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Potentiometric Titrations of some *o,o'*-Substituted Acid Azo Dyes

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ABSTRACT

Titrations based on both complex formation and ion-pair formation principles have been used in assaying nine anionic azo dyes, namely C.I. 13900, C.I. 15685, C.I. 15705, C.I. 15710, C.I. 16680, C.I. 18744, C.I. 18760, C.I. 18821 and Calmagite. The results show that the titrations of the dye anions can be performed using quaternary nitrogen salts as titrants, and can be monitored using a simple PVC membrane coated-wire electrode as a sensor in media buffered to an optimum pH value depending on the protolytic equilibria of the determinand. The complex formation titrations with copper(II) nitrate and copper(II) ion-selective electrode can also be carried out in either acetate or ammonia buffers. By comparing the results of both methods, more reliable conclusions can be made with regard to the sample purity.

1 INTRODUCTION

Azo dyes substituted in the *o,o'*-positions are an important group of dyes since they can be transformed into complexes with metal ions to enhance their colouristic properties. For this purpose, the *o*-substituent may be hydroxyl and the *o'*-substituent may be a hydroxyl, carboxy or amino group. By introducing one or more sulphonic acid groups into an azo dye or by making a solution of a dye containing carboxy or hydroxy groups alkaline, the compound is converted into the anionic form and can be precipitated with cationic agents, viz.

$$\mathrm{X^-}\ \text{(acid dye)} + \mathrm{Q^+}\ \text{(cationic titrant)} = \mathrm{QX}\ \text{(an ion-pair product)}$$

This is the principle of ion-pair formation-based titrations. If the ion pair formed is easily extractable into organic solvents, these titrations can be monitored potentiometrically using an electrode equipped with a liquid/plastic membrane.[1] As shown by Fogg and co-workers,[2,3] the assay values obtained by ion-pair titration agree fairly well with the results of other methods.

Acid azo dyes which contain chelating conformations have also been assayed using potentiometric complex formation-based titrations.[4,5] It seemed that titration with a copper(II) salt and a copper(II) ion-selective electrode was convenient also for *o,o'*-substituted azo dyes.[5]

Potentiometric measurements with ion-selective electrodes have become one of the most useful tools for rapid analysis of some dyes (for references, see Ref. 6). The aim of this paper is to demonstrate the possible use of methods mentioned above in assaying some industrially, as well as analytically, important acid azo dyes.

2 RESULTS AND DISCUSSION

2.1 Influence of pH

For the assay of chelating dyes by potentiometric complex formation type titrations, the use of copper(II) salts as titrants has several advantages. One is the fact that copper(II) reacts in a clean stoichiometric way with most dye ligands containing one chelating group (L), to form stable 1:1 complexes (CuL). The main equilibrium (charges are omitted)

$$L + Cu^{2+} = CuL, \qquad \beta_{CuL} = [CuL][Cu]^{-1}[L]^{-1}$$

may be influenced by side reactions of both the dye and metal ions. The values for a side reaction coefficient can be calculated if the equilibria of the side reaction are known and the equilibrium concentrations of the side reaction species can be estimated.[7] Once values of the side reaction coefficients α_L, α_{Cu} are known (see Table 1), it is easy to predict their influence on the conditional stability constant, β'_{CuL}, defined as

