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A STUDY OF THE COMPLEXATION REACTION OF MERCURY (II) WITH RHODAMINE B FROM THE POINT OF VIEW OF ITS UTILIZATION IN ASSAYING MERCURY BY THE LUMINESCENCE METHOD

Contents: 1. Introduction, 2. Experimental, 3. Discussion of results, 4. Conclusions; Streszczenie; References.

1. INTRODUCTION

Mercury is one of the most dangerous environmental pollutants, as it is easily accumulated in organisms, causing grave and chronic diseases. The source of mercury pollution of surface waters are certain industrial effluents and plant protection agents. The mercury level in sea water [9] amounts, for example to 0.05—0.10 $\mu\text{g dm}^{-3}$ (Baltic Sea). This value has been considered by some research workers to be natural mercury level in surface waters. Mercury may occur in the form of both inorganic and organic compounds, mostly as methyl- and phenylmercury salts [17].

Mercury atoms, having completed *d* orbitals, show a strong tendency to form complexes with the coordination number 2. The structure of the complexes may be linear or tetrahedral. Octahedral species are rarely encountered. The most stable complexes are formed with ligands containing atoms of halogens, carbon, nitrogen, phosphorus and sulphur [4, 3, 19]. A number of complexes with oxygen-containing anions have been reported [4], e.g. $[\text{Hg}(\text{SO}_3)_2]^{2-}$ and $[\text{Hg}(\text{NO}_3)_4]^{2-}$. A variety of amines have also been found to form complexes with Hg(II) [3], the affinity of mercury to nitrogen-containing ligands being stronger in aqueous solutions than that of other transition metals. Compounds of Hg(II) with β -diketones [14] do not display chelate-like structures, but are rather enolates, $\text{Hg}(\text{OCR}=\text{CHCOR})_2$. Recently, several works have been confined to the complexes of the metal with sulphur-containing ligands, such as benzylsulphanilthiobenzamide [18] and 2-mercaptobenzimidazole [7]. Most frequently, however, dyes have been used

which enter into reactions with complementary ions, which can be utilized for assaying mercury.

Tarayan and associates [15] studied a reaction of Hg(II) with methyl green in the presence of the Cl^- and Br^- ions. The complex formed, $[\text{R}^+\text{HgX}_3^-] \cdot \text{R}^+\text{X}^-$ was extracted with benzene. Extraction of the HgI_3^- and HgBr_3^- anions to an organic phase with such dyes as methylene blue, antipyrine dyes, butylrhodamine S, brilliant green, crystal violet and methyl green was investigated by Kisz and associates [11]. Shestidesatnaya and associates [16] employed bromophenyl blue and bromocresol green in the presence of phenanthroline for assaying mercury and suggested the formation of a chelate, $[\text{Hg}(\text{Fen})_2\text{R}]$. These studies were mainly carried out using extraction-photometric methods.

To assay small amounts of the metal by means of dyes, e. g. rhodamine B, the extraction-fluorimetric method was also used [10]. The luminescence method is markedly more sensitive than the photometric methods.

The objective of this paper was to examine the reaction of Hg(II) with rhodamine B and to establish optimum conditions for extraction of the complex formed with regard to the possibility of assaying mercury by means of this reaction using the luminescence method.

2. EXPERIMENTAL

The stock solutions of HgCl_2 and of rhodamine B were $1 \times 10^{-3}\text{M}$. Apart from these, 2N solutions of H_2SO_4 and NaCl were prepared.

An extractant was prepared by mixing together 2 volumes of benzene with one volume of diethyl ether.

A series of solutions for the measurements was prepared in 10-cm³ volumetric flasks. The volume of the aqueous phase was 5 cm³ and that of the extractant was 3 cm³. Tightly closed flasks were shaken for 1 min. After separation of the phases, the organic layer was transferred to a 1-cm cuvette with a cap and an absorptiometric or luminescence measurement was run.

The absorbance of the solutions was measured on a SPECORD UV-VIS spectrophotometer. Measurements of the luminescence were performed by using a special set-up.

The measurements of pH were carried out on an LBS-66 pH meter using glass (S-60) and calomel (K-60) electrodes.

