

UDC 547.1.541.13

Inorganic chemistry**EXTRACTION OF SOME BIVALENT METAL IONS WITH NEW
MULTI-COORDINATION BENZENE DERIVATIVES, RESISTANCE CONSTANT
OF THE COMPLEX AND IMPACT OF ANIONS ON IT****F.I.Shekiliyev, A.I.Rustamova, Sh.I.Gahramanova, E.A.Guliyeva**

(Presented by Academician of ANAS A.M.Aliyev)

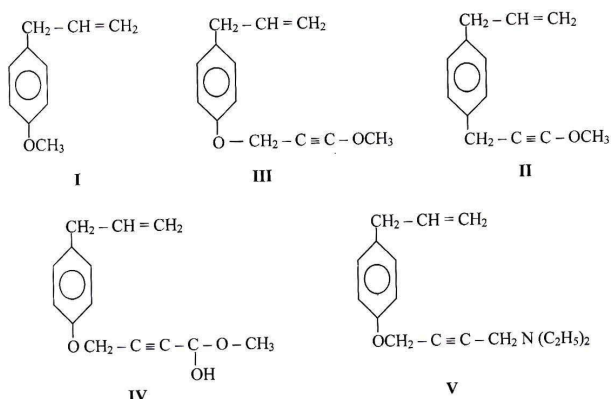
Resistance constant of the complex formed during the extraction of bivalent metal ions with new multi-coordination benzene derivatives and the effect of anions on it was studied in detail. It was determined that creation of resistant bond between crown ethers and metal ions depends on the number of active centers in functional group inside benzene ring and other structural factors.

Keywords: metal ions, extraction, active centers, multi-coordination derivatives, resistance constant

When stating about applicability of crown ethers with various structure and composition we must note the wide application of them as a high-selective extractant in analytical chemistry for separation of periodic system metal ions from solution. Extraction properties of these compounds are based on complex formation of metals ions with crown compounds and the main reason of this depends on interaction effect of active centers in the composition of metal ions with extractant. We studied extraction properties of these compounds and found that these compounds can effectively purify industrial waters polluted with several heavy metal ions [1,2]. We measured complex-forming constants (resistance constant) of several crown-ether-inorganic salt-solvent systems by using UB-spectroscopy, calorimetric, ion-selective electrodes and other methods. Maximum value of complex-forming constant with cation diameter equals to the cation diameter which is near to crown-ether surface value. There is some information about thermodynamics of these compounds. By using NMR-spectroscopy it was possible to measure kinetic parameters like complex-forming constant and dissociation constant [3]. As an organic fragment which is located outside polyether ring, has a hydrophobic nature, metal complexes of crown-ethers and even non-polar solvents dissolve in this way. In these cases anions (opposite ions)

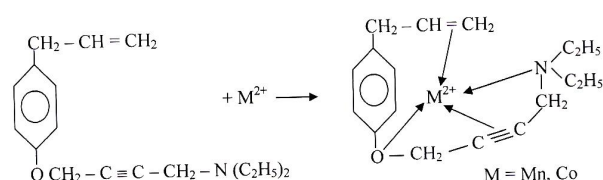
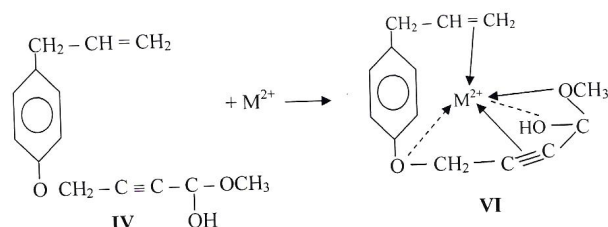
show high reactivity and acts as solvating solvents in the solution. These two properties are very important for using crown-ethers. For example, with the help of these complexes we may use inorganic salts as a reagent in different homogeneous reactions. These properties allow us to process new type reactions. By the impact of crown-ethers it is possible to dissolve many type compounds, such as inorganic salts, complexes of transition elements, metal-organic compounds and organic compounds of alkali metals. In this work by using allyl group OCH_2 , $\text{C}=\text{C}$, OCH_3 and OH -group benzene derivatives (I-V) we investigated the separation possibilities of some bivalent metal ions (M^{2+}) by extraction technique. According to the results of studies we determined that depending on a number of coordination centers in functional group in benzene ring, the presence of chelating group in molecule and its position we can determine the efficiency of extraction process. We consider that in these compounds extraction effect changed in a right proportion with a number of active centers in the compound. Macrocyclic or condensed benzene or substituting groups in cyclohexane ring influence considerably on resistance of crown-ether compounds. Advanced analysis of this influence was detected during complex formation of 4-substituted Benzo-15-crown-5 ether (B15C5) with sodium salt at acetone medium [4]. Inclusion of

