

Extraction of the Ionic Associates of the Azo Dyes with Strychnine

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The paper presents a study of the extraction of the ionic associates of strychnine with the acidic dyes having different number of the sulfo groups. Extraction constants of the ionic associates of strychnine were calculated and the procedure for the strychnine determination was developed.

The protonated cations of the bases form with the anions of the azo dyes and sulfophthaleins ionic associates that are extractable with a lipophilic organic solvent, usually chloroform. An ability to produce associates depends on the properties of a base as well as on the type of the used acidic dye. Some sulfophthaleins, e.g. bromothymol and bromophenol blue or bromocresol green, produce in the acidic solutions at $\text{pH} < 2$ nondissociated acids that are qualitatively extracted into the organic phase. On the contrary, azo dyes are dissociated in the aqueous solutions and are transferred into the organic solvent only in the form of associates with the cations of the bases [1].

The yield of the extraction depends, *inter alia*, on the polarity of the resulting compounds that might be to some extent influenced by the number of the sulfo groups in the dye molecule. Pitarch [2] investigated an effect of the position of one sulfo group in the azo dye molecule on the extractability of various organic bases with benzene. Thus, it

is important to take into consideration an effect of the number of the sulfo groups in the azo dye molecule on the extraction yield.

As an appropriate organic base we have chosen strychnine. Determinations of strychnine with eriochrome black [3], methyl orange [4], tropaeolin [5], bromocresol green [6], and bromothymol blue [7] are described in the literature. The associates have been always extracted with chloroform which does not enable extraction of the associates with a greater number of the sulfo groups. Therefore, we have chosen 1,1,2,2-tetrachloroethane that extracts more polar associates as well [8]. As the azo dyes, sulfo derivatives of 1-(1-naphthylazo)-2-naphthol have been chosen (Table 1).

EXPERIMENTAL

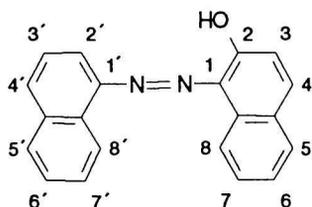
pH Values of the solutions were measured with an MW 870 pH-meter (Präcitronic, Dresden) equipped with a glass electrode GA 50N and a reference calomel electrode SE 20.

The electron absorption spectra of the investigated compounds were measured using a registering double-beam spectrophotometer Specord M40 (Zeiss, Jena). Absorbance was measured with a single-beam spectrophotometer Spekol 11 (Zeiss, Jena).

The content of the active component in the strychnine nitrate (The Pharmacopolia of CSFR, Zdravotnické zásobování, Prague) was estimated by means of perchloric acid titration in glacial acetic acid with acetic anhydride. The purity of the reagent was found to be 99.6 %.

Samples of the commercial azo dyes I–IV were three times recrystallized from methanol prior to use. Their homogeneity was tested using ascending thin-layer chromatography on Silufol plates (Kavalier, Votice). The mobile phase contained ethyl acetoacetate, methanol, and 28 % aqueous am-

Table 1. Selected Dyes and Their Designation



Dye name	C.I.	—SO ₃ Na		Designation
		number	location	
Producer	Dye No. [9]			
ACID RED 88 BASF, Germany	15 620	1	4'	I
ACID RED 44 Francolor, France	16 250	2	6,8	II
ACID RED 18 BASF, Germany	16 255	3	6,8,4'	III
ACID RED 41 Cassella, Germany	16 290	4	3,6,8,4'	IV

monia in the volume ratio 5 : 3 : 2. It has been found that the selected dyes did not contain contaminants.

1,1,2,2-Tetrachloroethane, pure (Apolda, Germany) was prior to use three times washed with water and distilled at a temperature of the boiling point of its azeotrope with water.

