

# Complexation equilibria in the systems Bi(III)—2-(2'-thiazolylazo)-4,6-dimethylphenol and Hg(II)—2-(4',5'-dimethyl-2'-thiazolylazo)-4,6-dimethylphenol

B. SANTANA, M<sup>a</sup> J. SÁNCHEZ, J. J. ARIAS, and F. GARCÍA-MONTELONGO

*Department of Analytical Chemistry, University of La Laguna,  
E38204-La Laguna*

Received 9 November 1987

In an ethanol—water medium ( $\varphi(\text{ethanol}) = 40 \text{ vol. } \%$ ) at  $I(\text{NaClO}_4) = 0.25 \text{ mol dm}^{-3}$  the system Bi(III)—2-(2'-thiazolylazo)-4,6-dimethylphenol forms the complex species Bi(OH)R ( $\log \beta_{111} = 10.96 \pm 0.09$ ) and Bi(OH)<sub>2</sub>R ( $\log \beta_{121} = 8.58 \pm 0.13$ ), and the system Hg(II)—2-(4',5'-dimethyl-2'-thiazolylazo)-4,6-dimethylphenol forms the complexes HgR ( $\log \beta_{101} = 10.95 \pm 0.05$ ) and Hg(OH)R ( $\log \beta_{111} = 8.07 \pm 0.02$ ).

В водно-спиртовой среде ( $\varphi(\text{этанола}) = 40 \text{ объ. } \%$ ) при  $I(\text{NaClO}_4) = 0,25 \text{ моль дм}^{-3}$  система Bi(III) с 2-(2'-тиазолилазо)-4,6-диметилфенолом образует комплексные соединения Bi(OH)R ( $\log \beta_{111} = 10,96 \pm 0,09$ ) и Bi(OH)<sub>2</sub>R ( $\log \beta_{121} = 8,58 \pm 0,13$ ), а система Hg(II) с 2-(4',5'-диметил-2'-тиазолилазо)-4,6-диметилфенолом образует комплексы HgR ( $\log \beta_{101} = 10,95 \pm 0,05$ ) и Hg(OH)R ( $\log \beta_{111} = 8,07 \pm 0,02$ ).

Even though heteroazo phenols have been widely used as analytical reagents [1, 2] for many metal ions in most cases little attention has been paid to their complexation equilibria in solution.

In this paper the complexation behaviour of 2-(2'-thiazolylazo)-4,6-dimethylphenol (TADMP) and 2-(4',5'-dimethyl-2'-thiazolylazo)-4,6-dimethylphenol (DMTADMP) [3] with Bi(III) and Hg(II), respectively, has been studied. Graphical and numerical analysis of the absorbance—pH dependences [4—6] enabled the establishment of the complex species in solution and the calculation of their stability constants.

## Experimental

Anal. grade Merck reagents (Darmstadt, GFR) and doubly distilled water were used throughout with no further purification.

Standard  $10^{-2} \text{ M}$  solutions of Bi(ClO<sub>4</sub>)<sub>3</sub> and of Hg(ClO<sub>4</sub>)<sub>2</sub> were prepared from the corresponding nitrates by perchloric acid treatment, and standardized complexometrically.

Stock  $10^{-3} \text{ M}$  solutions of TADMP (HR) and DMTADMP (HR) were prepared and purified (> 9 %, thin-layer chromatography and high resolution mass spectrometry) as described previously [3], in absolute ethanol.

A 2.5 M- $\text{NaClO}_4$  solution was used to maintain constant the ionic strength of the solutions  $I(\text{NaClO}_4) = 0.25 \text{ mol dm}^{-3}$ . Experiments were carried out at  $25 \pm 0.5^\circ\text{C}$ .

The absorbance of the solutions was measured using Beckman 25 (Fullerton, CA, USA) and Hitachi Perkin—Elmer 200 (Tokyo, Japan) recording spectrophotometers provided with 1 cm path length quartz cells.

A Radiometer PHM64 digital pH-meter (Copenhagen, Denmark) provided with a glass-calomel GK-2401-C combination electrode was used for pH measurements. Calibration of the electrode system in the ethanol—water medium ( $\phi(\text{ethanol}) = 40 \text{ vol. } \%$ ) used was carried out at  $25 \pm 0.5^\circ\text{C}$  according to *Bates et al.* [7].

