THE TITANOMETRIC DETERMINATION OF AZOBENZENE DERIVATIVES IN MIXED ACETONITRILE–METHANOL–WATER MEDIUM*

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Dedicated to Professor Dr J. Zýka on the occasion of his 60th birthday.

The possibility of titanometric determination of a number of azobenzene derivatives in a mixed acetonitrile–methanol–water medium, which ensures sufficient solubility of the substances determined, was studied. Trivalent titanium in the presence of sodium citrate was found to be optimal. Conditions were found for the automatic potentiometric titration of a number of azo-compounds using this reagent.

An earlier communication[1] was devoted to the chromometric determination of azobenzene derivatives. It was found that the direct titration is rather tedious and that nitro derivatives of azobenzene cannot be determined indirectly with divalent chromium even at increased temperatures. Consequently, this work deals with the possibility of titanometric determinations.

The standard redox potential for the Ti(IV)/Ti(III) system is higher than that for the Cr(III)/Cr(II) system, but the formal redox potential values can be markedly affected by addition of complexing agents[2], especially fluoride[3], EDTA (ref.[4]) and sodium tartrate or citrate[5]. Titanium(III) ions are among the most common reductants used in the analysis of dyes and dye industry intermediates[2,6–8]. Recently, attention has also been paid to the use of titanous ions in non-aqueous media of glycerol[9] or mixtures of glycerol with dimethylformamide[10,11].

As many of the studied substances have limited solubility in water, work must be carried out in a mixed water–organic solvent medium. Acetonitrile was found to be useful for dissolving the substances determined, as it is sufficiently resistant to the reductants used. However, cheaper and more easily obtainable methanol can be used as the titration medium. Under these conditions, the titration can be carried out using aqueous standard solutions.

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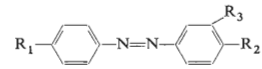
First, the possibility of indirect determination of azodyes of the type



surveyed in Table I, with titanium(III) ions in a medium acidified with sulphuric acid was verified. Because of the long time required for quantitative reduction in this medium, the possibility of speeding up the reaction by addition of a suitable complexing agent (ammonium fluoride, EDTA or sodium citrate or tartrate) was studied. The optimum conditions found for the titanometric determination of the studied azocompounds are given below.

EXPERIMENTAL

Reagents

Solutions of the studied azobenzene derivatives ($c = 5 \cdot 10^{-3}$ mol l^{-1}) in acetonitrile were prepared by dissolving an accurately weighed amount of the pure substance (Research Institute for Organic Synthesis, Pardubice-Rybitví) in this solvent (Laborchemie, Apolda, GDR) purified by the method described by Coetzee[12]. The purity of the substances used was controlled by thin-layer chromatography[13].

The standard titanium(III) chloride solution in 0·5M hydrochloric acid ($c(Ti^{3+}) = 0{\cdot}01$ mol $\cdot l^{-1}$) was prepared by diluting 10 ml of a 15% titanium(III) chloride solution with distilled water, adding 50 ml of concentrated hydrochloric acid and diluting with distilled water to 1 litre. The prepared solution was stored under an inert atmosphere over zinc amalgam and its titre was determined using potassium dichromate[2].

Titanium(III) chloride solutions of the same concentration in 0·1M hydrochloric acid, 0·1M ammonium fluoride, 0·1M-EDTA, 0·1M sodium citrate or 0·1M sodium tartrate medium were

TABLE I
Survey of the studied azodyes

Designation	R_1	R_2	R_3	Designation	R_1	R_2	R_3
I	NH_2—	OH—	H—	*VIII*	$(CH_3)_2N$—	CH_3CONH—	H—
II	CH_3—NH—	OH—	H—	*IX*	$(CH_3)_2N$—	F—	H—
III	$(CH_3)_2N$—	OH—	H—	*X*	$(CH_3)_2N$—	Cl—	H—
IV	NO_2—	OH—	H—	*XI*	$(CH_3)_2N$—	Br—	H—
V	OH—	OH—	H—	*XII*	$(CH_3)_2N$—	I—	H—
VI	$(CH_3)_2N$—	OH—	OH—	*XIII*	$(CH_3)_2N$—	—COOH	H—
VII	$(CH_3)_2N$—	NH_2—	H—	*XIV*	$(CH_3)_2N$—	$—SO_3Na$	H—