3. DISCUSSION OF RESULTS

A variety of modern instrumental techniques have recently been em-

ployed to assay mercury in water [5]. The techniques cannot, however, be employed under expeditional conditions and not each stationary hydrochemical laboratory is equipped with such expensive and precise equipment. Hence, it is the tendency to develop less sophisticated procedures that enable the assaying of trace amounts of mercury, including those in sea water.

As regards the method selected, a fluorescent compound could only provide a ligand coordinating with mercury. Among other compounds, dyes provide such ligands. In the extraction-photometric and extraction-fluorimetric methods, xanthene dyes [2] have found wi-

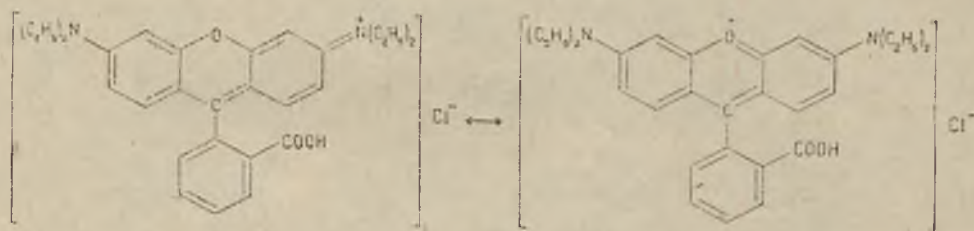


Fig. 1. Mesomeric structures of rhodamine B
Rys. 1. Struktury anezomeryczne rodaminu B

despread use. Rhodamine B is one of these dyes. Its mesomeric structures are shown in Fig. 1.

An aqueous solution of rhodamine B has an absorption maximum at $\lambda=554$ nm (Fig. 2) with molar absorptivity, ϵ , of about 10^5 l mol⁻¹ cm⁻¹. Rhodamine B has long been employed for assaying a variety of elements [1, 6, 8, 10, 12, 13]. With complex anions of the elements a cation of rhodamine B forms compounds referred to as ion pairs [8], ion associates [6, 10] or complexes [13, 1], which have been extracted from aqueous solution with organic solvents, mostly with benzene. In this work a benzene — ethyl ther (2:1 by vol.) mixture was used as an extractant. Ether accelerates and improves phase separation.

In Fig. 2 the spectrum of an aqueous solution of R_B ($C_{R_B}=2 \times 10^{-5}M$) mixed with a $HgCl_2$ solution ($C_{Hg}=1 \times 10^{-4}M$), curve 2, and spectra of extracts of appropriate rhodamine B solutions (curves 1', 2', 3' and 4') have also been shown. Curve 2'' provides a luminescence spectrum of the extracted $R_B - Hg(II)$ complex.

During extraction of a coloured solution of R_B ($C_{R_B} \leq 10^{-4}M$) with benzene and ether, the solution becomes colourless. The organic layer also does not become coloured although it contains about 90 per cent of the dye, as has been demonstrated by re-extraction of the separated organic layer with hydrochloric or sulphuric acid, or by isolation of rhodamine B by evaporation of the solvent and dissolution of the dry residue in water. This phenomenon can be explained in terms of an