Calculations were performed using a Digital VAS/VMX 11/780 (V.4.0) computer (Maynard, MA, USA). The experimental data were analyzed by applying the LETA-GROP-SPEFO program [6]. In this treatment composition and approximate equilibrium constant are given to the program which searches for the best set of constants and complexes which minimizes the error square sum,  $U(A)$ , defined as

$$U(A) = \sum_{N_p} (A_{\text{calc}} - A_{\text{exp}})^2$$

where  $A_{\text{exp}}$  represents the experimental absorbances and  $A_{\text{calc}}$  the corresponding values calculated by the computer assuming a certain set of complex species and constants.  $N_p$  is the number of experimental  $A$ —pH points given to the program. The program can be fed with a maximum of 110 experimental points.

In the first step calculations were performed using the species models and stability constants ascertained by graphical analysis. Nevertheless, in the second step, other combinations of complexes were tried searching for new species which could improve the fit to the experimental data. For each model of species tried, the program calculates both  $U(A)$  and  $\sigma(A)$ , the mean standard deviation, defined as

$$\sigma(A) = (U/N_p)^{1/2}$$

The best model is the one which gives the lowest values for both  $U(A)$  and  $\sigma(A)$ .

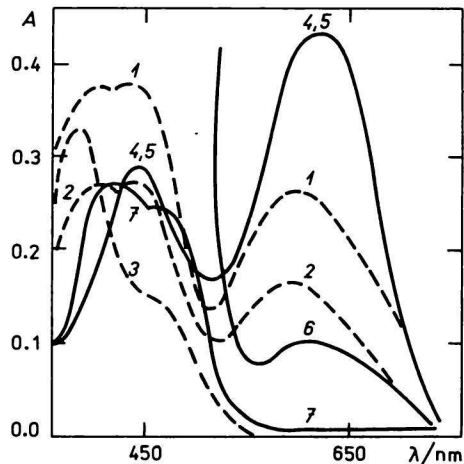
For each species model tested the computer output gives the values of  $U(A)$ ,  $\sigma(A)$ ,  $\log \beta_{pqr} \pm 3\sigma(\log \beta_{pqr})$  and  $\varepsilon(\lambda) \pm 3\sigma(\varepsilon(\lambda))$ ,  $\sigma$  being the mean standard deviation. The stability constants as calculated using relative equilibrium concentrations are dimensionless.

## Results and discussion

TADMP and DMTADMP and Bi(III) and Hg(II), respectively, cause greenish colourations,  $\lambda_{\text{max}} = 605 \text{ nm}$  and  $625 \text{ nm}$ , respectively, in solutions with  $\text{pH} \geq 3$  (Fig. 1).

The absorbance—pH curves (Fig. 2) carried out at  $\lambda = 605 \text{ nm}$  for several  $c(\text{Bi})/c(\text{TADMP})$  ratios show that complexation begins at  $\text{pH} \leq 0.5$  and stabilizes at  $\text{pH} \geq 2.5$  in reagent excess solution. The shape of the curves seems to indicate the presence of several complex species in solution.

Fig. 1. Absorption spectra for the systems: Bi(III)—TADMP (---), pH = 2.5,  $c(R) = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{Bi})/c(R)$ : 20 (1), 1 (2), reagent alone (3); and Hg(II)—DMTADMP (—), pH = 2.99,  $c(R) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{Hg})/c(R)$ : 50 (4), 25 (5), 0.2 (6), reagent alone (7). 40 vol. % ethanol—water,  $I(\text{NaClO}_4) = 0.25 \text{ mol dm}^{-3}$ .



For the Hg(II)—DMTADMP system the absorbance—pH curves (Fig. 3) indicate that complexation begins at  $\text{pH} \leq 0.5$  and stabilizes for  $\text{pH} \geq 2.6$ , and the shape of the curves also seems to indicate the presence of several complexes in solution.

The stoichiometry of the complex species as determined by the continuous variations and mole ratio methods (Fig. 4) shows the formation of only  $c(M)/c(R) = 1:1$  complex species in both systems.

