

betätigt ein Relais (mit Rückkopplung zum System), wenn sich auf Grund einer Änderung im untersuchten System die emittierte Frequenz ändert.

Résumé—On décrit un appareil pour le contrôle à distance d'opérations chimiques et pour le contrôle à distance de processus, au moyen d'un radio-récepteur accordé à la fréquence initiale d'un oscillateur qui traduit quelque paramètre physique du système contrôlé. Le récepteur fait fonctionner un relais (avec alimentation en retour au système) lorsque la fréquence émise change par suite d'un changement dans le système examiné.

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The extraction constant of mercury(II) *o-o'*-dimethyldithizonate into toluene

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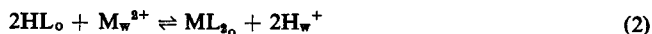
THE DETERMINATION of iodide, based on the measurement of dithizone liberated from its mercury(II) complex by means of the iodide to be determined, has been described by Agterdenbos *et al.*¹ Replacement of the dithizone by *o-o'*-dimethyldithizone [di(*o*-tolyl)thiocarbazone], H₂DMD, did not give a substantial improvement of the determination of iodide by the described method. In the course of this investigation an attempt was made to determine the extraction constant of the mercury(II) complex of H₂DMD into toluene. The unexpected results obtained are reported in this paper.

THEORY

If the extraction constant (subscripts o and w denote the organic and aqueous phases)

$$K = \frac{[ML_2]_o \cdot [H^+]_w^2}{[HL]_o^2 \cdot [M^{2+}]_w} \quad (1)$$

of the equilibrium



is very large, it can be measured only in the presence of an auxiliary complexing agent. Some cases of this type, with iodide as an auxiliary complexing agent, have been described, *e.g.*, by Takei and Kato²⁻⁷ and Bréant.⁸

It is easily derived that if H₂DMD is used for HL:

$$K = \frac{[Hg(HDMD)_2]_o \cdot [H^+]_w^2}{[H_2DMD]_o^2 \cdot \alpha \left(\frac{Hg_t}{v_o} - [Hg(HDMD)_2]_o \right)} \cdot \frac{v_w}{v_o} \quad (3)$$

where Hg_t is the total amount of Hg(II) in mmole; v_w and v_o denote the volumes of the aqueous and organic phase in ml; both volumes and [H⁺]_w are known from the amounts added. In this

expression α is given by:

$$\begin{aligned}\alpha &= \frac{\text{amount of Hg}^{2+} \text{ in aqueous phase}}{\text{total amount of Hg(II) not bound to HDMD}} \\ &= \frac{[\text{Hg}^{2+}]_w \cdot v_w}{\text{Hg}_t - [\text{Hg}(\text{HDMD})_2]_o \cdot v_o} \quad (4) \\ &= \frac{[\text{Hg}^{2+}]_w}{\left(\frac{\text{Hg}_t}{v_o} - [\text{Hg}(\text{HDMD})_2]_o\right) \cdot \frac{v_o}{v_w}}\end{aligned}$$

For the calculation of α , values given by Marcus^{9,10} were used for the stability constants of the mercury(II) iodide-complexes and for the partition coefficient $[\text{HgI}_2]_o/[\text{HgI}_2]_w$.

EXPERIMENTAL

Preparation of H₂DMD

o-o'-Dimethyldithizonone was synthesized from 2-methylaniline.¹¹ The final product was purified,¹² by shaking a solution in carbon tetrachloride several times with ammonia and re-extracting it with sulphuric acid into water. To prevent oxidation of the product it was found necessary to add the sulphuric acid at as low a temperature as possible. After purification the product was transferred into toluene. The absorption maxima in toluene were found at 632 and 464 nm, the peak-ratio was 2.4, ϵ_{632} was 41×10^3 l. mole⁻¹. mm⁻¹. Busev and Bazhanova¹³ report a maximum at 630 nm. The absorption maxima in carbon tetrachloride were found at 628 and 457 nm with a peak-ratio of 2.0. Takei and Kato report the maxima at 628 and 458 nm with a peak-ratio of 2.3. At 632 nm there is no absorbance due to Hg(HDMD)₂.

Determination of K

Reagents. Solutions of mercury(II) chloride, potassium chloride, sodium perchlorate and perchloric acid were prepared from analytical grade reagents. A solution of H₂DMD in toluene, about $2 \times 10^{-5}M$, was prepared as described above.