different alkyl groups into polyether ring strongly impacts on its surface conformation. If hydroxyl (OH) groups in macrocyclic ring widen the surface, inclusion of alkyl groups leads to accumulation of the surface due to conformation change. Substituting groups which are in direct relation with polyether ring, strongly impact on the conformation of polyheterocycle [5-8].



For example, 5 coordination VI compound more actively coordinates metal ion (M^{2+}) than other 4 coordination VII compound. Macrocyclic polyether type crown-ethers can solvate several metal cations with high selectivity [6]. Chemists consider these properties of crown-ethers and widely use these compounds in extraction chemistry. From the other point in the research works [7,8] conducted for investigation of the synthesis and practical use of new diaza-crown-ethers, two newly synthesized diaza-crown-ethers: 5,8 diaza-2,3,10,11-dibenzo-1,12-dioxa-15 crown-4 was used to produce octane-increasing admixture compositions of extracts containing ferrocene and its derivative [9]. In the early 1970s [10] selectivity law of macroheterocycles was formed. According to this law the creation of a bond between metal ions with macroheterocycle can be possible only when radii of metal ions conform to the size of crown-ether surface. But this law formed by Pedersen did not fully express the main regularities obtained by experimental studies of different researchers. Thus, further studies showed that the creation of a bond by metal ions is not determined by only Pedersen law and it also depends on configuration, conformation and

other structural factors of a reagent. That's why when changing the structure of crown-ethers these factors must be considered. Application of crown-ethers in analytical chemistry gave a new impulse for expansion of physical and physical-chemical analysis methods. Concentration of the element allows to increase 2-3 units the sensitivity of physical-chemical analysis methods. Crown-ethers are widely used in extraction chemistry, photometry, polarography, potentiometry, conductometry, and so on. There are many literature materials on properties, complex-formation with cations and extraction of crown-ethers and aza-crown ethers [11-15]. But some theoretical and practical tasks of extraction of crown-ethers have not been solved yet.



For example, experimental results on complex formation constant, in particular, extraction constant of crown-ethers in different solutions have not been systematized yet. There are less experimental materials on the extraction constants obtained during the extraction of crown-ethers. That's why many research works must be performed in this direction to state the value of extraction constant of metals, to determine the effect of solvents of anions and crown-ethers on extraction constant. Crown- and aza-ethers which dissolve in organic solvents are used for extraction of cations. During

extraction cation mixes with anion and enters into organic phase. During extraction we should consider the effect of anion and solvent on equilibrium of water phase and organic phase in the system. In this aspect there are many literature materials on complex formation constant of cations in water and organic solvents [12-15]. Pedersen observed the sizes of different crown-ether surfaces and obtained different values. According to the result he formed conformability principal of the value (radius) of crown-ether surface to cation radius – when the values of macrocycle surface and metal ion radius differ less, resistance (resistance constant) of the formed complex will be high. For example, if the difference of values of crown-ether surface radius is 0.45-0.50 Å, the difference of alkali, alkali-earth metal cation radii makes 0.15-0.20 Å. The values of crown-ethers obtained by Monte Carlo calculations, molecular mechanism and dynamics methods reach nearly to 0.25-0.40 Å. There is detailed information in literature [11-15] about the structures of complexes of crown-ethers and metal cations in solid state (monocrystal) with different anions. It is shown that crown-ethers may exist in different conformations and their surface value and structure varies depending on the conformation of crown-ether in the complex. It is expected that there are different possible conformations of free crown-ether molecules during the extraction in solutions and they try to transform to higher energy conformation due to the temperature and energy of each solution. For example, during formation of crown-ethers with metal complexes (ML^{+n}) several ether conformations participate in the process, but when monocrystal enhances during crystallization of a salt from solution, only one crown-ether conformation participates [12, 13, 14]. It should be stated that results of structural analysis of opposite ion salts must not be completely related to aqueous and other solutions. Impact of anions on the structure and resistance in solutions is lower than in monocrystals. The competition between metal ions with molecules of solvents with the purpose of entering to crown-ether surface should be considered. Large size of cation,

