA solution and in the background solution was analysed (refer to Figure 6). The results reveal the following details:

(I) Raman signals corresponding to the C-H and amino group (N-H) bonds of the aromatic ring of oPhDA were observed at 3106 cm^{-1} and 3046 cm^{-1}, respectively.

(II) Fe-N signals was detected at 1979 cm^{-1}, while C-N bond signals of oPhDA appeared at 1251 cm^{-1}. The glucose ring linear deformation of β–CD was identified at 422 cm^{-1}, C-O-C group at 470 cm^{-1}, and C-O bonds at 897 cm^{-1}. These details indicate the adsorption of β-CDoPhDA on the metal surface, forming Fe-O bonds.

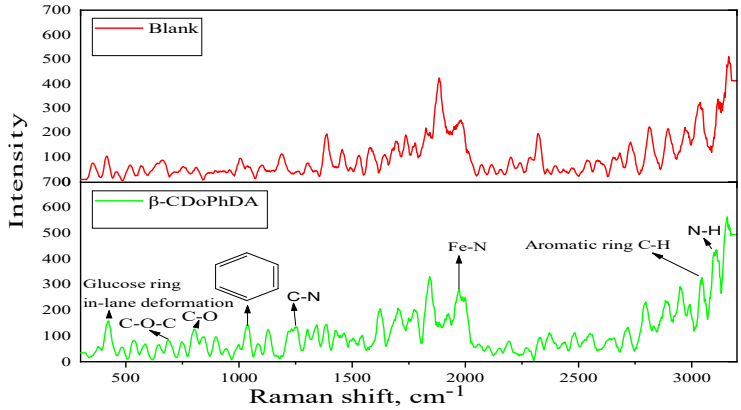


Figure 6. Raman spectra of a metal surface that is not thinned and is thinned by the β-CDoPhDA supramolecular complex.

The images obtained from scanning electron microscopy and their analysis (refer to Figure 7rasm) revealed that in β-CDoPhDA, the corrosion products and decay of steel in a non-thinned medium resulted in a thinned appearance (C-100 µm) when observed under the scanning electron microscope.

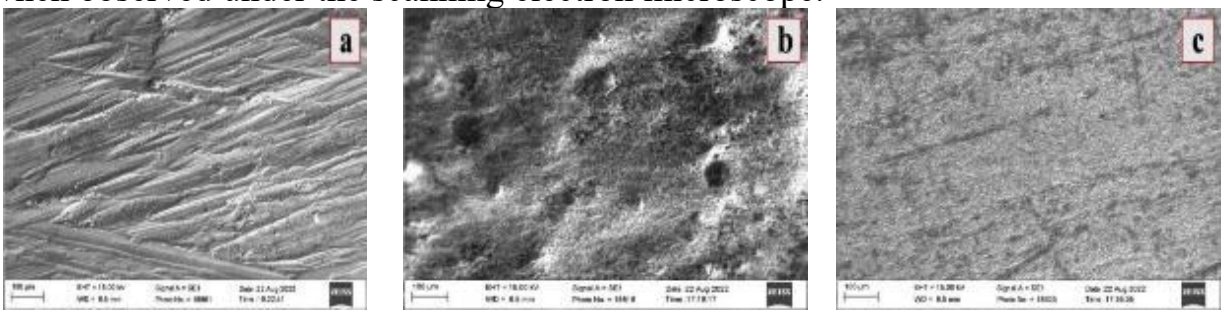


Figure 7. SEM pictures: (a) Clean metal surface of steel before immersion at 100 µm, (b) corroded surface of steel at 100 µm, (c) inhibited metal surface by β-CDoPhDA at 100 µm

It was observed that complex compounds are formed through the chemical and physical adsorption of the inhibitor in β-CDoPhDA onto the steel surface in the background solution. The formation of these complexes on the thinned steel surface led to a significant decrease in its corrosive nature and an increase in its stability against various environmental factors.

