OPTICAL INTERACTION BETWEEN THALLIUM IONS OF DIFFERENT OXIDATION STATES

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In 0.5—3.0 M perchloric acid solutions containing both thallic and thallous ions a positive non-additive absorbance has been found in the charge-transfer region (255—200 nm). The optical interaction can be observed immediately and remains constant for several days. Its extent increases with increasing the concentrations of thallium species and decreases if acidity and ionic strength is increased. In the presence of sufficient quantities of sulfate and chloride ions the optical interaction practically drops to zero. It is thought that the mixed valency complexes are formed by reactions of partially hydrolyzed thallic species as soft bases with the soft acid thallous ions.

Although the mixed valence complexes of several elements have been known since long, this interesting field of inorganic chemistry is far from being cleared up and only recently more attention is paid to this line from a quantitative point of view. This situation holds, also, for the chemistry of thallium. In 1949 MCCONNELL and DAVIDSON [1] looked for a non-additive absorbance in solutions containing thallium ions of different oxidation states in the hope of finding explanations for the slowness of the thallium(III)-thallium(I) electron exchange reaction and for its catalysis by halide ions. According to their investigations in the charge-transfer region (300—250 nm), there is no appreciable non-additive absorbance in mixed solution, neither in 1.6 and 3.2 F perchloric acid medium, nor in the presence of chloride ions.

Quite recently we have found [2] that the rate of reaction between thallium(III) ions and hydrogen peroxide in perchloric acid medium is considerably inhibited by addition of thallium(I) ions. This finding is rather surprising because up to now not a single reaction of thallium(III) had been known which was inhibited by thallium(I). To explain this disparate behaviour, we assumed the formation of mixed valence complexes and tried to find evidences for them. Results obtained by potentiometry, polarography and spectrophotometry are reported here.

Experimental

Materials: c.p. thallium(I) sulphate was converted by saturated barium perchlorate solution into thallium(I) perchlorate and one part of this stock solution was oxidized to thallium(III) anodically. Commercial perchloric acid was vacuumdistilled twice. Both perchloric acid and sodium perchlorate used to adjust the acidity and the ionic strength were chloride-free up to the sensitivity limit of the silver chloride test.

Potential measurements were made by ORION Model 801 digital pH meter using saturated calomel reference electrode carefully separated by an electrolytic bridge filled with sodium perchlorate to avoid the contamination of thallium solutions by chloride ions. Polarographic investigations were made by Radiometer Model P04 Polariter using sodium perchlorate supporting electrolyte and saturated calomel electrode as reference. Optical measurements were carried out by Unicam SP 500 and SP 800 spectrophotometers fitted with thermostatted cell compartments (25 ± 0.07 °C). To avoid the slight differences in the path lengths and the transmittances of different optical cells, the absorbances of the single thallium species and those of the mixed solutions were measured in the same cell, using corresponding perchloric acid and perchlorate solutions as reference. Spectra were taken in the range of 260—200 nm, however, only data obtained at 255, 250, and 245 nm, have been used for calculations; at these wavelengths the absorptivity of thallium(I) is small and the error caused by the stray light is negligible.

Experimental Results

According to our data, the Nernst—Peters equation for redox couples holds firmly in solutions containing both thallic and thallous ions, i.e. potentiometrically there is not the slightest hint of interaction of thallium species. The same results were obtained by polarography, too: the half-wave potentials of thallic and thallous ions remained unchanged when one of the components was present in at least 15-fold excess.

However, just the opposite results were found spectrophotometrically. When the concentration of thallium(I) was varied at constant thallic concentration, a positive non-additive absorbance was observed. Some typical results are shown in Fig. 1, where the positive deviation, ΔE, is the difference between the absorbance of solutions containing both thallium species and that calculated assuming additivity in the absorbances of these entities separately. The value of ΔE increases towards the shorter wavelengths. This can be seen in Fig. 2, which illustrates the spectra of thallium species and those of the mixed solutions, and the dependence of ΔE on the wavelength. The latter shows a maximum at about 220 nm in 0.5 M perchloric acid solution. However, this finding should be treated with precaution because