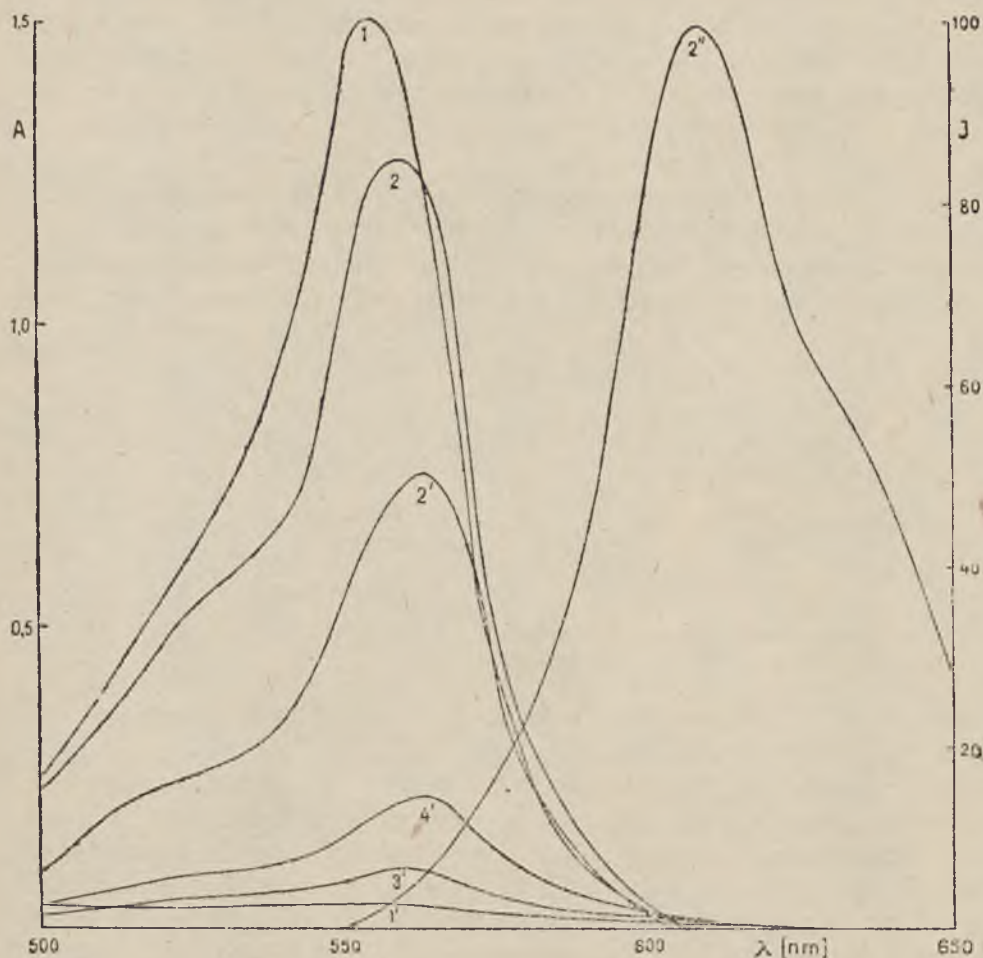


Fig. 2 Spectra of rhodamine B solutions; $C_{R_B} = 2 \times 10^{-5}M$.

1 — aqueous solution of R_B ; 1' — extract of solution 1;
 2 — aqueous solution of $R_B + Hg(II)$; $C_{Hg} = 1 \times 10^{-4}M$, $pH = 1.5$; 2' — extract of solution 2; 3' — extract of R_B solution, $pH = 1.5$; 4' — extract of the $R_B + Hg(II)$ solution, $C_{Hg} = 1 \times 10^{-5}M$, $pH = 1.5$; 2'' — emission spectrum of an extract of solution 2; $l = 1$ cm.

Rys. 2 Widma roztworów rodaminu B. $C_{R_B} = 2.10^{-5}M$.

1 — roztwór wodny R_B ; 1' — ekstrakt roztworu 1;
 2 — roztwór wodny $R_B + Hg(II)$, $C_{Hg} = 1.10^{-4}M$, $pH = 1.5$;
 2' — ekstrakt z roztworu 2;
 3' — ekstrakt z roztworu R_B , $pH = 1.5$;
 4' — ekstrakt z roztworu $R_B + Hg(II)$, $C_{Hg} = 1.10^{-5}M$, $pH = 1.5$;
 2'' — widmo emisyjne ekstraktu z roztworu 2; $l = 1$ cm.

equilibrium which sets up in the aqueous solution of R_B . The equilibrium is shown in Fig. 3.