$$\beta'_{CuL} = \beta_{CuL}\alpha_{Cu}^{-1}\alpha_L^{-1}$$

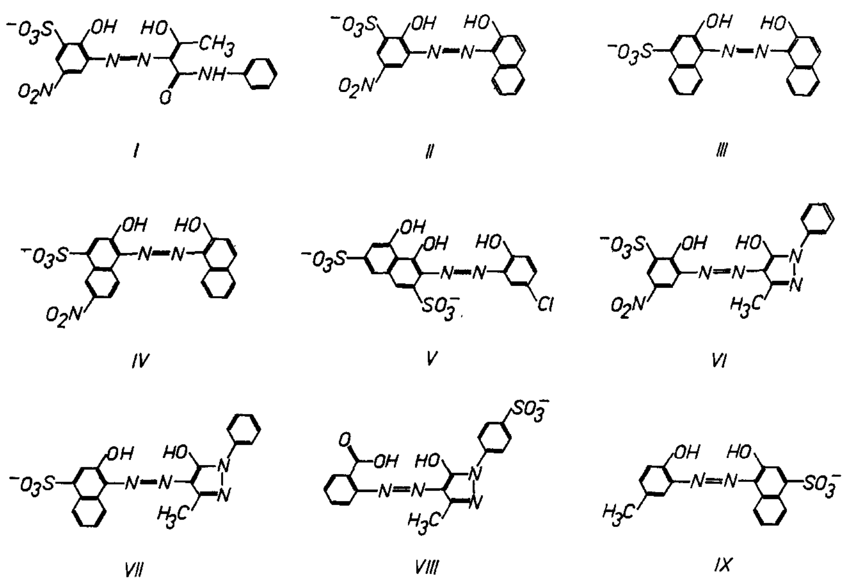
which is of importance in the shape of the titration curve. The influence of pH need not, of course, be neglected. An alkaline medium is desirable because the fully deprotonated species (L) participate in the complex formation. However, this cannot be fully accepted because of the hydrolytic reactions of copper(II) ions. In the presence of ammonia buffer, amino-copper(II) complexes are formed. In accord with theoretical presumptions,

TABLE I

Dissociation Constants and Side-Reaction Coefficients of the Dyes Studied

Dye	*Molar mass (as an acid) (g mol^{-1})*	*Dissociation constants, given as pK_a (L), i =*			*Ref.*	*Side-reaction coefficient $\log \alpha_{L(H)}$, for*		*$\Delta \log \alpha_L$*
		3	*2*	*1*		*pH 5*	*pH 9*	
I	422·38	—	4·10	13·5	13	8·55	4·50	−4·05
II	390·13	—	4·38	12·5	13	7·59	3·50	−4·09
III	394·11	—	7·3	13·5	14	10·80	4·51	−6·29
IV	439·41	—	6·2	13·0	14	9·23	4·00	−5·23
V	474·85	8·0	10·5	11·9	15	15·40	4·45	−10·95
VI	419·37	—	3·63	9·98	13	5·00	1·02	−3·98
VII	424·44	—	5·46	11·44	13	7·03	2·44	−4·59
VIII	402·39	—	3·26	10·82	13	5·83	1·83	−4·00
IX	358·37	—	8·1	12·4	16	—	—	—
			7·9	12·3	17	—	—	—
			7·74	12·5	13	10·24	3·52	−6·72

Side-reaction coefficients for copper(II) ion are $\log \alpha_{Cu(CH_3COO^-)} = 0{\cdot}62$ for pH 5 and an acetate buffer containing $[CH_3COO^-] = 0{\cdot}0454$ M, or $\log \alpha_{Cu(NH_3)} = 8{\cdot}51$ for pH 9 and an ammoniacal buffer containing $[NH_3] = 0{\cdot}935$ M in the solution titrated, respectively. The formation of copper(II) hydroxo-complexes was negligible in both cases. The difference is then $\Delta \log \alpha_{Cu} = 7{\cdot}89$.



Structure 1

the end-point breaks were usually higher in solutions buffered with acetate, but the differences were not very significant. The reverse observation for the dye V (Structure 1) sample also agreed with theory based conclusions.

Also, in ion-pair formation-based titrations of the dyes, the pH values play an important role. Since univalent cationic titrants are used, the charge of the dye anion significantly influences the titration stoichiometry. With one exception (dye V), all the dyes studied contained one sulphonic acid group, i.e. they were present as univalent anions in a medium sufficiently acidified with dilute hydrochloric acid (see values of the dissociation constants of the dyes listed in Table 1). It can also be seen from Table 1 that the dye may be present as a bivalent anion if the pH is kept just between the $pK_a(H_2L^-)$ and $pK_a(HL^{2-})$ values. In fact, titrations with univalent quaternary salts are feasible, and the end-points are shifted because of another stoichiometry (1:2), but the potential breaks are much smaller.