The results of energy-dispersion spectroscopy (EDS) and their analysis were conducted. According to the EDS analysis of the metal surface in a non-toxic environment, the oxygen (O) content was found to be significantly higher (28.5%), while the iron (Fe) content was much lower (68.1%), indicating severe oxidation of the Steel 20 surface (see Figure 8). However, after the addition of inhibitors to the corrosion solution in β-CDoPhDA, there was a notable increase in the Fe content (77%) and a significant decrease in the concentration of oxygen (8.6%). This indicates that the metal surface was almost non-oxidized, meaning it was not corroded. The presence of oxygen atoms can be attributed to the adsorption of β–CDoPhDA on the Steel 20 surface. Additionally, there was a sharp increase in the carbon (C) content (9.8%) in Steel 20, providing further evidence of the adsorption of β–CDoPhDA on the surface of Steel 20.

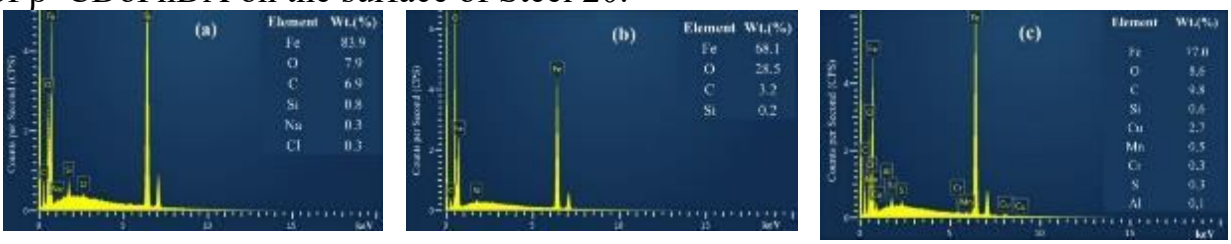


Figure 8. EDS results of early (a), corrosive (b), and β-CDoPhDA ingested(c) plates of the metal surface.

The fifth chapter of the dissertation is titled **"Quantum Chemical Analysis of the Thinning Process"** and it presents the data obtained from the quantum chemical analysis of synthesized supramolecular complexes.

Density functional theory (ZFN) analyses were conducted on both neutral and protonated forms of β–CDoPhDA. The results obtained from this method revealed that the protective properties of corrosion inhibitors are dependent on their structure and physicochemical properties. The optimized structures of the neutral and protonated forms of the inhibitor, as well as the LUMO (lowest unoccupied molecular orbital), HOMO (highest occupied molecular orbital), and molecular electrostatic potential (MEP) structures, were obtained for β–CDoPhDA (refer to Figure 9). The optimized structures of β–CDoPhDA indicated that the inhibitor exhibits a high polarization index, which suggests its strong thinning properties in β-CDoPhDA. The thinning properties are influenced by the steric parameters, positions of functional groups, and the characteristics of aromatic rings and heteroatoms in the optimized neutral or protonated forms of oPhDA within the β–CD space.

In β–CDoPhDA, the theoretical physicochemical properties of the neutral and protonated supramolecular complex of the inhibitor were determined (refer to Table 5). Based on the obtained results, the following conclusions were drawn:

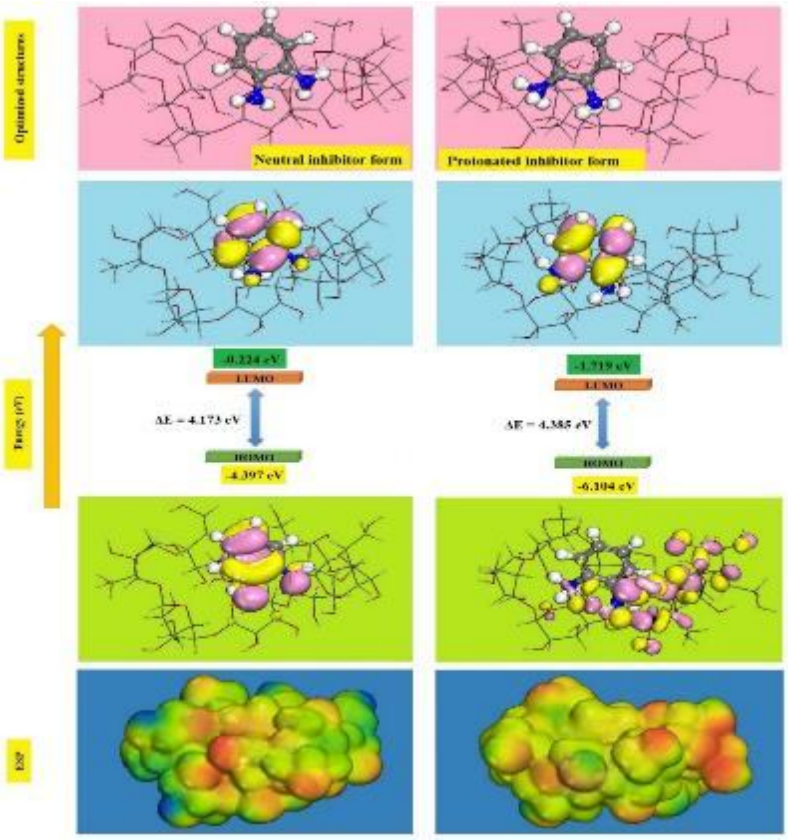


Figure 9. Optimized structures, LUMO, HOMO and ESP pictures of a supramolecular complex with β–CDoPhDA for neutral and protonated inhibitor forms.

(I) The protonated form of β–CDoPhDA has been identified as a highly electromechanical molecule. In the corrosion protection mechanism, protonated molecules interact favourably with the metal surface.

(II) The chemical hardness and softness properties of β–CDoPhDA undergo changes during the protonation process due to the impact of amino group protonation on the chemical hardness and softness in β–CDoPhDA. These changes significantly affect the thinning properties of β–CDoPhDA.

(III) The values of ΔN (change in electron density) and ΔE (change in energy) were found to be higher in the protonated form. This provides evidence of the anti-corrosion property of the host β-CDoPhDA.

Table 5. Calculated theoretical parameters of the neutral and protonated supramolecular complex with β–CDoPhDA inhibitor forms.

Theoretical parameters	Neutral form	Protonated form
I (eV), Molecular ionization potential	4.397	6.104
A (eV), Electron affinity	0.224	1.719
χ (eV), Electronic negativity	2.310	3.911
η (eV), Chemical hardness	2.086	2.192
σ (eV), Chemical softness ΔN, Fraction of electron transfer	0.479 0.321	0.456 0.336

In the molecular dynamic simulation, adsorption configurations of the neutral and protonated forms of the inhibitor were determined on the Fe (110) surface in

β–CDoPhDA (refer to Figure 10). The results showed that the amino group of the guest molecule and the hydroxyl functional groups of β–CD are the primary centres responsible for adsorption onto the Steel 20 surface in β–CDoPhDA. Both the neutral and protonated forms of the inhibitor exhibited adsorption parallel to the metal surface. The reduction of corrosion occurs due to the formation of a protective layer, resulting from the inhibition of chloride ions and water molecules on the metal surface. The selected inhibitor forms a protective barrier between the other aggressive ions and the metal surface, facilitated by a stable solid layer formed on the metal surface. Consequently, the exposure of the metal to the solution decreases. Additionally, in β–CDoPhDA, it was observed that the behaviour of the neutral and protonated forms of the inhibitor is influenced by temperature changes in the MD simulation process.

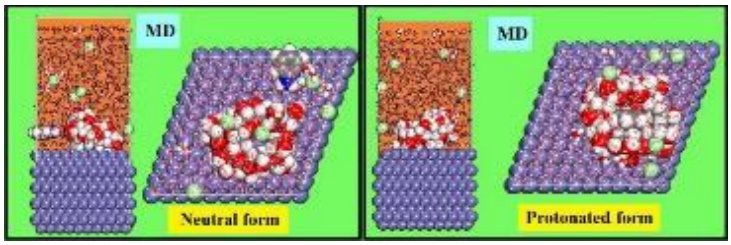


Figure 10. Results found in β–CDoPhDA by MD simulation of the adsorption of neutral and protonated sugars of the inhibitor on the Fe (110) surface.