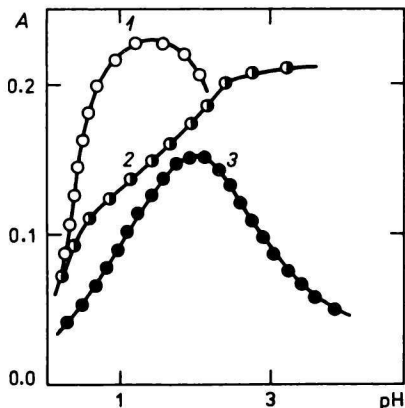


Fig. 2. Absorbance—pH curves for the system Bi(III)—TADMP, 40 vol. % ethanol—water,  $I(\text{NaClO}_4) = 0.25 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 605 \text{ nm}$ ,  $c(R) = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{Bi})/c(R)$ : 20 (1), 1 (2), 0.08 (3).

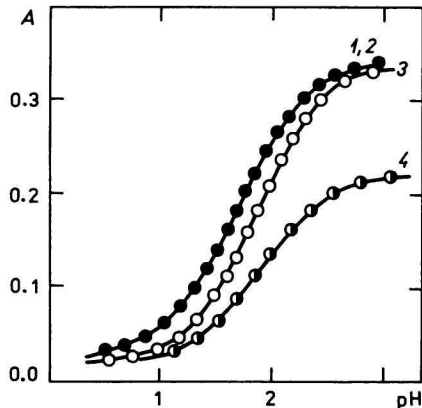


Fig. 3. Absorbance—pH curves for the system Hg(II)—DMTADMP, 40 vol. % ethanol—water,  $I(\text{NaClO}_4) = 0.25 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 625 \text{ nm}$ ,  $c(R) = 2 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c(\text{Hg})/c(R)$ : 25 (1), 20 (2), 10 (3), 0.2 (4).

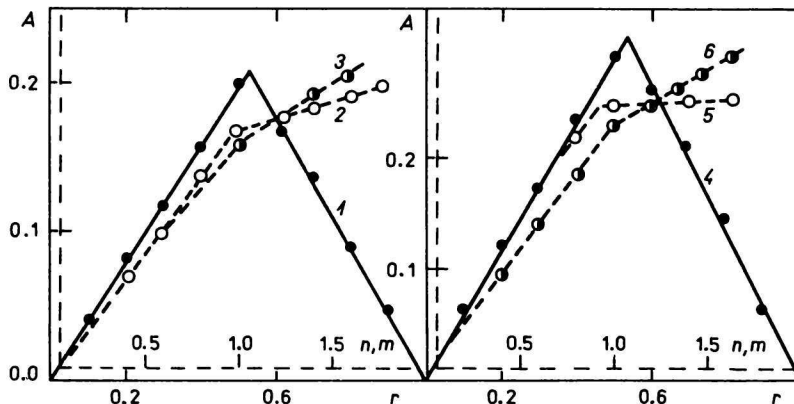


Fig. 4. Stoichiometry of the systems: Bi(III)—TADMP, pH = 1.7: continuous variations:  $c(\text{Bi}) + c(\text{R}) = 8 \times 10^{-5} \text{ mol dm}^{-3}$  (1); mole ratio:  $c(\text{R}) = \text{const.} = 4 \times 10^{-5} \text{ mol dm}^{-3}$  (2); mole ratio:  $c(\text{Bi}) = \text{const.} = 4 \times 10^{-5} \text{ mol dm}^{-3}$  (3); and Hg(II)—DMTADMP, pH = 2.9: continuous variations:  $c(\text{Hg}) + c(\text{R}) = 2 \times 10^{-5} \text{ mol dm}^{-3}$  (4); mole ratio:  $c(\text{Hg}) = \text{const.} = 1 \times 10^{-5} \text{ mol dm}^{-3}$  (5); mole ratio:  $c(\text{R}) = \text{const.} = 1 \times 10^{-5} \text{ mol dm}^{-3}$  (6).  
 $r = c(\text{R})/(c(\text{R}) + c(\text{M}))$ ,  $m = c(\text{M})/c(\text{R})$ ,  $n = c(\text{R})/c(\text{M})$ .

For the calculation of the stability constants of the complex species involved in each system the method of graphical analysis of the absorbance—pH dependences of *Sommer et al.* [4, 5] was used firstly, from which the existence of species BiR ( $\log \beta_{101} = 9.83$ ) and Bi(OH)R ( $\log \beta_{111} = 8.73$ ) in the system Bi(III)—TADMP, and of species HgR ( $\log \beta_{101} = 11.06$ ) in the system Hg(II)—DMTADMP was established, from points in the ranges  $1.0 \leq \text{pH} \leq 2.5$  and  $1.5 \leq \text{pH} \leq 3.0$ , respectively, in each absorbance—pH curve.

