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Determination of Rylan Type Metal-Complex Dyes Using Potentiometric Ion-Pair Formation Titration

K. Vytřas,[a] F. Novák,[b] J. Kalous[a] & H. Macounová[a]

[a] Department of Analytical Chemistry, University of Chemical Technology,
532 10 Pardubice, Czech Republic
[b] Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitvi, Czech Republic

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ABSTRACT

Simple coated-wire electrodes were used to monitor the titrations of seven metal-complex dyes, namely, Rylan Black R, Rylan Blue TR, Rylan Bordeaux B, Rylan Brown B, Rylan Orange R, Rylan Red 2B and Rylan Olive 2G. These chromium(III) complexes of o,o′*-dihydroxy acid azo dyes are present as tervalent anions in aqueous solution. The determination is based on the precipitation of ion pairs with a univalent cationic titrant (Septonex). High potential breaks were observed on the titration curves, with well-defined end-points corresponding to a titration dye–titrant stoichiometric ratio of 1:3; the reproducibility of the results obtained in assaying the dye samples was very satisfactory. A new standardization procedure of the titrant solution against picric acid is also suggested.*

1 INTRODUCTION

Metal-complex dyes originate from azo dyes with a chelating conformation (usually hydroxy, carboxy or amino groups in the *ortho* positions to the azo group), which are able to form complexes with metal ions; chromium(III), cobalt(II) and copper(II) are the most usual.[1] The synthesis offers various combinations, especially when 1:2 metal–dye complexes are prepared; Rylan dyes are 1:2 metal–complex dyes of Czech origin[2,3] and contain two sulpho-groups in their molecule. This has a favourable effect on the solubility of the dyes under cold conditions (up to 100 g dm^{-3}). The dyes are used for dyeing and printing wool, polyamide and natural silk, and for dyeing of wool blends.

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For assaying the dye, spectrophotometry is widely used, but the method is not absolute since the molar absorptivities have to be determined using pure samples. The availability of such samples is probably one of the main difficulties in assessing the accuracy of dye assay procedures. As is well known, many assay methods give precise results, but the value obtained often depends on the chemical method used, owing to reactions of impurities.[4] For metal-complex dyes, atomic absorption spectrometry could also be employed for the determination of the central metal ion; however, such procedures are not fully acceptable because the excess metal ion which is not bonded to a dye molecule is also determined.

Potentiometric methods involving ion-selective electrodes in the control of dyestuffs production have been recently reviewed;[5] on this basis, ionic dyes may advantageously be determined by titrations based on ion-pair formation. The application of this method for assaying metal-complex dyes using simple potentiometric sensors has been investigated and the results are presented in this paper.

2 RESULTS AND DISCUSSION

2.1 Titration curves

Due to the presence of two sulpho groups and the chelating conformation between two *o,o′*-dihydroxy azo group and chromium(III), all the metal-complex dyes investigated form salts of good solubility, giving tervalent anions (L^{3-}) in aqueous solution. Because of their lypophilic character, the anions can be precipitated with a cationic titrant. In precipitation titrations, it is well known that the magnitude of the potential break is governed predominantly by the solubility of the precipitate formed. However, as has been shown recently,[6] the role of the extraction equilibria must also be taken into account when the precipitate of the ion-pair type is extractable into the electrode membrane mediator.

On precipitating the tervalent dye anion with a lypophilic cationic titrant (Q^+), it could be assumed that well extractable products (Q_3L) are formed. Titration curves with high potential breaks and well-defined end-points were obtained (Fig. 1), the equilibrium voltage of the measuring cell being established quickly after each addition of titrant.