prepared analogously with addition of the required amount of the corresponding complexing agent. The pH value of the latter four solutions was adjusted to 5·5 by addition of hydrochloric acid. The titre of these solutions was always determined before use in the following manner: 5·00 ml of ferrous sulphate solution ($c(Fe^{2+}) = 0{\cdot}01$ mol l^{-1}) in 0·1M hydrochloric acid, previously reduced with zinc amalgam so that it did not give a positive reaction with thiocyanate ions, were measured into a titration vessel. An amount of 1·00 ml of potassium dichromate solution ($c(K_2Cr_2O_7) = 0{\cdot}01/6$ mol l^{-1}) was added to this solution along with 10 ml methanol. The solution was bubbled for 5 min with nitrogen and was then titrated potentiometrically with the solution whose titre was to be determined to a potential of +100 mV.

The other chemicals used were all of *p.a.* purity.

Apparatus

The potentiometric titrations were carried out in a thermostatted titration vessel using an automatic titration apparatus consisting of the TTT 1c automatic titrator and an ABU 1b autoburette (Radiometer, Copenhagen, Denmark). A platinum indicator and saturated calomel reference electrode were used. The temperature was maintained constant using a U3 thermostat (Mechanik Prüfgeräte, Medingen, GDR).

TABLE II

Accuracy and reproducibility of the indirect titanometric determination in 0·5M sulphuric acid medium

Compound	Added mg	Found mg	Δ^a %	s_r^b %
I	1·066	1·072	0·56	0·066
II	1·136	1·144	0·70	0·044
III	1·207	1·220	1·08	0·033
IV	—[c]	—	—	—
V	1·071	1·080	0·84	0·028
VI	1·287	1·283	0·31	0·054
VII	1·202	1·197	0·42	0·042
VIII	1·402	1·405	0·21	0·071
IX	1·216	1·221	0·41	0·082
X	1·299	1·307	0·62	0·031
XI	1·521	1·524	0·20	0·066
XII	1·756	1·770	0·80	0·034
XIII	1·347	1·351	0·30	0·044
XIV	1·637	1·645	0·49	0·061

[a] Average relative error in the determination for $n = 7$. [b] Estimated relative standard deviation in the determination for $n = 7$. [c] The reduction is not quantitative after 30 min even with heating to 60°C.

Procedure

Indirect titanometric determination in 0·5M *sulphuric acid medium.* An amount of 1·00 ml of the stock solution of the studied substance in acetonitrile was measured into the titration vessel, 15 ml of 0·5M sulphuric acid were added and the solution was bubbled for 5 min with nitrogen. Then 5·00 ml of a standard titanium(III) chloride solution in 0·5M hydrochloric acid were added from an autoburette and, after complete disappearance of colour (*c.* 10—30 min, if necessary with heating), 5·00 ml of a ferric chloride solution ($c = 1 \,.\, 10^{-2}$ mol l^{-1}) in 0·1M hydrochloric acid were added; unreacted ferric ions were back-titrated with a standard titanium(III) chloride solution in 0·5M hydrochloric acid to a potential of +200 mV. Simultaneously, a blank determination was carried out analogously and the reagent consumption was calculated from the difference.

Comparison of the rate of reduction of trivalent titanium in the presence of various complexing agents. An amount of 10 ml methanol was added to 1·00 ml of the stock solution of the studied substance in acetonitrile in a thermostatted vessel and the solution was bubbled for 5 min with nitrogen. Then 5·00 ml of standard solution of titanium(III) chloride in a suitable medium was added from the autoburette and the time necessary for discolouration of the solution was measured.

Indirect titanometric determination in the presence of various complexing agents. An amount of 1·00 ml of the stock solution of the studied substance in acetonitrile was measured into the

TABLE III

Time necessary for reduction of the studied substances by titanium(III) ions in various media at laboratory temperature