2.2 Assays

A further advantage of potentiometric titrations is that coloured impurities which do not form complex or ion pairs, but would affect spectrophotometric measurements, do not interfere. However, an important role is played by the stability of the dye solutions. On this basis, the titrations of dyes I, VI, VII and VIII were performed without difficulties. On the other hand, the aqueous solutions of the dyes II, III, IV and IX were less stable,

TABLE 2
Summarized Results of Potentiometric Titrations

Dye	*Sample number*	*Optimum conditions*					*Other results*					*Comment*[d]
		Titrant	*Buffer*	*pH*	*ΔE (mV)*[a]	*Assay (%) (n)*[b]	*Titrant*	*Buffer*	*pH*	*ΔE (mV)*	*Assay (%) (n)*	
I	751/163	Septonex	HCl	1	280–300	89·7±0·8 (4)	Septonex	Borate	9	70–80	87·9±2·4 (3)	Declared:
							Cu(II)	Ammonia	9	70–90	85·5±5·2 (3)	90·1%
	751/80	Septonex	HCl	1	280–300	83·2±0·4 (3)	Cu(II)	Ammonia	9	70–90	84·8±2·5 (3)	89·4%
II	706/154	Septonex	HCl	1	240–250	67·1±1·2 (4)	Cu(II)	Acetate	5	100–110	69·3±2·0 (3)	Declared:
								Ammonia	9	80–90	67·2±2·0 (3)	68·7%
							Septonex	Ammonia	9	120–130	68·6±2·6 (3)	
III	706/202	Septonex	HCl	2	210–240	69·6±1·3 (3)	Cu(II)	Ammonia	9	70–90	68·0±4·5 (3)	—
		Cu(II)	Acetate	5	70–80	70·5±0·9 (3)						
IV	690/270	—	—	—	—	—	Septonex	Acetate	5	140–160	74·2±3·9 (3)	Less soluble,
								HCl	2	140–150	68·2±4·4 (3)	Less stable
							Cu(II)	Acetate	5	120–130	67·5±4·8 (3)	In alkaline
							Septonex	Ammonia	9	100–110	73·0±5·6 (3)	Medium
V	Lachema	Cu(II)	Ammonia	9	80–90	45·1±1·3 (3)						
			Acetate	5	40–50	~44 (1)						
VI	SB8/865	Septonex	HCl	1	240–260	82·3±0·8 (3)	Cu(II)	Acetate	5	80–120	83·9±1·6 (3)	Declared:
								Ammonia	9	90–120	81·1±1·8 (3)	83·2%
							Septonex	Phosphate	7	90–100	82·7±1·9 (3)	
VII	Lachema	Septonex	HCl	1	230–250	48·3±1·9 (3)	Cu(II)	Ammonia	9	90–100	47·4±2·0 (3)	—
								Acetate	5	50–60	47·7±2·7 (3)	
VIII	706/239	Septonex	HCl	1	130–150	54·0±0·4 (3)	CPC[c]	Phosphate	7	120–130	55·5±2·0 (3)	Declared:
							Cu(II)	Ammonia	9	80–100	54·9±2·0 (3)	57·5%
							Septonex	Phosphate	7	60–70	54·7±2·1 (3)	
	21251	Septonex	HCl	1	130–150	50·0±0·7 (3)	Cu(II)	Acetate	5	100–120	52·6±2·1 (3)	
IX	Lachema	CPC	HCl	2	180–190	29·6±0·8 (3)	Cu(II)	Ammonia	9	80–90	30·6±2·8 (3)	—

[a] End-point potential break.