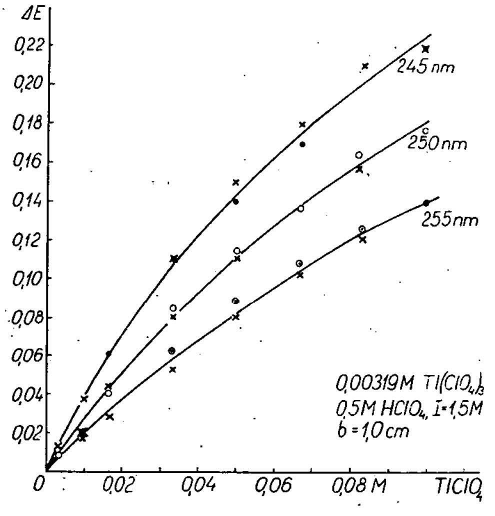

Fig. 1

of the stray light error. The non-additive absorbance can be observed immediately and remains constant even for several days. — Similarly, a curve of saturation value is obtained when the concentration of thallium(III) ions is increased at a constant quantity of thallous ions. — The extent of the optical interaction depends on the acidity of the solution. The value of ΔE decreases considerably with increasing the acid concentration from 0.5 to 3.0 M, and over 3 M no interaction can be observed at all. With increasing the ionic strength, a decrease in ΔE was found in the range of 1—4 M perchlorate concentration, further increase in the ionic strength did not cause any observable change. The non-additive absorbance increases with increasing absolute concentration of thallium(III) ions. This is shown in Fig. 3.

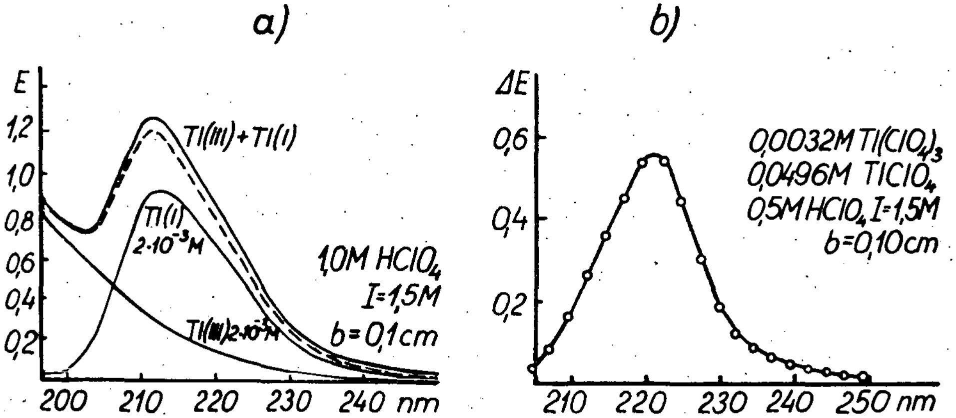

Fig. 2

Although the absorbance of the thallium (III) species considerably increases with the rising temperature, ΔE shows no observable change in the range of 20—40 °C.

On adding sulphate ions to the mixed solution, the value of ΔE decreases and practically drops to zero if sulphate is used in about tenfold excess with respect to the thallium(III) concentration. A still stronger suppressing effect is exerted by chloride ions which are able to quench the interaction in as small as equimolar quantity.

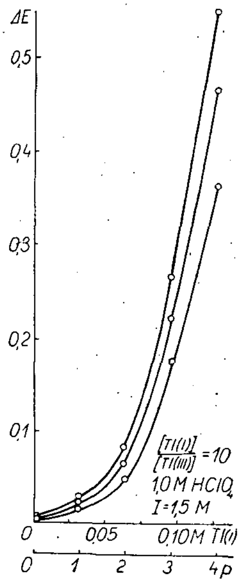

Fig. 3

Discussion

The optical interaction between thallium(III) and thallium(I) ions in perchloric acid medium can be interpreted on the basis of the acid-dependence observed. Thallic ion, like other polyvalent metal ions is an acid of considerable strength and hydrolyses easily even in the presence of dilute perchloric acid, resulting in the corresponding weak bases, the mono and dihydroxo species:

$$Tl^{3+}\cdot aq \overset{K_1}{\rightleftharpoons} TlOH^{2+}\cdot aq + H^+ \tag{1}$$

$$TlOH^{2+}\cdot aq \overset{K_2}{\rightleftharpoons} Tl(OH)_2^+\cdot aq + H^+ \tag{2}$$