Compound	τ				
	hydrochloric acid min	EDTA min	fluoride min	tartrate s	citrate s
I	10	19	1	50	15
II	7	24	0·8	40	10
III	16	29	2	30	20
IV	>30	>30	23	360	240
V	7	16	1	30	15
VI	5	20	3	60	20
VII	11	24	4	60	20
VIII	14	26	4	40	15
IX	25	>30	7	50	20
X	28	>30	1	40	15
XI	28	>30	4	50	20
XII	>30	>30	3	80	25
XIII	>30	>30	4	80	10
XIV	>30	>30	4	70	20

titration vessel, 10 ml methanol were added (in determination with a standard titanium(III) chloride solution in 0·1M hydrochloric acid medium, 1 ml of 1M hydrochloric acid was also added) and the solution was bubbled for 5 min with nitrogen. Then 5·00 ml of a standard solution of trivalent titanium in a suitable medium was added. After loss of colour, the solution was left to stand for 5 min, 10·00 ml of ferric chloride solution ($c(Fe^{3+}) = 0{\cdot}01$ mol l^{-1}) in 0·1M hydrochloric acid was added and the unreacted excess was titrated with a standard trivalent titanium solution in the given medium to a potential of +100 mV. A blank was carried out simultaneously and the reagent consumption was found from the difference.

Direct titration with trivalent titanium in the presence of citrate. An amount of 1·00 ml of stock solution of the studied substance in acetonitrile was measured into the titration vessel. 10 ml methanol were added and the solution was bubbled for 5 min with nitrogen and potentiometrically titrated with a standard solution of titanium(III) chloride in 0·1M sodium citrate at pH 5·5.

RESULTS AND DISCUSSION

The reagent consumption in direct and indirect titrations corresponds to reduction of the azo group according to Eq. (*A*) and of any nitro group present according to Eq. (*B*):

$$R_1{-}N{=}N{-}R_2 + 4\,Ti^{3+} + 4\,H^+ \rightarrow R_1NH_2 + R_2NH_2 + 4\,Ti^{4+} \qquad (A)$$

$$R{-}NO_2 + 6\,Ti^{3+} + 6\,H^+ \rightarrow RNH_2 + 6\,Ti^{4+} + 2\,H_2O \qquad (B)$$

TABLE IV

Results of the indirect titanometric determination

Compound	Added mg	Found, mg[a]			
		A[b]	B	C	D
I	1·067	1·073	1·077	1·074	1·074
II	1·136	1·143	1·147	1·144	1·144
III	1·207	1·218	1·221	1·217	1·218
IV	1·216	—[c]	—[c]	1·222	1·223
V	1·071	1·081	1·082	1·078	1·079
VI	1·287	1·284	1·292	1·288	1·287
VII	1·202	1·199	1·204	1·203	1·201
VIII	1·402	1·407	1·407	1·401	1·404
IX	1·217	1·223	—[c]	1·221	1·222
X	1·299	1·309	—[c]	1·305	1·306
XI	1·521	1·526	—[c]	1·524	1·525
XII	1·756	—[c]	—[c]	1·769	1·769
XIII	1·347	—[c]	—[c]	1·352	1·353
XIV	1·637	—[c]	—[c]	1·645	1·645

[a] Average of three determinations; [b] titrant medium: A 0·1M-HCl, B 0·1M EDTA, C 0·1M fluoride, D 0·1M tatrate; [c] the determination could could not be carried out.

In the indirect determination in 0·5M sulphuric acid medium, the excess reagent must be left to react for 10–30 min and sometimes (substances *III*, *XI*–*XIV*), the reaction mixture must be heated to 60°C. The reaction of substance *IV* is not quantitative after 30 min even with heating to 60°C. The accuracy and reproducibility of this determination are given in Table II, where the listed values are the average of 7 determinations, from which the standard deviation was also calculated.

The times required for decolouration of the reaction mixture, found by the procedure given in the experimental part, are given in Table III. It follows from this table that the rate of reduction of the studied substances with titanium(III) ions in the presence of complexing agents increases in the order EDTA < fluoride < tartrate < < citrate. The rate of reduction in the presence of EDTA under the given conditions is even less than the rate of reduction in hydrochloric acid medium.

It was found that substances *I*–*III* and *V*–*IX* can be determined indirectly at laboratory temperature using a standard solution of titanium(III) ions in 0·1M hydrochloric acid, but that the excess reagent must be left to react for a rather long time.