The experimental data were analyzed next by applying the LETAGROP-SPEFO program. For each system 110 experimental points coming from the respective absorbance—pH dependences (Figs. 2 and 3) in the ranges  $0.5 \leq \text{pH} \leq 3.0$  for the Bi(III)—TADMP system and  $0.5 \leq \text{pH} \leq 3.5$  for the Hg(II)—DMTADMP, were fed to the program as well as the corresponding  $c(\text{M})$  and  $c(\text{R})$  values for each set of points coming from each absorbance—pH dependence.

As seen in Table 1 the best fit for the system Bi(III)—TADMP is obtained with the model including species Bi(OH)R and Bi(OH)<sub>2</sub>R simultaneously. The model including the species BiR and Bi(OH)R deduced by graphical analysis does not fit the experimental results. Table 2 shows that for the system Hg(II)—DMTADMP the best fit is obtained for the model including species HgR and Hg(OH)R simultaneously. In any case the fit is not improved by introducing other species such as higher hydroxylated complexes ( $\text{M}(\text{OH})_n\text{R}$ ,  $n \geq 2$ ), protonated ( $\text{MH}_n\text{R}$ ,  $n \geq 2$ ) and/or polynuclear ( $\text{M}_m(\text{OH})_n\text{R}_r$ ,  $m \geq 2$ ,  $n \geq 2$ ,

Table 1

Results of the numerical treatment of the data for the different models of species tested for the system Bi(III)—TADMP\*

Species	$U(A)**$	$\sigma(A)**$	$\log \beta_{pqr} \pm 3\sigma(\log \beta_{pqr})$	$\varepsilon(605) \pm 3\sigma(\varepsilon)***$
BiR	0.55	0.09	10.89 $\pm$ 0.18	—
Bi(OH)R			11.04 max 15.4	—
BiR	0.28	0.06	10.91 $\pm$ 0.26	—
BiHR			20.83 max 23.19	—
BiR	0.37	0.07	11.79 max 12.06	—
Bi(OH) <sub>2</sub> R <sub>2</sub>			11.83 max 12.61	—
BiR	0.15	0.05	11.49 $\pm$ 0.22	7200 $\pm$ 1400
Bi(OH)R			8.68 $\pm$ 0.22	9800 $\pm$ 200
Bi(OH)R <sub>2</sub>			8.98 max 15.42	—
BiR	0.23	0.05	11.67 max 11.99	—
Bi(OH)R			—	—
Bi(OH) <sub>2</sub> R			5.72 max 6.18	—
Bi(OH)R	0.0027	0.008	10.96 $\pm$ 0.09	6143 $\pm$ 60
Bi(OH) <sub>2</sub> R			8.58 $\pm$ 0.13	1186 $\pm$ 76

\*  $N_p = 110$  experimental points, experimental conditions as in Fig. 2.

\*\* Absorbance unities.

\*\*\*  $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$ .

Table 2

Results of the numerical treatment of the data for the different models of species tested for the system Hg(II)—DMTADMP\*

Species	$U(A)**$	$\sigma(A)**$	$\log \beta_{pqr} \pm 3\sigma(\log \beta_{pqr})$	$\varepsilon(625) \pm 3\sigma(\varepsilon)***$
HgHR <sub>2</sub>	0.23	0.04	12.07 $\pm$ 0.23	—
HgR	0.12	0.036	11.07 $\pm$ 0.09	10000 $\pm$ 100
HgHR			24.40 $\pm$ 0.23	—
HgHR <sub>2</sub>	0.0018	0.014	12.51 $\pm$ 0.17	—
HgR <sub>2</sub>			11.31 $\pm$ 0.08	9600 $\pm$ 250
HgR <sub>2</sub>	0.0091	0.009	8.05 max 12.44	—
HgR			10.79 max 11.13	6800 $\pm$ 35
Hg(OH)R			9.39 max 9.21	8100 $\pm$ 211
HgR	0.0025	0.006	10.95 $\pm$ 0.05	10817 $\pm$ 44
Hg(OH)R			8.07 $\pm$ 0.02	4274 $\pm$ 108

\*  $N_p = 110$  experimental points, experimental conditions as in Fig. 3.