[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 n parallel determinations (in parentheses) at a significance level of 0·05 (95% probability).[18]

[c] Cetylpyridinium chloride.

[d] Catalogue values (approximative): dye I, 40%[8] or 45%;[9] dye III, 50%[8] or 60%;[9] dye V, 75%[8] or 60%;[9] dye IX, 60%.[8]

since the solubility of these dyes is smaller. The solubility can be increased by addition of hydroxide, but to the detriment of the stability of the dye solution. To obtain reliabile results, it is therefore necessary to work with freshly prepared solutions.

The titrations based on ion-pair formation are accompanied by higher end-point potential breaks. That is why they are more convenient for assaying the dye samples when compared with titrations using copper(II) salts (see Table 2). This is valid for all the dyes studied, except for dye V which contains two sulphonic acid groups. In this case, the potential breaks are also higher, but the results are not reproducible. Thus, the ion-pair formation titrations with quaternary nitrogen salts can be recommended as an assay procedure for all univalent dye anions.

In some cases, the assay values obtained during this work could be compared to those declared by the manufacturer (for two samples of the dye I, and for dyes II, VI and VIII, see Table 2). A comparison with the catalogue values[8,9] differs significantly because the composition of dyes of different origin usually differs significantly also.[10]

3 EXPERIMENTAL

3.1 Apparatus

Potentiometric titrations were performed using an OP-208/1 pH meter (Radelkis, Budapest) equipped with measuring and reference electrodes. For ion-pair formation titrations, the indicator sensor was prepared as described previously[11] using an aluminium conductor coated with a membrane obtained from a solution of poly(vinyl chloride) (0·085 g) and 2,4-dinitrophenyl octyl ether (0·2 cm^3) in tetrahydrofuran (3 cm^3). In complex formation titrations, the copper(II) ion-selective electrode Crytur 29-27 (Monokrystaly, Turnov) was used. In both cases, a Crytur RCE-102 double-junction calomel electrode filled with saturated potassium chloride and 0·1 M sodium nitrate was used as a reference half-cell.

3.2 Solutions

Quaternary nitrogen salt titrants were prepared as *c.* 0·01 M solutions and standardized potentiometrically against sodium tetraphenylborate solution, which had been standardized against thallium(I) nitrate solution.[1] Two salts were used, namely, 1-(ethoxycarbonyl)pentadecyltrimethylammonium bromide (Septonex), or cetylpyridinium chloride (CPC).

Copper(II) nitrate titrant was prepared by dissolving appropriate amounts of pure copper (*c.* 0·635 g) in nitric acid (65%, 3 cm^3), and diluting the solution to 1 dm^3.

The reaction medium was buffered using 0·1 M or 1 M hydrochloric acid, or acetate (pH 5), phosphate (pH 7), ammonia or borate (pH 9) buffers.

3.3 Dyes

Azo dyes used industrially as starting compounds in the syntheses of metal-complex dyes, and other *o,o′*-dihydroxy azo dyes used for analytical purposes as metallochromic indicators were studied. The industrial samples were obtained from VÚOS (Pardubice-Rybitví) and the indicator samples were from Lachema (Brno). The C.I. Constitution Number, C.I. Generic Name (or common name if not included in the Colour Index)[12] and chemical constitutions are:

(I) C.I. 13900, C.I. Acid Yellow 99, 1-anilino-2-[(2-hydroxy-3-sulpho-5-nitrophenyl)azo]-3-hydroxy-2-buten-1-one, Na salt.

(II) C.I. 15685, C.I. Acid Red 184, 1-[(2-hydroxy-3-sulpho-5-nitrophenyl)azo]-2-naphthol, Na salt.

(III) C.I. 15705, C.I. Mordant Black 17, 3-hydroxy-4-[(2-hydroxy-1-naphthyl)azo]-1-naphthalenesulphonic acid, Na salt.