2.2 Titration stoichiometry and assays

Because of the univalent nature of the cationic titrant, a corresponding stoichiometric 1:3 dye–titrant ratio was expected, and confirmed on some of

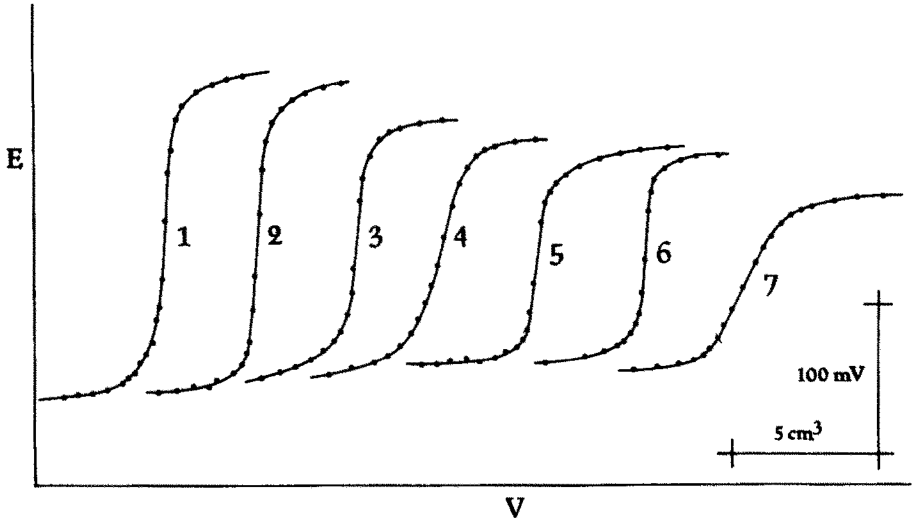


Fig. 1. Potentiometric titration curves of Rylan type metal-complex dyes: 1, Rylan Olive 2G (VII); 2, Rylan Bordeaux B (III); 3, Rylan Blue TR (II); 4, Rylan Black R (I); 5, Rylan Brown B (IV); 6, Rylan Red 2B (VI); 7, Rylan Orange R (V); *c*. 20–30 mg of the dye sample in 50 cm^3 of the solution titrated with 0·01M Septonex.

the samples with nominal dye content (the percentage content of which was based on both spectrophotometric measurements and colouristic estimations). These were compared on 12 samples of the newly developed metal-complex dye, Rylan Khaki, now introduced Rylan Olive 2G (see Table 1, in which the strengths of the dye samples were compared with a reference dye and determined spectrophotometrically at 470 and 600 nm in solution, and subjectively by colouring wool).

The good solubility of all of the metal-complex dyes investigated, the good stability of their aqueous solutions and especially, the favourable course of the potentiometric titrations contributed significantly to obtaining very reproducible results (the assay values are given in Table 2). It was, however, observed that, after a large number of experiments, the electrodes became covered by a honey-like precipitate, and the potential break of the titration curves then continuously decreased. This could be overcome by rinsing the measuring cell, as well as the titration beaker, with a stream of ethanol from a syringe.

2.3 Standardization procedure

Attention was also paid to the standardization procedure for the titrant solution. In this paper, the cationic titrant (Septonex) was standardized potentiometrically against a standard solution of picric acid. Although the

TABLE 1

Comparison of the Strength of Rylan Olive 2G as Determined by Various Methods

Sample number	*Content of the dye*[a] *(%)*	*Strength of the dye (%)*[b] *determined by*			
		Potentiometric titration	*Spectrophotometrically*		*Colouring wool*[c]
			470 nm	*600 nm*	
690/290	58·6	100·0	100	100	The type
706/313	77·6	75·6	76	72	75–80
314	76·2	76·9	75	73	75–80
316	77·6	75·6	78	74	80
317	77·6	75·5	73	75	70–75
318	80·3	73·0	72	72	70
319	79·6	73·4	73	72	70
320	84·6	69·3	70	69	70
321	82·1	71·4	68	69	65–70
322	80·8	72·5	70	68	65–70
323	81·9	71·6	70	69	70–75
324	80·3	73·0	70	70	70–75
342A	83·2	70·5	70	68	70

[a] Arithmetic mean of two parallel determinations.

[b] Compared relatively to the reference type dye (sample number 690/290), defined as the amount of the dye necessary to obtain the same colour perception, i.e. the percentual concentration ratio c (type dye)/ c (sample).

[c] Expressed as the intervals of the subjective evaluation of the sample dye strength.