Based on the obtained results, it was determined that the MD simulation of the selected supramolecular systems exhibits higher resistance to temperature changes. It was observed that, even with variations in temperature, the adsorption of the inhibitor on the metal surface remained nearly unchanged.

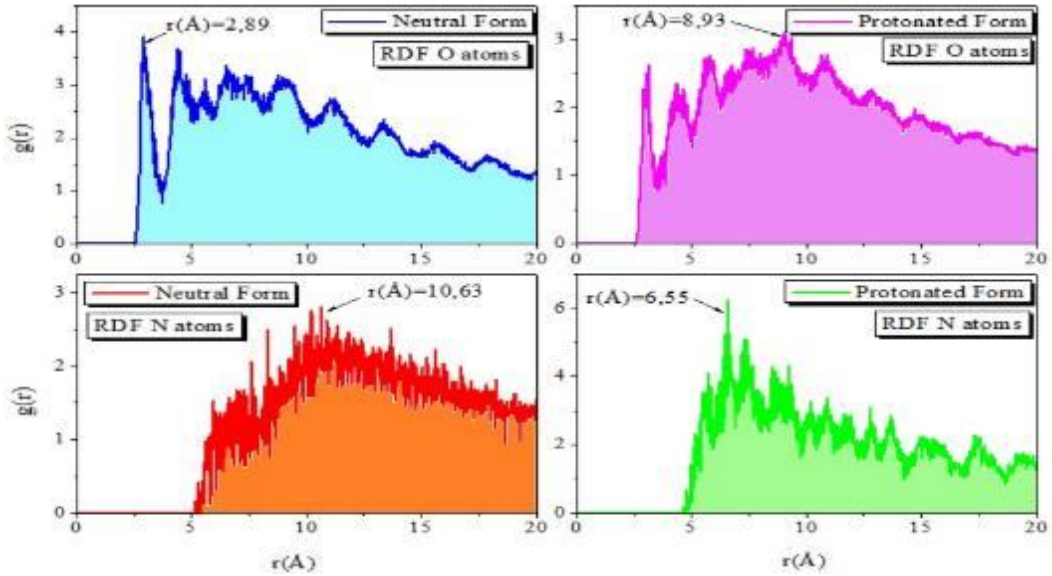


Figure 11. RDF of the N and O atoms of the neutral and protonated supramolecular complex with β–CDoPhDA inhibitor forms on the Fe(110) surface, obtained via MD simulation.

In order to further analyses the MD simulation results, a radial scattering function (RDF) analysis was conducted, which led to theoretical calculations of the Fe-N and Fe-O bond values on the Fe (110) surface (refer to Figure 11). In β–CDoPhDA, obtained through the MD simulation method, the formation of Fe-O and Fe-N bonds

was observed using the RDF method through the adsorption of the inhibitor on the surface of the neutral and protonated supramolecular complex Fe(110). The results revealed that, in the neutral form, the bond length for Fe-O was determined to be 2.89 Å, while for Fe-N, it was 10.63 Å. On the other hand, in the protonated form, the bond length was found to be 8.93 Å for Fe-O and 6.55 Å for Fe-N. This phenomenon confirms that the O and N atoms effectively interact with the metal surface, forming strong chemical bonds.