Electrolytic dissociation leads probably to splitting off of the H^+ ion to form a transient zwitterion R_B^\pm which is subsequently converted

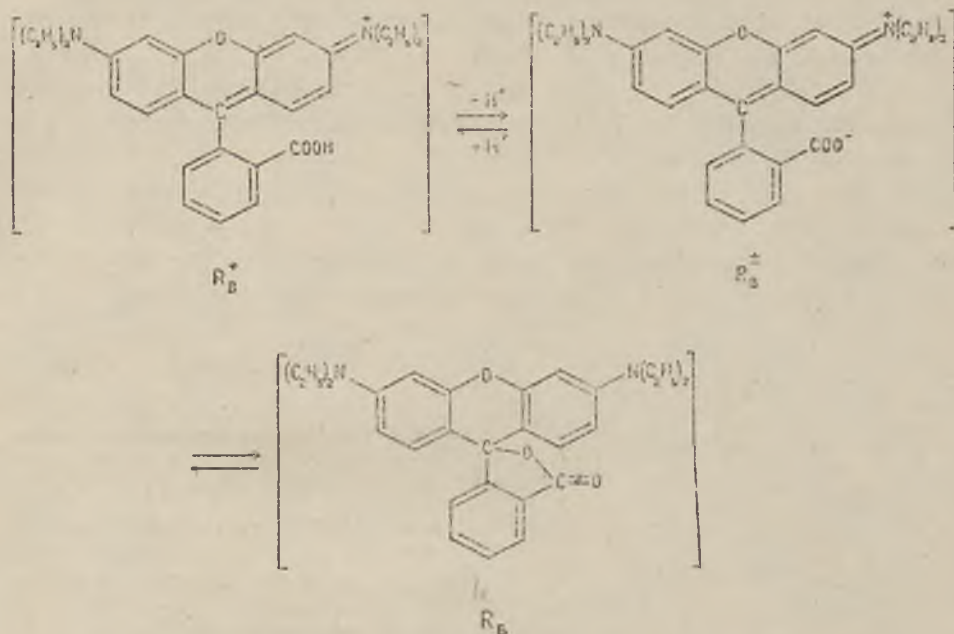


Fig. 3 Equilibrium forms of rhodamine B in aqueous solution.
 Rys. 3. Formy równowagowe rodaminy B w roztworze wodnym.

to a lactone form of R_B having a structure similar to that of fluorescein and its derivatives (uranin, eosin, erythrosin). In the lactonic form (R_B), rhodamine B becomes colourless probably owing to disturbance of the system of conjugate double bonds. This system undoubtedly affected colour-producing properties of rhodamine and its solutions to a great extent. In this form R_B is freely soluble in nonpolar solvents, such as benzene. Consequently, during extraction with the benzene — ether mixture, the equilibrium shifts to the lactonic form thus leading to decolouration of the solution.

At concentrations higher than $10^{-4}M$ a faint pink colour appears in the organic layer after extraction. This is probably due to the weakly polar nature of ether which may thus solvate rhodamine B causing displacement of the charges similar to that observed in the zwitterion R_B^\pm which is coloured.

After treatment of the decolourized solution with sulphuric acid and shaking it with the organic layer, intense colouration of the aqueous phase was restored. The acid splits the lactonic bond and shifts equilibrium towards the formation of the R_B^+ cation, i.e. the coloured form of rhodamine B. A small portion of this cationic form also passes to the organic layer since it acquires a faintly perceptible slightly pink colouration, as was confirmed by the spectrum (Fig. 2, curve 3').

Of the three forms of rhodamine B in equilibrium, the R_B^+ ion shows the strongest complex forming capacity. The spectra of the extracted complexes of R_B with $Hg(II)$ are shown in Fig. 2 (curve 2', $C_{Hg} = 1 \times 10^{-4} M$; curve 4', $CHg = 1 \times 10^{-5} M$). To examine the reaction of rhodamine B with $Hg(II)$ in greater detail, the effect of acidity was first studied. To a range of solutions of rhodamine B ($C_{RB} = 1 \times 10^{-5} M$) and of $HgCl_2$ ($1 \times 10^{-4} M$), variable amounts of 2N H_2SO_4 were added. Similar amounts of the acid were added to solutions of rhodamine B alone. The absorbance of the extracted complex and the rhodamine itself is shown in Fig. 4. The measurements were performed at 564

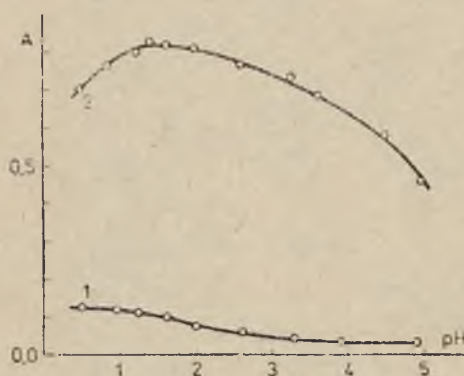


Fig. 4. Dependence between extraction of rhodamine B (1) and of its complex with $Hg(II)$ (2) and pH of aqueous solution.