According to BIEDERMANN [3], and ROGERS and WAIND [4], olation does not occur. It can be calculated that the quantities of mono- and dihydroxo species amount to 4.6 and 0.1%, resp., in 1.5 M perchloric acid solution.

We assume that the weak bases formed by equilibria (1) and (2) undergo reactions with the soft acid thallium(I) ions:

$$TlOH^{2+} + Tl^+ \rightleftharpoons Tl{-}O{-}Tl^{2+} + H^+ \tag{3}$$

$$Tl(OH)_2^+ + Tl^+ \rightleftharpoons HO{-}Tl{-}O{-}Tl^+ + H \tag{4}$$

$$HO{-}Tl{-}O{-}Tl^+ + Tl^+ \rightleftharpoons Tl(O{-}Tl)_2 + H^+ \tag{5}$$

This assumption seems to be supported by another independent observation, namely that the precipitation-pH of thallium(III)-hydroxide is shifted to higher and higher values when the solution contains thallous ions, too, in increasing quantity.

The experience that the interaction cannot be detected by potentiometry and polarography can be explained as follows: i) both methods are of restricted sensitivity because of the logarithmic relationship between the oxidation-reduction (or half wave) potential and the activities of species involved in the couple; ii) equilibrium (3) presumedly prevailing in the interaction reduces the activities of oxidized and reduced species of thallium equally, therefore the potential must remain constant in spite of the formation of the mixed valence complex.

There is some parallelism between the thallic-thallous electron exchange reaction and our optical observations, which may help to elucidate the nature of the mixed valance complexes. The rate of exchange increases when the acidity is decreased and a dramatic increase in the zero-time exchange rate is caused when the solution is neutralized until the precipitation of thallium(III). These observations were explained by previous authors [5] by the fact that the $TlOH^{2+}$ ion is about eight times more reactive than the $Tl^{3+}\cdot aq$ species, which statement involves a transition state complex as described in equilibrium (3).

On the other hand, it was pointed out by WAIND [6] that the uptake of water is necessary for the formation of the transition state:

$$Tl^{3+}\cdot aq + Tl^+\cdot aq + H_2O \rightleftharpoons y$$

consequently any change in the activity of water results in alteration of the exchange rate.

The large increase in the zero-time exchange rate at pHs where $Tl(OH)_3$ starts to precipitate was explained by VOGT and BORN [7] by a rapid homogeneous exchange between thallium (I) and $Tl(OH)_3$ species. However, it is necessary to take into consideration the finding of JONASSON and STRANKS [8], too, that the thallic-thallous exchange reaction can be efficiently catalyzed by finely divided insoluble thallium(III) oxide.

It is also worth mentioning that the rate of exchange reaction decreases with increasing the ionic strength, just as was found in the case of the non-additive absorbance. This behaviour can be explained partly by the decrease of K_1 with increasing ionic strength, partly by an ion-pair formation between thallic and perchlorate ions.

Both sulphate and chloride ions, if used in sufficient quantity, can cancel the optical interaction. This is easy to be understood because both ions are able to suppress the hydrolysis of thallium(III) and interfere with equilibria (3)—(5).

Considering that the dihydroxo species is present only in small quantity, equilibria (4) and (5) were omitted in the first trial and so we have obtained for $\varDelta E$:

$$\varDelta E = \frac{\varepsilon_Q - \varepsilon_A - \varepsilon_B}{2}\left(A + B + k - \sqrt{(A+B+k)^2 - 4AB}\right) \tag{6}$$

where ε_Q is the molar absorptivity of the mixed valence complex, ε_A is the apparent absorptivity of thallium(III) species and ε_B is that of thallium(I). A and B are the analytical concentrations of thallium(III) and thallium(I) and k is defined as

$$k = \frac{[\mathrm{H}^+]\{K_1 + [\mathrm{H}^+]\}}{K_3 K_1} \tag{7}$$

The unknown values of k and ε_Q were computed by a fitting program using a Minsk 22 computer. The obtained values are compiled in Table I.

