Correspondence

Rio de Janeiro, June 27, 1998 Dear sir:

The paper "Spectrophotometric Determination of Iodate in Talbe Salt", wrote by Rosa Lina G.N.P. Silva, A. Fernando de Oliveira, and Eduardo Almeida Neves that appeared in *J. Braz. Chem. Soc.* **1998**, 9(2), 171 has called my attention because of the molar absortivities found by these authors for the ion I_3 - at the wavelengths 288 and 352 nm. As can be seen from the tables presented below, these values are much higher than those obtained by other authors.

Table 1.

λ / nm	ε/M ⁻¹ cm ⁻¹	Ref.
287.5	40 000	1
288	40 000	2
288	38790	3
288	40 000	4
288	1.103×10^5	Silva et al.

Table 2.

λ / nm	ε/M ⁻¹ cm ⁻¹	Ref.
350	25 750	3
351	27 000	4
352	26 400	2
352	7.320×10^4	Silva et al.
353	26 400	1
353	2.58×10^4	5

As the iodate content in the table salt is measured by the UV-Vis spectroscopy at these wavelengths it would be convenient for these authors to justify why their molar absortivity values are so different.

Respectfully, Roberto de Barros Faria Departamento de Química Inorgânica Universidade Federal do Rio de Janeiro.

References:

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- 2. Allen, T.L.; Keefer, R.M. "The Formation of Hypoiodous Acid and Hydrated Iodine Cation by the Hydrolysis of Iodine", *J. Am. Chem. Soc* **1955**, *77*, 2957-2960.
- 3. Palmer, D.A.; Ramette, R.W.; Mesmer, R.E. "Triiodide Ion Formation Equilibrium and Activity Coefficients in Aqueous Solution", *J. Solution Chem* **1984**, *13*(9), 673-683.
- 4. Troy, R.C.; Kelley, M.D.; Nagy, J.C.; Margerum, D.W. "Non-Metal Redox Kinetics: Iodine Monobromide Reaction with Iodide Ion and the Hydrolysis of IBr", *Inorg. Chem.* **1991**, *30*(25), 4838-4845.
- 5. Thomas, T.R.; Pence, D.T.; Hasty, R.A. "The Disproportionation of Hypoiodous Acid", *J. Inorg. Nucl. Chem.* **1980**, *42*, 183-186 (note that the correct ε value for the 353 nm band is equal to 2,58 x 104 and not 2,58; it can be obtained from Eqs. (1) and (2)).

Author's Replay

Our molar absortivity data, ϵ , are correct and are referred not exactly for the I_3^- anion but indirectly for IO_3^- as they are the slopes of analytical curves for iodate in salt NaCl. The reported data are based on the following redox reaction that takes place between iodate with iodide in acidic medium:

$$IO_3^- + 5 I^- + 6 H^+ \rightarrow 3 I_2 + 3 H_2O$$

 $3 I_2 + 3 I^- \rightarrow 3 I_3^-$
 $IO_3^- + 8 I^- + 6 H^+ \rightarrow 3 I_3^- + 3 H_2O$

On this basis it is clear that 1 IO_3^- ion generates 3 I_3^- . Thus our indirect iodide ϵ data should be divided by 3 when referred to I_3^- :

At 352 nm,
$$\varepsilon = (73\ 200\ /\ 3) = 24\ 400\ L\ mol^{-1}\ cm^{-1}$$

At 288 nm, $\varepsilon = (110\ 300\ /\ 3) = 36\ 767\ L\ mol^{-1}\ cm^{-1}$

These values are colse to those from the literature, $40\,000\,\mathrm{or}\,38\,790\,\mathrm{at}\,288\,\mathrm{nm}$ and $26\,400\,\mathrm{or}\,25\,800\,\mathrm{at}\,352\,\mathrm{nm}$. Small differences are acceptable due to different experimental conditions, viz. ionic. strength and the presence of chloride ion in our working soutions which can compete to some extent with iodide to form a complex like I_2CI^- .

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