$C_{RB} = 1 \times 10^{-5} M$; $C_{Hg} = 10^{-4} M$; $l = 1$ cm
 $\lambda = 564$ nm.

Rys. 4. Zależność ekstrakcji rodaminu B (1) i jej kompleksu $R_B - Hg(II)$ (2) od pH roztworu wodnego.

$C_{RB} = 1 \times 10^{-5} M$; $C_{Hg} = 10^{-4} M$; $l = 1$ cm
 $\lambda = 564$ nm.

nm. As seen, the highest absorbance is observed over the pH range 1—2 of the aqueous layer curve 2), i.e. within this range the largest number of the $R_B - Hg(II)$ complexes passes to the organic layer. The contribution of the rhodamine itself is rather small (curve 1).

Kisz and associates [11] demonstrated the essential effect of the iodide and bromide ions on the extraction of coloured $Hg(II)$ complexes. The effect of the chloride ions was not studied in such detail, as their contribution was markedly smaller. In this paper, however,

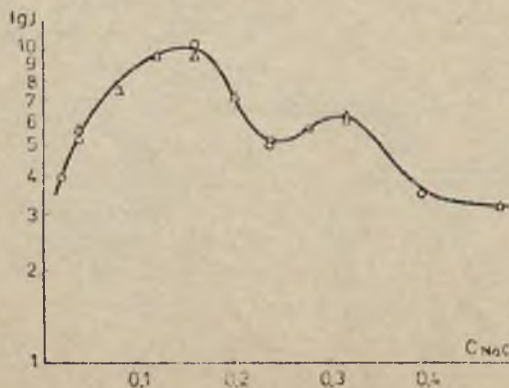


Fig. 5. Dependence between extraction of the $R_B - Hg(II)$ complex and $NaCl$ concentration in the aqueous solution.

$C_{RB} = 1 \times 10^{-5} M$; $C_{Hg} = 1 \times 10^{-4} M$
 $\lambda = 608$ nm; pH = 1; $l = 1$ cm

Rys. 5. Zależność ekstrakcji kompleksu $R_B - Hg(II)$ od stężenia $NaCl$ w roztworze wodnym.

$C_{RB} = 1 \times 10^{-5} M$; $C_{Hg} = 1 \times 10^{-4} M$
 $\lambda = 608$ nm; pH = 1; $l = 1$ cm

this effect should be accounted for, since the procedure is to be employed for assaying Hg(II) in sea water.

This effect was studied by the luminescence method at 608 nm and pH 1, using fixed concentrations of HgCl_2 , C_{Hg} , and of R_B , C_{R_B} , equal to $1 \times 10^{-4} \text{M}$ and $1 \times 10^{-5} \text{M}$, respectively. Particular series of the solutions differed in the NaCl concentration. There were two maxima shown in Fig. 5, one stronger over the NaCl concentration range 0.1–0.2M and the other, weaker, over the range 0.30–0.34M. One may assume that the chloride ions act as the complementary ones, affecting stability of the complex being formed. The Hg(II)/Cl⁻ ratio was determined by the equilibrium shift method (Fig. 8, line 2), The ratio for the NaCl concentrations in aqueous solutions not exceeding 0.2M is 1:3. At higher concentration a straight line was obtained by this method, probably owing to the occurrence of reactions of a higher order. Data in Fig. 5 suggest, however, that the $[\text{HgCl}_3]^-$ ion, which participates in the formation of an ion pair with rhodamine B, forms a complex which is more stable and more extractable to the organic layer.