oxygen, sulphur and nitrogen charges in crown-ethers forms the complex-formation energy and impacts on resistance constant of the complex. Hydration (solvation) of cation and reagent (crown-ether) also effects on the resistance constant of the complex. We may evaluate the impact of above mentioned factors on the system (complex-formation) by using quantum-mechanical and Monte Carlo calculations as well as methods of molecular mechanics and dynamics [14]. For example, during complex-formation (at 1:1 ratio) metal ion which is in interaction with all heteroatoms of the system and differs less from radius of conformation surface of crown-ether or equal to the surface radius may locate on surface of heterocycle. If radius of cation is bigger than the surface radius, then ion goes out of surface of macrocycle, if radius of cation is less than radius of macrocycle surface, then cation locates on any part of macrocycle surface and interreacts with heteroatom of crown-ether [12-15]. Some works [12, 13, 15] were devoted to dependence of resistance constant of complexes formed by alkali and alkali-earth elements with crown-ethers in water and other solutions on cation radius or dependence of cation radius on ratio of surface radius of crown-ether. Thus, according to results of experiments and literature materials we conclude that during extraction of metal cations the use of crown-ethers as a reagent allows to increase distribution coefficient. Considering the abovementioned statements the complex formation in extraction processes of metal ions with crown-ethers, studying the influence of anions and solvents on extraction constant in detail and systematically will be possible.

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BƏZİ İKİVALENTLİ METAL İONLARININ YENİ ÇOXKOORDİNASİYALI BENZOL TÖRƏMƏLƏRİ İLƏ EKSTRAKSİYASI, ALINAN KOMPLEKSİN DAVAMLILIQ SABİTİ VƏ ONA ANİONLARIN TƏSİRİNİN TƏDQIQI

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İkivalentli metal ionlarının yeni çoxkoordinasiyalı benzol törəmələri ilə ekstraksiyası zamanı əmələ gələn kompleksin davamlılıq sabiti və ona anionların təsiri ətrafı tədqiq edilmişdir. Müəyyən edilmişdir ki, kraun-efirlərin metal ionları ilə davamlı rabitə yaratması əsasən onların konfigurasiyasından, konformasiyasından, benzol həlqəsinə yeridilmiş funksional qrupdakı aktiv mərkəzlərin sayından və digər struktur faktorlardan asılıdır.

Açar sözlər: metal ionları, ekstraksiya, aktiv mərkəzlər, çoxkoordinasiyalı törəmələr, davamlılıq sabiti

ЭКСТРАКЦИЯ НЕКОТОРЫХ ИОНОВ ДВУХВАЛЕНТНЫХ МЕТАЛЛОВ НОВЫМИ МНОГОКООРДИНАЦИОННЫМИ ПРОИЗВОДНЫМИ БЕНЗОЛА, ИССЛЕДОВАНИЕ КОНСТАНТЫ УСТОЙЧИВОСТИ ПОЛУЧЕННЫХ КОМПЛЕКСОВ И ВЛИЯНИЯ НА НИХ АНИОНОВ

Ф.И.Шекилиев, А.И.Рустамова, Ш.И.Каграманова, Е.А.Кулиева

Исследованы константы устойчивости полученных комплексов, образовавшихся при экстракции некоторых двухвалентных металлов новыми многокоординационными производными бензола, и влияние на них анионов. Установлено, что образование прочных связей с ионами металлов зависит, в основном, от их конфигураций, конформаций, числа активных центров в функциональной группе, введенных в бензольное кольцо, и прочих структурных факторов.

Ключевые слова: ионы металлов, экстракция, активные центры, многокоординационные производные, коэффициент устойчивости