(IV) C.I. 15710, C.I. Mordant Black 1, 3-hydroxy-4-[(2-hydroxy-1-naphthyl)azo]-7-nitro-1-naphthalenesulphonic acid, Na salt.

(V) C.I. 16680, C.I. Mordant Blue 13, 3-[(5-chloro-2-hydroxyphenyl)-azo]-4,5-dihydroxy-2,7-naphthalenedisulphonic acid, di Na salt.

(VI) C.I. 18744, C.I. Mordant Orange 29, 4-[(2-hydroxy-3-sulpho-5-nitrophenyl)azo]-1-phenyl-3-methyl-5-pyrazolone, Na salt.

(VII) C.I. 18760, C.I. Mordant Red 7 (Eriochrome Red B), 4-[(2-hydroxy-4-sulpho-naphthyl)azo]-1-phenyl-3-methyl-5-pyrazolone, Na salt.

(VIII) C.I. 18821, C.I. Mordant Yellow 8 (Alizarine Chrome Fast Yellow R), 4-[(2-carboxyphenyl)-azo]-1-(4-sulphophenyl)-3-methyl-5-pyrazolone, Na salt.

(IX) Calmagite, 3-hydroxy-4-[(2-hydroxy-5-methylphenyl)-azol]-1-naphthalenesulphonic acid, Na salt.

The samples were free of colour impurities (checked by thin-layer chromatography). For titrations, the dyes were dissolved to obtain *c.* 0·001 M solutions.

3.4 Titration procedures

According to the titration stoichiometry expected, appropriate volumes of the dye stock solutions (50, 25 cm^3, or other volume) were transferred into a

100-cm^3 titration vessel, diluted with water to 50 cm^3 if necessary, and adjusted with a desired buffer (5 cm^3). The titrations were performed manually using magnetic stirring, the titrants being added using a 10-cm^3 burette.

4 CONCLUSIONS

It was demonstrated that potentiometric titrations using ion-selective electrodes as sensors can advantageously be used to assay the dye samples. The procedures are rapid and simple. The lower stability of some dye solutions has also to be considered, because it may be a cause of less precise or even erroneous results. The ion-pair formation-based titrations give more precise results because the corresponding potential end-point breaks are higher than those in complex formation titrations (see Fig. 1). Another advantage is that these titrations can be monitored with simple sensors of the coated-wire type which can easily be prepared even in simply equipped laboratories.

Both methods used are simple and inexpensive, and it is concluded that they may find further analytical applications in control laboratories of the dye industry.

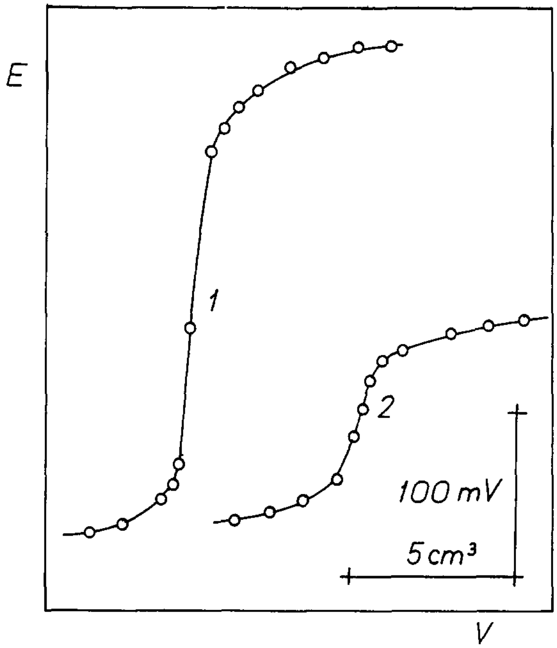


Fig. 1. Comparison of potentiometric titration curves of the dye VI sample solution titrated with (1) Septonex, pH 1 (diluted HCl), and (2) copper(II) nitrate, pH 5 (acetate buffer).

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