TABLE 2

Characterization of Titration Curves and List of Assays of the Dyes

Sample		*Molar mass*[a] *(g/mol)*	*Titration curve*		*Assay*[b] *(%)*
			Overall potential break (mV)	*Steepness near the end-point (mV/0·1 cm³)*	
I	Rylan Black R	993·7	160–170	7–8	49·7±0·9
II	Rylan Blue TR	903·7	190–200	14–19	44·8±0·8
III	Rylan Bordeaux B	963·8	200–210	23–28	54·5±0·9
IV	Rylan Brown B	973·7	150–160	20–22	65·8±0·7
V	Rylan Orange R	953·3	90–110	4–5	53·3±0·3 53·4±1·7[c]
VI	Rylan Red 2B	958·7	140–150	16–19	49·9±0·2
VII	Rylan Olive 2G	976·7	190–220	30–38	58·6±0·4

[a] Given for the trisodium salts.

[b] Results given as a reliability interval $\bar{x} \pm u_0 R$, where $\bar{x}$ is the arithmetic mean, R the range $(x_{\max} - x_{\min})$ and u_0 the Lord's critical value for three parallel determinations at a significance level of 0·05 (95% probability).

[c] Repeated after long delay with the new dye stock and titrant solutions.

potential break in these titrations was not too high (120–140 mV) or too steep (c. 10 mV per 0·1 cm^3 of the titrant near the end-point), very reproducible results for the titrant concentration were obtained. The above standardization procedure was verified by potentiometric titration against sodium tetraphenylborate solution, which had been standardized against thallium(I) nitrate solution.[7] Statistically viewed, the differences in the resulting titrant concentrations were not significant.

3 EXPERIMENTAL

3.1 Apparatus

Potentiometric titrations were performed using an OP-208/1 pH meter (Radelkis, Budapest). The simple sensing electrode of the coated-wire type were prepared as described previously,[8] using an aluminium conductor as a support for the membrane, which was obtained from a solution of poly(vinyl chloride) (0·09 g) and 2,4-dinitrophenyl octyl ether (0·2 cm^3) in tetrahydrofuran (3 cm^3). An RCE-102 calomel electrode (Crytur, Turnov) of double-junction construction, filled with saturated potassium chloride and 0·1 M sodium nitrate solutions, was used as a reference half-cell.

3.2 Titrant

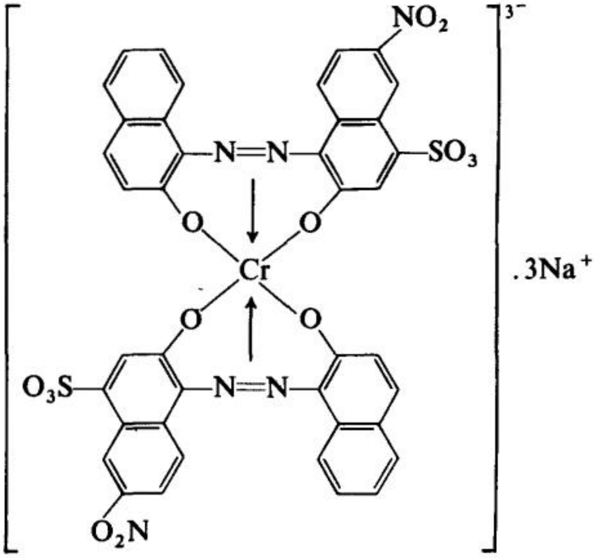
1-Ethoxycarbonyl)pentadecyltrimethylammonium bromide (Septonex; Slovakofarma, Hlohovec), c. 0·01 M solution, was prepared and standardized potentiometrically against a 50 cm^3 portion of the standard $1{\cdot}017 \times 10^{-3}$ M solution of picric acid, which was prepared by dissolving 0·1165 g of the analytical-reagent grade preparation (Lachema, Brno) in 500 cm^3 of water.