In order to investigate a pH dependence of the partition ratio, we have consecutively added into eighteen Erlenmeyer flasks 1 cm³ of aqueous solution of the dye, 1 cm³ of strychnine nitrate solution, and 0–50 mm³ of HCl or NaOH. The total volume was adjusted with water to 20 cm³ and the mixture was extracted for 1 h with 20 cm³ of 1,1,2,2-tetrachloroethane. pH of the water phase has been measured and after the separation of the phases their absorbance was measured at the corresponding wavelengths (λ_{\max} given in Table 2).

The molar absorption coefficients ϵ of the associates were calculated from the slope of the calibration dependence of the absorbance of the dye extracted as an ionic associate on its analytical concentration. The following solutions were mixed: 0.1–1.0 cm³ of dye solution ($c = 1 \text{ mmol dm}^{-3}$), 20 mm³ of HCl ($c = 0.2 \text{ mol dm}^{-3}$), 1 cm³ of base solution ($c = 20 \text{ mmol dm}^{-3}$). The mixture volume was adjusted with water to 3 cm³. After 1 h extraction with 3 cm³ of 1,1,2,2-tetrachloroethane the absorbance of the organic layer has been measured.

The relative molar absorption coefficients ϵ' were measured in a similar way but 0.1–1.0 cm³ of base solution ($c = 1 \text{ mmol dm}^{-3}$) and 1 cm³ of dye solution ($c = 2 \text{ mmol dm}^{-3}$) were mixed. Further procedure was identical with that described above.

RESULTS AND DISCUSSION

Azo dyes I–IV are well soluble in water and are not extracted with 1,1,2,2-tetrachloroethane. Together with the strychnine cations they are extracted in the form of the ionic associates. Those are red-coloured and their absorbance maximum lies in the range of $\lambda = 508\text{--}524 \text{ nm}$. The absorbance values of the aqueous and organic phases can be obtained at the same wavelength and thus a partition ratio D of the dye in its free form in an aqueous solution and of its associate in the organic phase can be calculated.

An extraction curve of the ionic associate reflects a dependence of the partition ratio D on pH value. The $\log D$ values were calculated as a logarithm of the ratio of absorbance values of the aqueous and organic phases.

From Fig. 1 an evident difference can be seen between the curve 1 that expresses an extraction

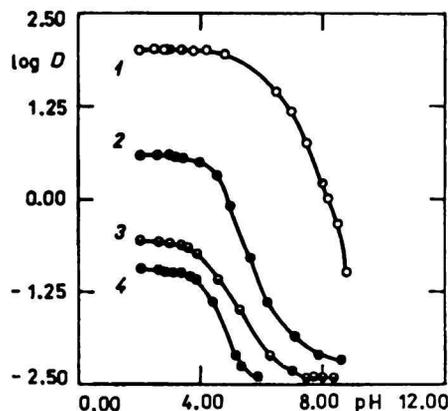


Fig. 1. Extraction curves of the strychnine associates with the following dyes: 1. I ($c_L = c_B = 1.25 \text{ mmol dm}^{-3}$), 2. II ($c_L = 3 \text{ mmol dm}^{-3}$, $c_B = 6 \text{ mmol dm}^{-3}$), 3. III ($c_L = 5 \text{ mmol dm}^{-3}$, $c_B = 15 \text{ mmol dm}^{-3}$), 4. IV ($c_L = 10 \text{ mmol dm}^{-3}$, $c_B = 40 \text{ mmol dm}^{-3}$).

of the associate of I with strychnine and the curve 2 corresponding to the associate of the disulfo dye II. The extraction yields of the polysulfo dyes III and IV are significantly lower than those of I and II. It is obvious from the figure that at $\text{pH} > 4$ dissociation of the ionic associates occurs and the extraction yields decrease. Further measurements were performed at pH 3.

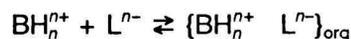
The value of the partition ratio D may be expressed in terms of the molar absorption coefficients ϵ and ϵ' [10], where a relative coefficient ϵ' includes an extraction yield, while ϵ corresponds to the quantitative extraction

$$D = \frac{\epsilon}{\epsilon - \epsilon'}$$

The relative molar absorption coefficient ϵ' changes with the variation of pH, concentration of the base or dye, and is valid for the separate experimental points. On the contrary, the value of the molar absorption coefficient ϵ may be considered to be constant for the quantitative extractions of the azo dye in the form of an ionic associate.