Table I

N°	$HClO_4$ (M)	I (M)	(nm)	k	K_3	$Q(M^{-1} \cdot cm^{-1})$
24	0,5	1,5	255	0,06015	57	134
27	0,5	1,5	255	0,06884	50	138
25	0,5	1,5	250	0,055	62	180
29	0,5	1,5	245	0,224	15	201
18	1,0	1,5	255	0,2536	50	117
39	1,0	1,5	255	0,2677	47	110
40	1,0	1,5	250	0,2775	46	164
37	1,0	1,5	250	0,2297	55	151
41	1,0	1,5	245	0,2196	58	187
38	1,0	1,5	245	0,2195	58	186
30	1,5	1,5	255	0,2629	105	104
71	1,5	1,5	250	0,2400	115	119

According to the figures of Table I, the K_3 values are fairly constant when the perchloric acid concentration is 0.5 and 1.0 M, but there is a large deviation at higher acidity. The molar absorptivities obtained show the same trend as the wavelength-dependence of the non-additive absorbance, but the change of the ε_Q values with the acidity points again to the roughness of approximation. These facts indicate that, in spite of the minute quantity of the dihydroxo species, the contribution of this entity to the overall absorbance cannot be neglected. The implication of equilibria (4) and (5) into the computation may help to overcome the mentioned discrepancies. Now we are working on this more involved four-dimension fitting.

programme. However, it may happen that this more rigorous approximation will not furnish much better data, the ΔE values being burdened with a large experimental error of about ±5—8%.

Our results contradict to the findings of McConnell and Davidson [1]. But this contradiction is only apparent. Namely, the absorbances of the mixed solutions were measured by the mentioned authors up to 255 nm in 3.2 M and only up to 265 nm in the presence of 1.6 M perchloric acid. This circumstance taken into account, their experiences perfectly agree with our results, i.e. at 3 M or higher acidity we did not find any interaction either, however, in 1.6 M perchloric acid, where the interaction does exist, its extent at 265 nm hardly exceeds the error of conventional spectrophotometric measurements. Consequently, if these measurements had been extended towards the shorter wavelengths only by as few as 10 nm, the interaction would certainly have been observed, too.

The question why no general thallium(I) inhibition is observed in reactions involving thallium(III), if mixed valence complexes are formed in fact, can be answered by the low stability of the interaction compounds. Thallium(I) is expected to inhibit reactions with partners which form, if at all, only loose adducts with the thallium(III). This was found in the H_2O_2—Tl(III) system. Of course, when the substrate forms a fairly stable complex with thallium(III), e.g. in the case of formic acid (where pK = 5), thallium(I) inhibition cannot be observed. At present there are no sufficient data to explain the lack of thallous inhibition in reactions of thallium(III) with uranium(IV) and mercury(I).

Experiments using thermal methods to collect further evidences for the existence of mixed valence complexes of thallium are in progress.

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ОПТИЧЕСКОЕ ВЗАИМОДЕЙСТВИЕ МЕЖДУ РАЗНЫМИ ОКИСЛЯМИ ТАЛЛИЯ

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В 0,5—3,0 М растворах хлорной кислоты, содержащих ионы таллия(III) и таллия(I), положительная неаддитивная оптическая плотность была найдена в области зарядного переноса (255—200 nm). Оптическое взаимодействие наблюдается сразу и остается постоянным в течении несколько дней. Мера его увеличается с увеличением концентрации таллиевых веществ, и понижается с уменьшением кислотности и ионной силы. В присутствии достаточного количества сульфатного и хлоридного ионов, оптическое взаимодействие практически падает на нуль. Предположено, что смешанные комплексы образуются в результате реакций между частично гидролизированными ионами таллия(III), действующими как «мягкая» щелочь и таллием(I), выступающим как «мягкая» кислота.