AMPEROMETRIC TITRATION OF MERCURY (II) WITH MPCMDEDTC SOLUTION IN DIMETHYL SULFOXIDE

Abstract. The article studies the voltammetric behavior of 4-methoxyphenyl carboxymethyl diethyldithiocarbamate (MPCMDEDTC) in dimethyl sulfoxide (DMSO) on the presence of background electrolytes with different acid-base properties in the anodic polarization region of a platinum microdisk electrode. MPCMDEDTC is oxidized in 0.125 M LiClO₄ solution forming one clearly pronounced anode wave with \( E_{1/2} = 0.85 \) V, while the wave height varies in proportion to the concentration of the depolarizer. A procedure has been developed of amperometric titration of mercury (II) with a standard MPCMDEDTC solution in DMSO using two indicator electrodes.

Keywords: mercury (II), 4-methoxyphenyl carboxymethyl diethyldithiocarbamate, lithium perchlorate, n-propanol, dimethyl sulfos, microdisk electrode, indicator electrode, potential half-wave, depolarizer, background electrolytes.

Relevance of the work
Electroanalytical methods, amperometric titration in particular, can be used to determine different elements in broad concentration range and, with an appropriate selection of analysis conditions, they also become highly selective.

Since mercury, which is often found in natural and technological environments in quantities exceeding the permissible exposure limit (PEL), is toxic, monitoring and determination of its content is a relevant issue throughout the world.

Earlier, some features of amperometric titration of a number of cations in glacial acetic acid [1–2] and in N-propanol medium [3–4]. Представляло интерес исследовать возможность амперометрического титрования раствором 4-methoxyphenyl carboxymethyl diethyldithiocarbamate (MPCMDEDTC) in a medium of non-aqueous solvents with acid-base properties.

This work is devoted to studying the possibility of amperometric titration of mercury (II) with two indicator electrodes with a MPCMDEDTC solution.
in a medium widely used in electrochemical studies of an aprotic dipolar solvent, dimethyl sulfoxide (DMSO), which exhibits weak basic properties.

The initial 0.002 M mercury (II) nitrate solution was obtained by dissolving a portion of Hg(NO₃)₂·H₂O (chemically pure) in DMSO in DMSO and standardized by an aqueous solution of potassium iodide amperometrically [5]. Solutions of lower concentrations were obtained by diluting the original immediately before use. A standard 0.005 M solution of MPCMDEDTC was prepared by accurately weighing the reagent. Stock solutions of background electrolytes (10% LiClO₄; 7.5% CH₃COONa and CH₃COOH) were prepared by dissolving the corresponding salts in DMSO.

Amperometric titration with two indicator rotating platinum electrodes was carried out according to the setup described in [6]. Titration was carried out with a piston microburette [7] with an accuracy of 0.0005 ml. the final volume of the solution prepared for titration was 10.0 ml.

To obtain the current-voltage curves of MPCMDEDTC, a complex of mercury (II) with MPCMDEDTC and free ions of mercury (II) for the anodic and cathodic polarization of a platinum microdisk electrode (l = 1.0 mm), we used a three-electrode cell and a PPT-1 polarograph, the reference electrode was SCE.

**Results and discussion.** It can be seen from the obtained experimental data that the current-voltage curves of mercury (II) ions in DMSO are restored at E₁/₂ = 0.12 V. he cathode wave of mercury (II) chelating agent is shifted by approximately 0 with respect to the wave of free mercury (II) ions. 2 V towards more negative potentials. MPCMDEDTC anode wave is not clearly expressed due to the partial application of the oxidation current of the solvent itself, which begins to flow at a noticeable rate even at 0.8 V. The mercury (II) chelating agent also oxidizes at the platinum anode at slightly higher potential values (E₁/₂ = 0.92 V), and therefore its wave is expressed even less clearly than the wave of free MPCMDEDTC.

Taking into account the voltammetric behavior of all components of the reaction of formation of mercury (II) chelating agent, it can be concluded that amperometric titration of mercury (II) should be carried out at a half-wave potential in the range of E₁/₂ = 0.80–0.90 V. Under such conditions, to the point of equivalence, the indicator current will be due to the simultaneous reduction of titrated mercury (II) ions at the cathode and the oxidation of the resulting mercury (II) chelating agent at the anode. Since in this case the concentration of mercury (II) will continuously fall from its initial to almost zero value, and the concentration of mercury (II) chelating agent, on the contrary, will increase, the indicator current will first increase to a certain maximum value, reached at the time of titration of approximately half of all mercury (II), and then fall in this case, a continuously increasing current is observed, due to the reduction of mercury (II) chelating agent at the cathode and the oxidation of free MPCMDEDTC on the anode.

When mercury (II) is titrated against a background of 0.125 M LiClO₄ a fairly clear titration curve is obtained with a smooth curve in the vicinity of the titration end point, which indicates a slightly lower strength of mercury (II) chelating agent in DMSO compared with its strength in water. The titration endpoint, determined by the generally accepted graphic method, corresponds to the formation of a normal complex of mercury (II) with MPCMDEDTC with a ratio of mercury (II): MPCMDEDTC = 1/1. Unlike solutions containing lithium perchlorate as a background, solutions of mercury (II) nitrate against the background of sodium acetate and acetic acid are titrated much worse: the titration curve is less clear and the equilibrium time sharply increases after each titrant addition. This is explained by the ability of mercury (II) to form very strong complexes with acetate ions.

In order to assess the reproducibility and correctness of the developed method, various amounts of mercury (II) were titrated against a background of 0.1 M lithium perchlorate with a 3-fold repetition of
The results of titrations of mercury (II) with the standard MPCMDEDTC solution showed that the difference between the taken and found amounts of mercury (II) in all cases does not go beyond the confidence interval, which indicates the absence of systematic errors.

Amperometric titration of mercury (II) with MFKMDEDTK solution can be used in the analysis of certain paints, pharmaceuticals and perfumes containing mercury that are poorly soluble in water.

Список литературы:

1. Геворгян А. М., Хадеев В. А. Растворимость и полярографическое поведение комплексона III на платиновом микроаноде в среде безводной уксусной кислоты. Доклады АН УзССР, 1973. – Т. 12. – 22 с.
2. Геворгян А. М., Талипов Ш. Т., Хадеев В. А. Биамперометрическое титрование цинка, индия и меди комплексоном III в неводной среде. Заводск. лаборатория, 1976. – Т. 42. – 646 с.
3. Геворгян А. М., Хадеев В. А., Костылев В. С. Вольтамперное поведение ЭДТА на платиновом микроаноде в среде пропилового спирта. Доклады АН УзССР, 1979. – Т. 3. – 48 с.
4. Геворгян А. М., Хадеев В. А., Костылев В. С. ЭДТА – аналитический реагент кальция и магния в неводной амперометрии. Доклады АН УзССР, 1979. – Т. 5. – 49 с.
5. Сонгина О. А., Захаров В. А. Амперометрическое титрование. – М.: Химия. 1979. – 237 с.
6. Геворгян А. М., Рахматов Х. Б., Сирлибаев Т. С., Цагараев Э. Г. Амперометрическое титрование в неводных средах. – Ташкент: Изд-во ТашГУ. Часть 2. 1993. – 135 с.
7. Геворгян А. М., Матмуратов Ш. А., Калладин В. Г. Неводное амперометрическое определение ртути(II) феноксивинилом // Тез. докл. международ. конф., посвящённой 100-летию академика О. А. Сонгиной. – Алматы. 2001. – 44 с.