CONLUSIONS

1. Based on beta cyclodextrin, a new complex-type β–CDoPhDA, along with β–CDME, β–CDDPhC, β–CDNA, and β-CDAA supramolecular inhibitors, was synthesized. The structure of these inhibitors and their complexes with amines was characterized using IR, ^{1}H NMR, Raman spectroscopy, and TGA methods.
2. Corrosion inhibition properties of selected compounds in 0,5 M HCl medium related various temperatures and concentrations were studied. The process of inhibition with 100 mg/l concentration of β-SDoFDA shows that the values of E_a (57.72 kJ/mol) and ΔH_a (55.08 kJ/mol) create a high energetic barrier for the corrosion of steel 20. Moreover, the thermodynamic functions of the adsorption process (ΔG^o_{ads} = -26.52 kJ/mol) indicate that both physical and chemical adsorption occur simultaneously in the process.
3. Potentiodynamic polarization and electrochemical resistance spectroscopy techniques was revealed that the supramolecular complexes significantly influence cathode (β_a = 185.6 mV) and anode (β_c = -152.6 mV) processes. These effects demonstrate that the inhibitors form a protective layer on the metal surface, effectively reducing contact between the metal and corrosive particles in the medium.
4. The surface morphology of Steel 20 in both non-thinned and thinned environments was analysed using SEM, EDS, AFM, and Raman spectroscopy. The results indicate that the inhibitors form a thin protective layer on the metal surface, providing a high level of protection against water and corrosion ions.
5. Density functional theory calculations have shown that the protonated forms of the supramolecular complexes exhibit excellent thinning properties. Bond lengths (Fe–O 8.93 Å and Fe-N 6.55 Å in inhibitors in β–CDoPhDA) have been obtained through MD simulation.
6. Based on the comprehensive investigations, the tested inhibitors was recommended for use in inhibiting the corrosion process in closed-circuit metal structures and devices at the Navoi Mining and Metallurgical Combine JSC, Almaliq Mining and Metallurgical Combine JSC, and the Uzbekistan-Switzerland joint venture, “GISSARNEFTGAZ”.

РАЗОВЫЙ НАУЧНЫЙ СОВЕТ НА ОСНОВЕ НАУЧНОГО СОВЕТА DSc.03/30.12.2019.K.01.03 ПО ПРИСУЖДЕНИЮ УЧЕНЫХ СТЕПЕНЕЙ ПРИ НАЦИОНАЛЬНОМ УНИВЕРСИТЕТЕ УЗБЕКИСТАНА

НАЦИОНАЛЬНЫЙ УНИВЕРСИТЕТ УЗБЕКИСТАНА

ЭЛИБОЕВ ИЛЁС АСКАРОВИЧ

ЭЛЕКТРОХИМИЧЕСКИЕ И АДСОРБЦИОННЫЕ СВОЙСТВА СУПРАМОЛЕКУЛЯРНЫХ КОМПЛЕКСОВ НА ОСНОВЕ ЦИКЛОДЕКСТРИНА

02.00.04 – Физическая химия
02.00.11-Коллоидная и мембранная химия

АВТОРЕФЕРАТ ДИССЕРТАЦИИ ДОКТОРА ФИЛОСОФИИ (PhD) ПО ХИМИЧЕСКАМ НАУКАМ

Ташкент – 2024

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ВВЕДЕНИЕ (аннотация диссертации доктора философии (PhD))

Цель исследования Заключается в синтезе супрамолекулярных комплексов на основе циклодекстрина, изучении их электрохимических и адсорбционных свойств для защиты стали от коррозии в сильнокислой среде.

Объектом исследования выбраны супрамолекулярные комплексы бета-циклодекстрин ортофенилендиамина (β-ЦДоФДА), бета-циклодекстрин меламина (β-ЦДМЭ), бета-циклодекстрин-1,5-дифенилкарбазида (β-ЦДДФК), бета-циклодекстрин нафтиламина-1 (β-ЦДНА) и бета-циклодекстрин ацетанилида (β-ЦДАС).

Научная новизна исследования заключается в следующем:

впервые была выявлена эффективность супрамолекулярных комплексов β-ЦДоФДА, β-ЦДМЭ, β-ЦДДФК, β-ЦДНК и β-ЦДАС в качестве новых ингибиторов коррозии стали 20;

высокие ингибирующие свойства синтезированных супрамолекулярных комплексов подтверждаются снижением плотности коррозионного тока ($i_{\text{корр.}} = 0{,}85\ \mu\text{A/cm}^2$), увеличением значений сопротивления перезарядки ($R_{\text{ЗАл}} = 126{,}4\ \ \Omega/\text{cm}^2$), степени защиты ($\eta_{\text{Грав.}} = 96{,}93$) и уровня покрытия поверхности ($\theta_{\text{Грав.}} = 0{,}97$);

механизмы ингибирования супрамолекулярных комплексов были определены с помощью квантово-химических расчетов, АКМ- и СЭМ-микрофотографий поверхности металла, ЭДС и спектров комбинационного рассеяния света;