3.3 Dyes

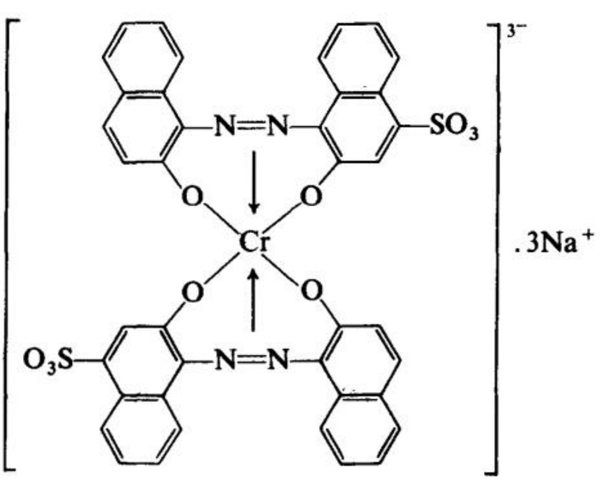
The samples of Rylan metal-complex dyes investigated were as follows:

(I) Rylan Black R, C.I. Acid Black 194, a 1:2 chromium(III)–C.I. 15710 (C.I. Mordant Black 1) complex dye, tri Na salt;
(II) Rylan Blue TR, C.I. 15707, C.I. Acid Blue 193, a 1:2 chromium(III)–C.I. 15705 (C.I. Mordant Black 17) complex dye, tri Na salt;
(III) Rylan Bordeaux B, C.I. 18762, C.I. Acid Violet 90, a 1:2 chromium(III)–C.I. 18760 (C.I. Mordant Red 7) complex dye, tri Na salt;
(IV) Rylan Brown B, C.I. Acid Brown 355, a 1:1:1 chromium(III)–C.I. 15710 (C.I. Mordant Black 1)–C.I. 18744 (C.I. Mordant Orange 29) complex dye, tri Na salt;

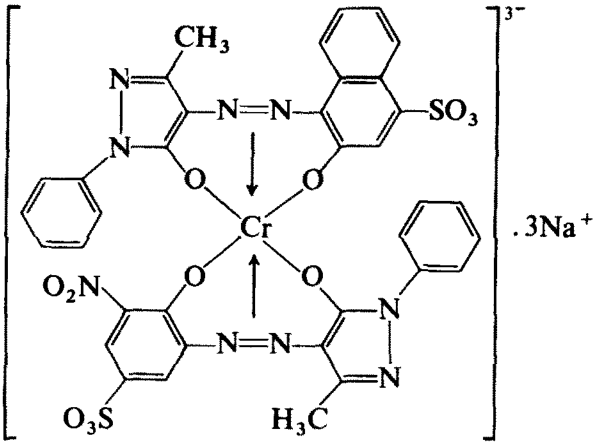
(V) Rylan Orange R, C.I. Acid Orange 142, a 1:2 chromium(III)–C.I. 18744 (C.I. Mordant Orange 29) complex dye, tri Na salt;
(VI) Rylan Red 2B, C. I. Acid Red 432, a 1:1:1 chromium(III)–C.I. 18740 (C.I. Acid Orange 72)–C.I. 18760 (C.I. Mordant Red 7) complex dye, tri Na Salt;
(VII) Rylan Khaki, now introduced as Rylan Olive 2G, C.I. Acid Green 121 a 1:1:1 chromium(III)–C.I. 13900 (C.I. Acid Yellow 99)–C.I. 15710 (C.I. Mordant Black 1) complex dye, tri Na salt.