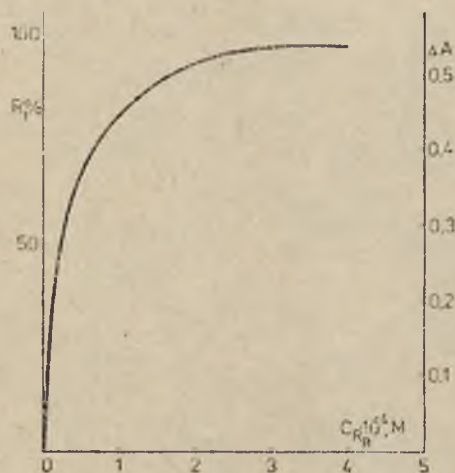


Fig. 6 The effect of rhodamine B on percentage extraction of the $\text{R}_B\text{--Hg(II)}$ complex.

$C_{\text{Hg}} = 2 \times 10^{-5} \text{M}$; pH = 1.5; $\lambda = 564 \text{ nm}$
 $l = 1 \text{ cm}$.

Rys. 6. Wpływ stężenia rodaminu B na procent ekstrakcji kompleksu $\text{R}_B\text{--Hg(II)}$.

$C_{\text{Hg}} = 2 \times 10^{-5} \text{M}$; pH = 1.5; $\lambda = 564 \text{ nm}$
 $l = 1 \text{ cm}$.

Fig. 6 illustrates the effect of the rhodamine B concentration on percentage extraction of the $\text{R}_B\text{--Hg(II)}$ complex at fixed concentrations of HgCl_2 ($C_{\text{Hg}} = 2 \times 10^{-5} \text{M}$), NaCl ($C_{\text{NaCl}} = 0.15 \text{M}$), at pH 1.5. The saturation of the extractant with the complex occurs at $C_{\text{R}_B} \approx 2 \times 10^{-4} \text{M}$. The highest percentage extraction of the complex amounts to about 90 percent after taking into account the contribution to the extraction of the rhodamine B itself.

Quantitative contribution of rhodamine B in the complex was established by the methods of isomolar series of solutions and equilibrium shift. As seen from the Job's curve, the Hg(II)/ R_B ratio in the complex is 1:1. This was confirmed by the equilibrium shift method where the

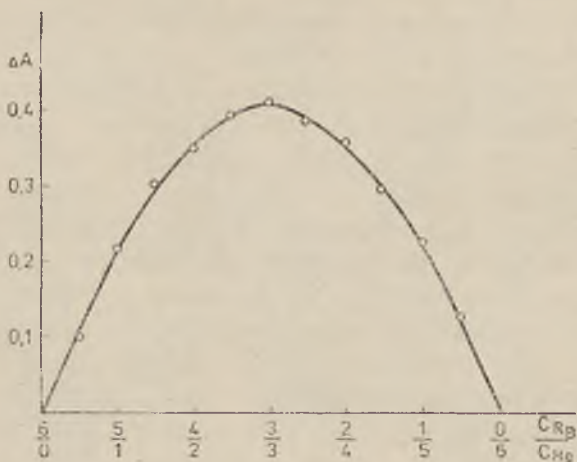


Fig. 7 Absorption curve of isomolar series of solutions of Rb and Hg(II); $C_{Hg} + C_{Rb} = 3 \times 10^{-5}M$; pH = 1.5; $\lambda = 564$ nm.

Rys. 7. Krzywa absorpcji serii izomolowych roztworów Rb i Hg(II); $C_{Hg} + C_{Rb} = 3 \times 10^{-5}M$; pH = 1.5; $\lambda = 564$ nm.

slope of the straight line in Fig. 8 is equal to unity. Accordingly, one can conclude that the following complex of Hg(II) is formed under these conditions: $[(HgCl_3)^- R_B^+]$. During extraction of the complex, equilibrium was attained within 30 min and the luminescence intensity did not change. Shaking of the aqueous layer with the organic extractant for 60 s allowed maximum extraction of the complex.