моделированием Монте-Карло были определены позиции адсорбции нейтральной и протонированной форм ингибитора на поверхности металла;

впервые с помощью МД моделирования теоретически было рассчитано взаимодействие супрамолекулярного комплекса β-ЦДоФДА с поверхностью Fe, доказано, что длина связи Fe-N составляет 8,93 Å, а длина связи Fe-O 6,55 Å;

Внедрение результатов исследования. На основании полученных результатов изучения механизмов ингибирования коррозии стали 20 супрамолекулярных комплексов на основе циклодекстрина в сильнокислых средах гравиметрическими, электрохимическими, методами поверхностного анализа и квантово-химическими расчетами:

супрамолекулярные комплексы на основе циклодекстрина: β-циклодекстрин ортофенилендиамин, β-циклодекстрин меламин, β-циклодекстрин 1,5-дифенилкарбазид, β-циклодекстрин нафтиламин-1 и β-циклодекстрин ацетанилиды для коррозионного процесса в металлических конструкциях и устройствах в лаборатории Узбекско-Швейцарское совместного предприятия «ГИССАРНЕФТГАЗ» прошли испытания в качестве ингибитора (справка №730-01/11 от 6 ноября 2023 года Узбекско-Швейцарского СП «ГИССАРНЕФТГАЗ»). По результатам лабораторных испытаний супрамолекулярные комплексы обладают высоким уровнем

защиты и покрытия поверхности при высоких температурах и низких концентрациях, лучше защищают от коррозионных процессов в металлических конструкциях и устройствах в сильнокислых средах, чем ингибиторы, применяемые в промышленности, и подлежат применению на практике в сферах, где есть потребность в защите металлических конструкций и устройств от коррозии;

Полученные супрамолекулярные комплексы на основе циклодекстрина прошли испытания в Центральной научно-исследовательской лаборатории Акционерного общества «Навоийский горно-металлургический комбинат» (АО «Навоийский горно-металлургический комбинат», номер 23/01-01-07/575 от 13 ноября 2023 года). В результате было показано, что по сравнению с промышленно используемыми ингибиторами объекты исследования обладают более высокой способностью защищать металлы от коррозии при различных температурах и в кислых средах;

Растворы супрамолекулярных комплексов на основе циклодекстрина концентрацией 100 мг/л внедрены в практику в качестве средства предотвращения коррозии металлоконструкций, используемых в системах водооборота, системах охлаждения и отопления сернокислотного цеха №1 АО «Алмалыкский горно-металлургический комбинат». Цинковый завод (справка № СЛ-1282 от 16 ноября 2023 года АО «Алмалыкский горно-металлургический комбинат»). В результате эти соединения получили положительную оценку как эффективные ингибиторы предотвращения коррозии металлических конструкций в системах циркуляции воды, системах охлаждения и отопления;

антикоррозионные свойства и механизмы адсорбции новых супрамолекулярных комплексов использованы в проекте № ОТ-Ф7-85 «Синтез и физико-химические свойства алифатических и гетероциклических ингибиторов коррозии металлов на основе аминометиленфосфатной кислоты» с целью физико-химических исследований. механизма ингибирования и определения электрохимических свойств (Справочник № 03/10-2023 от 23 августа 2023 года Министерства высшего образования, науки и инноваций Республики Узбекистан). Полученные результаты позволяют использовать выбранные ингибиторы для защиты металлических материалов от коррозии в нефтегазовой отрасли;

Структура и объем диссертации. Диссертация состоит из введения, 5 глав, заключения, списка использованной литературы и приложения. Объем диссертации составляет 118 страниц.

E’LON QILINGAN ISHLAR RO‘YXATI
СПИСОК ОПУБЛИКОВАННЫХ РАБОТ
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3. Eliboyev I.A., Akbarov X.I., Xoliqov A.J., Berdimurodov E.T. β-siklodekstrin va naftilamin asosidagi yashil ingibitor sintezi / “Kimyo fanini o‘qitishning istiqbollari: Kecha, bugun, ertaga” mavzusidagi Respublika ilmiy-amaliy konferensiyasi. – Jizzax, 2022. – B. 258-260.

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