For each dye the ϵ values were expressed as the slope magnitudes of the calibration lines for I, II, III, and IV with an excess of aqueous solution of strychnine nitrate, extracted into 1,1,2,2-tetrachloroethane at optimum pH 3.0.

The extraction process itself can be expressed by the equation



where an extraction constant K_{ex} is

$$K_{\text{ex}} = [\text{BH}_n^{n+} \text{L}^{n-}]_{\text{org}} [\text{L}^{n-}]^{-1} [\text{BH}_n^{n+}]^{-1}$$

The value of the extraction constant is affected by the by-processes, such as protolysis, extrac-

Table 2. Characteristics of the Ionic Associates of Strychnine with the Chosen Azo Dyes

Parameter	I	II	III	IV
$\epsilon/(\text{m}^2 \text{ mol}^{-1})$	1911	1671	1591	1224
$s/(\text{m}^2 \text{ mol}^{-1})$	8	9	11	9
$\epsilon'/(\text{m}^2 \text{ mol}^{-1})$	1900	1016	177	29
$s'/(\text{m}^2 \text{ mol}^{-1})$	6	9	14	2
r	0.99	0.99	0.97	0.97
D	172.7	1.551	0.111	0.089
R	0.99	0.61	0.10	0.08
$\log K'_{\text{ex}}$	9.24	5.19	2.94	2.67
n	1	5	660	625
$L_D/(\mu\text{g cm}^{-3})$	0.80	1.46	7.89	8.54
$\lambda_{\text{max}}/\text{nm}$	515	515	508	524

s, s' - standard deviations of the molar and relative molar absorption coefficients, r - correlation coefficient, R - extraction yield, n - number of extractions necessary for a quantitative yield, L_D - detection limit.

tion of the entering substances, association in the water phase, dimerization of the ions, etc. Therefore, it is more convenient to use a relative extraction constant K'_{ex} that includes these lateral equilibria

$$K'_{\text{ex}} = c(\text{BH}_n^{n+} \text{ L}^{n-}) c(\text{BH}_n^{n+})^{-1} c(\text{L}^{n-})^{-1}$$

Its establishing includes determination of the orientation value. For this purpose it is possible to use a constant calculated and measured using a method of the continual variations that is described in our previous communication [10]. Using this constant we could define more exactly the value of K'_{ex} that was calculated from the series of measurements with the equal concentrations of the base and the dye. For mono- and disulfo derivatives, the value of the logarithm of this constant was greater than 3.5, which is in accordance with the data of Gasparič *et al.* [11]. The associates of the tri- and tetrasulfo derivatives are extracted practically with the yield lower than 1 %. Their constants have therefore been calculated at the excess of the base and a smooth increase of the amount of the dye. It has been found that only mono- and disulfo derivatives are of the practical importance for the determination procedure. Strychnine associates with the dyes having greater number of the sulfo groups are practically not extracted into an organic solvent. In all studied cases, strychnine played a role of a monovalent

cation as it has also been proved by means of the determination with silver nitrate [8].

Furthermore, we have developed a procedure for the determination of strychnine using azo dyes containing one, two, three or four sulfo groups. The extraction characteristics, such as molar and relative molar absorption coefficients, extraction yield values, detection limits, etc. are presented in Table 2. Substantial differences have been observed at the extraction of strychnine with distinct sulfonic azo dyes. Thus, by choosing an appropriate dye, one can influence first of all the extraction yield.

In conclusion we can assert that for the determination of strychnine, knowledge of the relative extraction constant is important. Using azo dyes with one or two sulfo groups it is possible to determine strychnine quantitatively. With the increasing number of the sulfo groups, the stoichiometry is retained, however, low yield of the associates of these derivatives does not enable their practical utilization.

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