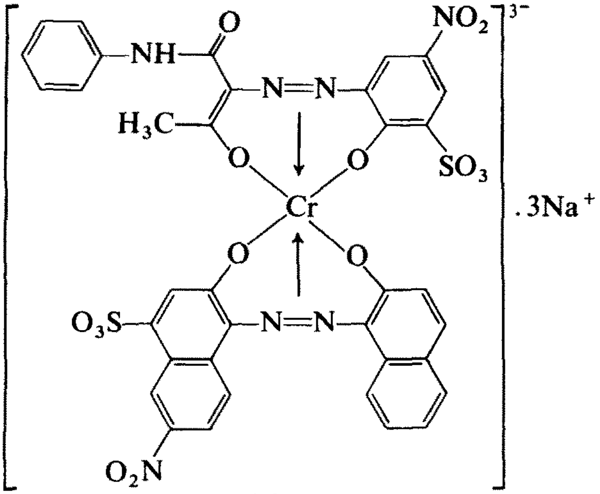
Scheme 1



Scheme 2



Scheme 6



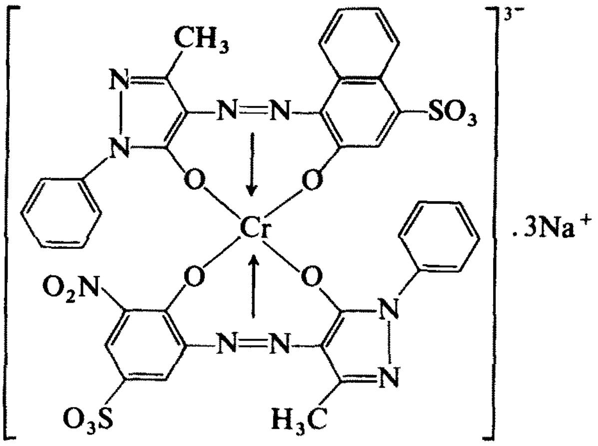
Scheme 7

The formulae of all the above dyes are given. (Schemes 1–7 correspond to the dyes I–VII).

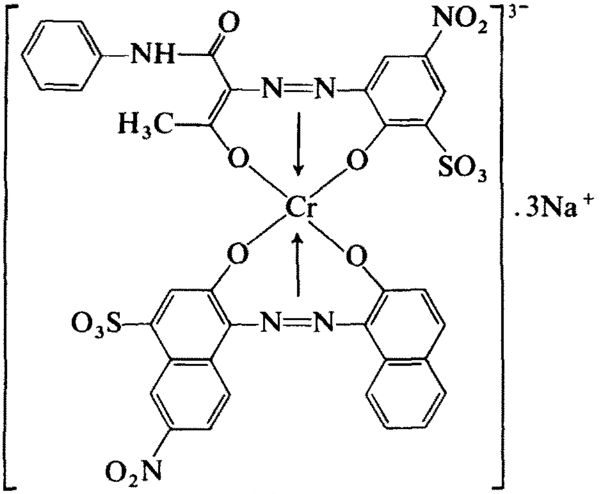
All the samples were obtained from VÚOS (Pardubice-Rybitví); thin-layer chromatography showed them to be essentially free of other colour impurities; only when very concentrated solutions were applied were some colour spots, due to the starting azo dyes or intermediates, detectable, in such small amounts that no quantitative assessment was considered necessary.

3.4 Titration procedure

The stock dye solution, was prepared from a known amount of the dye sample (*m* (sample), 200–300 mg) dissolved in 500 cm^3 (*V* (stock)) of water.



Scheme 6



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For potentiometric titration, an appropriate volume (V(pip), usually 50 cm^3) of the stock solution was titrated against 0·01 M Septonex, with stirring. In order to obtain reproducible titration curves, it was necessary to rinse the measuring cell and the titration vessel with ethanol after each second repeated titration.

The percentage content ($p_{\%}$) of the dye in a sample was calculated according to the formula:

$$p_{\%} = 100\tfrac{1}{3}\, V\,(\text{Sept})\; c\,(\text{Sept})\; M\,(\text{dye}) \times \frac{V\,(\text{stock})}{V\,(\text{pip})} \Big/ m\,(\text{sample})$$

where V(Sept) is the amount of the Septonex titrant used at the end-point, c (Sept) is its concentration, and M (dye) the molar mass of the dye.

4 CONCLUSIONS

From the results obtained, a simple coated-wire electrode can be recommended as a sensor to determine metal-complex acid azo dyes by potentiometric titration, using a quaternary ammonium salt as titrant. This is especially interesting in connection with a recent paper,[9] in which similar potentiometric titrations of acid *o,o'*-dihydroxy azo dyes were reported. It follows that both starting dyes and final products in the syntheses of metal-complex dyes can be assayed using simple potentiometric methods based on ion-pairing principles, which allows the use such titrations in the control of dyestuff production. In view of the importance of metal-complex dyes on an industrial scale,[10] reliable analytical methods for such dyes are necessary, and the potentiometric titration reported here affords a rapid and inexpensive procedure for the assay of these dyes.

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