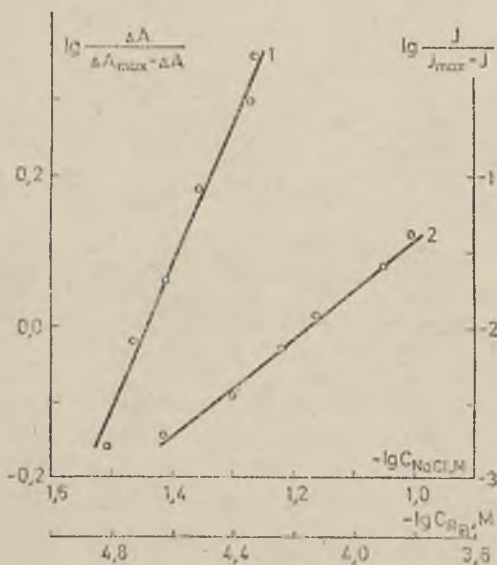


Fig. 8. Dependence between partition coefficient of mercury and equilibrium concentration of Rb (curve 1; $C_{Hg} = 2 \times 10^{-5}M$) and of the NaCl concentration (line 2; $C_{Rb} = 1 \times 10^{-5}M$, $C_{Hg} = 1 \times 10^{-4}M$)

Rys. 8. Zależność współczynnika podziału rtęci od równowagowego stężenia Rb (prosta 1, $C_{Hg} = 2 \cdot 10^{-5}M$) i od stężenia NaCl (prosta 2, $C_{Rb} = 1 \cdot 10^{-5}M$; $C_{Hg} = 1 \cdot 10^{-4}M$).

The complexation reaction of Hg(II) with rhodamine B may provide a basis for the determination of mercury in sea water by the luminescence method after checking the selectivity of the method with respect to other heavy metals present in the environment.

4. CONCLUSIONS

Mercury (II) was found to form the $[(\text{HgCl}_3)^- \cdot \text{R}_B^+]$ complex with rhodamine B in the presence of the Cl^- ions. The complex is easily extractable with a benzene — ether mixture. The maximum absorbance of the complex in the extractant occurs at 564 nm.

The most intense extraction of the complex occurs within the pH range 1—2 and within the NaCl concentration range 0.1—0.2 M.

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BADANIA REAKCJI TWORZENIA KOMPLEKSU RĘĆ (II) — RODAMINA B POD KĄTEM ZASTOSOWANIA JEJ W OZNACZANIU RĘĆCI METODĄ LUMINESCENCYJNĄ

Streszczenie

W pracy przeanalizowano warunki zachodzenia reakcji kompleksowania pomiędzy rodaminą B a Hg (II) pod kątem wykorzystania jej do oznaczania niewielkich ilości rtęci w wodzie morskiej metodą luminescencyjną. Jako mieszaniny ekstrakcyjnej użyto mieszaniny benzenu i eteru etylowego w stosunku 2:1. Badania absorpcyjne prowadzono na spektrometrze Specord UV VIS, pomiary luminescencyjne na specjalnie zmontowanej aparaturze a pehametryczne na pH-metrze LBS-66.

Ustalono, że w zakresie pH: 1—2 występuje najintensywniejsza ekstrakcja kompleksów $\text{R}_B\text{—Hg}$ (II) z fazy wodnej. Przejście badanego kompleksu do warstwy organicznej również zależy od stężenia jonów chlorkowych, które prawdopodobnie spełniają rolę jonu uzupełniającego. Najlepsze efekty uzyskuje się przy stężeniu NaCl w wodzie od 0,1—0,2 M.

Nasylenie badanym kompleksem mieszaniny ekstrahującej, stosując stałe stężenie HgCl_2 ($C_{\text{Hg}}=2 \cdot 10^{-5}\text{M}$) i optymalne warunki (pH=1,5; $C_{\text{NaCl}}=0,15\text{M}$), uzyskano przy stężeniu R : $C_{\text{R}_B} \approx 2 \cdot 10^{-4}\text{M}$. Maksymalny procent ekstrakcji kompleksu wynosi około 90%. Na podstawie metody serii izomolowych roztworów oraz przy pomocy metody przesunięcia równowagi ustalono, że w wyniku reakcji pomiędzy R_B i Hg (II) tworzy się związek kompleksowy o składzie $[(\text{HgCl}_3)^- \cdot \text{R}_B^+]$.

Uzyskane wyniki pozwalają stwierdzić, że zbadaną reakcję można spożytkować do ilościowego oznaczania rtęci w wodzie morskiej metodą luminescencyjną.

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