Procedure. To 25 ml (v_o) of H₂DMD in toluene were added 25 ml (v_w) of an aqueous solution containing slightly less than the stoichiometric amount of mercuric chloride, from 0.09 to 1.8 m-mole of potassium iodide, from 0.025 to 2.5 mmole of perchloric acid and enough sodium perchlorate to make the ionic strength 0.5. The phases were shaken together in a separatory funnel, and after separation the absorbance of the toluene phase was measured at 632 nm.

Calculations

From the absorbance at 632 nm the value of $[\text{H}_2\text{DMD}]_o$ was found. With this value of $[\text{H}_2\text{DMD}]_o$ and the total amount of H₂DMD added the value of $[\text{Hg}(\text{HDMD})_2]_o$ could be calculated. The values of Hg_t and $[\text{H}^+]$ were found from the amount of reagent added and from the values of v_w and v_o . From the amount of iodide added, the value of v_w and the physical constants given in the theoretical part, the values of α was calculated. In this way, all values necessary for the calculation of K [see equation (3)] were known.

RESULTS AND DISCUSSION

Results are given in the columns headed *a* in Table I. The mean value of $\log K$ is 27.9, the standard deviation $s = 2.1$. Furthermore the value K' , given by

$$\log K' = \log K + n\text{pH} + q\text{pI} \quad (5)$$

(where $\text{pI} = -\log[\text{I}^-]_w$), was calculated for $n = 2$ and $q = 2$. The results shown in the columns headed *b* of Table I show that K' has a mean value of 34.3 and $s_1 = 0.32$. This may be explained by assuming that the dithizonate is completely converted into the extractable compound $\text{Hg}(\text{HDMD})_2 \cdot 2\text{HI}$, with the same spectrum as $\text{Hg}(\text{HDMD})_2$. There is no further evidence to support this, however.

If it is not assumed that n and q are integers, insertion of the values $n = 1.7$ and $q = 2.2$ in (5) gives a mean value of $\log K' = 34.2$ with $s_2 = 0.15$, a value significantly lower than the value 0.32. Interpretation of the non-integers seems still more difficult than that of the integers, however (columns *c*).

TABLE I.—VALUES OF LOG K AND LOG K'

pH	pI			1.5			1.8			2.4		
	a	b	c	a	b	c	a	b	c	a	b	c
0	31.6	33.8	34.0	31.0	34.0	34.3	30.2	33.8	34.2	29.1	33.9	34.4
0.5	31.0	34.2	34.3	30.3	34.3	34.4	29.6	34.2	34.4	28.3	34.1	34.4
1.0	30.1	34.3	34.2	29.3	34.3	34.3	28.3	33.9	34.0	27.1	33.9	34.1
1.5	29.3	34.5	34.3	28.5	34.5	34.3	27.6	34.2	34.1	26.3	34.1	34.1
2.0	28.6	34.8	34.4	27.8	34.8	34.5	27.0	34.6	34.4	25.6	34.4	34.3
2.5	27.4	34.6	34.1	26.7	34.7	34.2	25.8	34.4	34.0	24.5	34.3	34.0
3.0	26.4	34.6	33.9	25.8	34.8	34.2	25.1	34.7	34.2	23.9	34.7	34.3

a: log K .

b: log K' for $n = 2$ and $q = 2$.

c: log K' for $n = 1.7$ and $q = 2.2$.

Though no interpretation of the results obtained can be given, this paper may suggest that the method described here for the determination of extraction constants should be used with caution.

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Summary—An attempt was made to determine spectrophotometrically the extraction constant of mercury(II) *o-o'*-dimethyldithizonate into toluene by means of a known excess of iodide as a masking agent. The results found, however, could not be explained by a simple reaction between mercury(II) *o-o'*-dimethyldithizonate and iodide.

Zusammenfassung—Es wurde versucht, mit Hilfe eines bekannten Jodidüberschusses als Maskierungsmittel die Extraktionskonstante von Quecksilber (II)-*o-o'*-dimethyldithizonat in Toluol spektrophotometrisch zu bestimmen. Die Ergebnisse ließen sich jedoch nicht mit einer einfachen Reaktion zwischen Quecksilber (II)-*o-o'*-dimethyldithizonat und Jodid erklären.

Résumé—On a fait un essai pour déterminer spectrophotométriquement la constante d'extraction de l'*o,o'*-diméthyl-dithizonate de mercure(II) en toluène au moyen d'un excès connu d'iodure comme agent de dissimulation. Toutefois, les résultats trouvés n'ont pu être expliqués par une simple réaction entre l'*o,o'*-diméthyl-dithizonate de mercure(II) et l'iodure.

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