\*\* Absorbance unities.

\*\*\*  $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$ .

$r \geq 2$ ) complexes. The values calculated for the corresponding stability constants as well as the respective molar absorption coefficients as calculated by the program, are included in Tables 1 and 2.

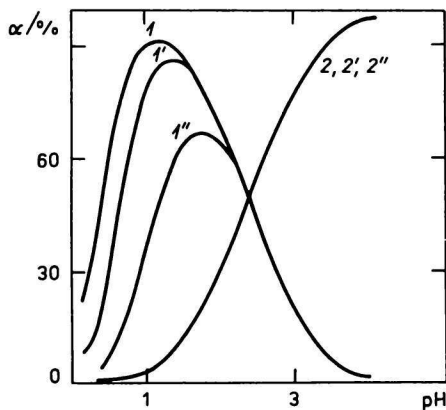


Fig. 5. Distribution diagram for the system Bi(III)—TADMP:  $c(\text{Bi}) = 25c(\text{R}) = 8 \times 10^{-4} \text{ mol dm}^{-3}$  (1, 2);  $c(\text{Bi}) = 0.08c(\text{R}) = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$  (1', 2');  $c(\text{Bi}) = c(\text{R}) = 4 \times 10^{-5} \text{ mol dm}^{-3}$  (1'', 2''); Bi(OH)R (1, 1', 1''), Bi(OH)<sub>2</sub>R (2, 2', 2'').

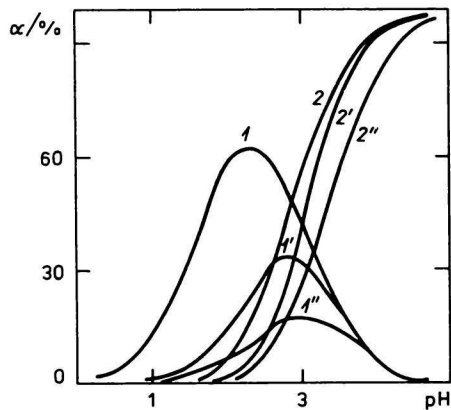


Fig. 6. Distribution diagram for the system Hg(II)—DMTADMP:  $c(\text{Hg}) = 25c(\text{R}) = 2 \times 10^{-4} \text{ mol dm}^{-3}$  (1, 2);  $c(\text{Hg}) = 0.2c(\text{R}) = 1 \times 10^{-3} \text{ mol dm}^{-3}$  (1', 2');  $c(\text{Hg}) = c(\text{R}) = 4 \times 10^{-5} \text{ mol dm}^{-3}$  (1'', 2''); HgR (1, 1', 1''), Hg(OH)R (2, 2', 2'').

The distribution diagram of species (Figs. 5 and 6) as established using the HALTAFALL program [8] shows how species Bi(OH)R predominates at  $\text{pH} < 2.5$  and species Bi(OH)<sub>2</sub>R predominates in solutions at  $\text{pH} > 3$ . For the system Hg(II)—DMTADMP species Hg(OH)R predominates at  $\text{pH} > 3$ .

*Acknowledgements.* The authors wish to acknowledge financial support of this work by CAICYT (Spain) grant No. 4133/79.

## References

1. Hovind, H. R., *Analyst* (London) **100**, 769 (1975).
2. Shibata, S., in *Chelates in Analytical Chemistry*, Vol. 4. (Flaschka, H. and Barnard, A. J., Editors.) P. 1. M. Dekker, New York, 1972.
3. Santana, B., Sánchez, M<sup>a</sup> J., Arias, J. J., and García-Montelongo, F., *Collect. Czechoslov. Chem. Commun.* **53**, 258 (1988).
4. Mushran, S. P. and Sommer, L., *Collect. Czechoslov. Chem. Commun.* **34**, 3693 (1969).
5. Sommer, L., Langová, M., and Kubáň, V., *Collect. Czechoslov. Chem. Commun.* **41**, 1317 (1976).
6. Sillén, L. G. and Warnqvist, B., *Ark. Kemi* **31**, 377 (1968).
7. Bates, R. G., Bennetto, H. P., and Sankar, M., *Anal. Chem.* **52**, 1598 (1980).
8. Ingri, N., Kakolowicz, M., Sillén, L. G., and Warnqvist, B., *Talanta* **14**, 1261 (1967).