TABLE V

Accuracy and reproducibility of the indirect titanometric determination (titrant in 0·1M sodium citrate, pH 5·5)

Compound	Added mg	Found mg	Δ^a %	s_r^b %
I	1·066	1·070	0·38	0·120
II	1·136	1·141	0·44	0·091
III	1·207	1·216	0·75	0·075
IV	1·216	1·224	0·66	0·084
V	1·071	1·079	0·75	0·107
VI	1·287	1·286	0·07	0·110
VII	1·202	1·202	0 00	0·132
VIII	1·402	1·405	0·21	0·101
IX	1·216	1·221	0·41	0·102
X	1·299	1·304	0·39	0·099
XI	1·521	1·524	0·20	0·092
XII	1·756	1·769	0·74	0·078
XIII	1·347	1·350	0·22	0·102
XIV	1·637	1·645	0·49	0·083

[a] Average relative error in the determination for $n = 7$; [b] estimated relative standard deviation for $n = 7$.

TABLE VI

Accuracy and reproducibility of the direct titanometric titration (titrant in 0·1M sodium citrate at pH 5·5)

Compound	Temp. °C	Added mg	Found mg	Δ^a %	s_r^b %	E_f^{oc} mV	ΔE^d mV
I	20	1·066	1·068	0·19	0·056	−140	35
I	65	1·066	1·069	0·28	0·056	−145	35
II	20	1·136	1·142	0·53	0·062	−150	30
II	65	1·136	1·140	0·35	0·053	−160	35
III	20	1·207	1·217	0·83	0·058	−160	55
III	65	1·207	1·216	0·75	0·050	−175	60
IV	20	—	—	—	—	—	—
IV	65	1·217	1·223	0·49	0·066	−125	50
V	20	1·071	1·079	0·75	0·075	+125	60
V	65	1·071	1·078	0·65	0·084	+135	60
VI	20	1·287	1·286	0·08	0·062	+105	55
VI	65	1·287	1·284	0·23	0·054	+120	60
VII	20	1·202	1·201	0·08	0·058	−105	40
VII	65	1·202	1·201	0·08	0·056	−105	40
VIII	20	1·402	1·405	0·21	0·064	−105	40
VIII	65	1·402	1·406	0·29	0·057	−100	40
IX	20	1·216	1·220	0·33	0·058	− 70	35
IX	65	1·216	1·220	0·33	0·049	− 70	40
X	20	1·299	1·305	0·46	0·062	− 30	35
X	65	1·299	1·304	0·39	0·046	− 35	40
XI	20	1·521	1·522	0·07	0·046	+ 35	40
XI	65	1·521	1·523	0·13	0·053	+ 30	40
XII	20	1·756	1·769	0·74	0·039	+ 40	40
XII	65	1·756	1·767	0·63	0·051	+ 45	40
XIII	20	1·347	1·353	0·45	0·052	− 80	50
XIII	65	1·347	1·349	0·15	0·045	− 80	55
XIV	20	1·637	1·645	0·49	0·043	− 95	30
XIV	65	1·637	1·644	0·43	0·043	− 95	40

[a] Average relative error in the determination for $n = 7$; [b] estimate of the relative standard deviation for $n = 7$; [c] formal redox potential of the tested substances read from the titration curve at half the consumption required to the equivalence point; [d] potential change around the equivalence point corresponding to addition of 0·02 ml of standard solution, ($c(Ti^{3+}) = 0{\cdot}01$ mol l^{-1}).

In the presence of EDTA, titanium(III) ions also react very slowly and, moreover, only substances *I–III* and *V–VIII* can be determined in the presence of this complexing agent at laboratory temperature. All the studied substances can be determined in the presence of fluoride at laboratory temperature, but the potential stabilizes very slowly during the back-titration, which takes 20 min or longer. All the substances can be determined in the presence of tartrate at laboratory temperature, but a precipitate is formed on addition of a large amount of methanol and the potential stabilizes rather slowly during the back-titration. The results for the titanometric determination of the studied substances in the presence of various complexing agents are given in Table IV, where the values listed are the average of 3 determinations.

Titanium(III) ions in citrate medium were most useful; the reaction is fastest and the potential stabilizes very rapidly during back-titration. The accuracy and reproducibility of the indirect determination of the studied substances with the reagent are given in Table V, where the results listed are the average of 7 determinations, from which the standard deviations were also calculated.

The rapid reduction during the indirect determination with titanium(III) ions suggested the possibility of direct titration. It was found that all the studied substances except substance *IV* can be determined at laboratory temperature. The latter can be titrated at 60°C. The results are listed in Table VI, where the values given are the average of 7 determinations, from which the standard deviations were also calculated.

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