Sulfonephthalein dyes. II.*
Protolytic equilibria of methylxylenol blue

K. VYTŘAS and J. VYTŘASOVÁ

Department of Analytical Chemistry, Institute of Chemical Technology,
532 10 Pardubice

The protolytic equilibria of methylxylenol blue in the aqueous and concentrated acid media were studied spectrophotometrically and potentiometrically. The values of the corresponding dissociation constants were determined. Colour reactions of methylxylenol blue with some metal ions were preliminary followed.

Methylxylenol blue or 3,3'-bis-N,N'-di(carboxymethyl)aminomethyl-p-xylenolsulfonephthalein belongs to the group of metallochromic indicators prepared by *Körbl* and *Přibil* [1] *via* condensation of common sulfonephthalein dyes with formaldehyde and iminodiacetic acid. Recently it has been newly prepared by *Cherkesov* and co-workers [2] and named p-xylenolphthalexon S. Two indicators from this group, xylenol orange and methylthymol blue, have found a wide application very soon in the volumetric analysis and as reagents for spectrophotometric determinations of the trace concentrations of metal ions.

Lately, methylxylenol blue has also been often applied, especially in Japan laboratories. The formation of coloured complex compounds of methylxylenol blue has been utilized in the methods worked up for the spectrophotometric determination of iron [3], bismuth [4, 5, 27], mercury [6], calcium [7], gallium [8], zirconium [9—11], thorium [5, 12], cerium [13], lanthanoides [14], scandium and yttrium [15]. Methylxylenol blue, together with xylenol orange and methylthymol blue, belongs to the most sensitive reagents for the fluoride determination in waters [16] by means of the colour chelates of zirconium(IV) ions. The simultaneous spectrophotometric determination of aluminium and beryllium in mixtures was also studied [28].

Necessary assumption of a more thorough study of the complex compounds of methylxylenol blue is to know its protolytic equilibria. They are studied in this communication.

Experimental and results

Reagents, instrumentation, and methods of measurements

Methylxylenol blue

The preparation of the highest possible purity was required for the study of acid-base properties of methylxylenol blue. Nevertheless, three colour components were separated from the commercial preparation (Lachema, Brno) on a chromatographic purity check carried out on paper W2 in the system butanol—acetic acid—water (2 : 1 : 1). The most intensive was the spot with the lowest value of $R_F = 0.28$ (methylxylenol blue), the

---

* For Part I see Ref. [19].

middle spot ($R_F = 0.62$, semimethylxylenol blue) had *ca.* one third of its intensity. When a larger amount of the commercial preparation was deposited on the start of the chromatogram, the third spot with the highest value of $R_F = 0.82$ was observed. A check with the standard showed that it was the unchanged *p*-xylenol blue. Since both the semiform and the mother compound have the properties of acid-base indicators, results of the study of protolytic equilibria would greatly be distorted.

We attempted the preparative chromatographic separation but with very low yields. Finally, the following procedure proved to be satisfactory for the preparation of the chromatographically pure methylxylenol blue: commercial preparation (*ca.* 5 g) was dissolved in saturated solution of sodium acetate (20 ml). After addition of ethanol (300 ml), the mixture was allowed to stand for two days. The syrupy sediment settled in the meantime on the bottom of the beaker. The sediment was separated, washed with ethanol and ethanol—ether mixture, and air-dried. The yield was low (*ca.* 15%) but the product appeared to be free of colour impurities on the chromatographic check.

Stock solutions of methylxylenol blue with 0.08 g of the purified preparation in 100 ml were stabilized by a small admixture of nitric acid.

Spectrophotometric measurements were performed with a VSU-1 (Zeiss, Jena) spectrophotometer. The absorption spectra were measured in Britton—Robinson buffer solutions with the ionic strengths adjusted by additions of sodium perchlorate to the constant value $I = 0.2$. The pH measurements were carried out with a pH-meter OP-205 (Radelkis, Budapest) equipped with glass and saturated calomel electrodes. The H_- acidity function was considered in the last, strongly alkaline solution, while in the acidic region, the conventional activity scale of pH was replaced by the H_0 acidity function in the medium of formic and sulfuric acids [17]. The solutions of 1 M-HCl and 0.1 M-NaOH were prepared for potentiometric titrations. The solution of acid was dosed by a piston burette with a micrometer screw, its total volume being 1.5 ml.

Colour transitions of methylxylenol blue

The colour changes of sulfonephthalein dyes in solutions depend on the effect of the dissociation or protonization upon the symmetry of the molecule and the overall electron distribution in its chromophore system [18]. The protonization of quinoide oxygen in the acidic region and proton dissociation from the hydroxyl group in alkaline solutions are usually accompanied by the most marked colour changes. These colour changes, analogous to the equilibria of *p*-xylenol blue [19], are associated, in the case of methylxylenol blue, with a number of other protonization reactions. These equilibrium reactions can be interpreted analogously to the equilibria of related dyes [20—22]. Dissociation constants characterizing the reactions are marked in the structural formula of methylxylenol blue (Scheme 1).
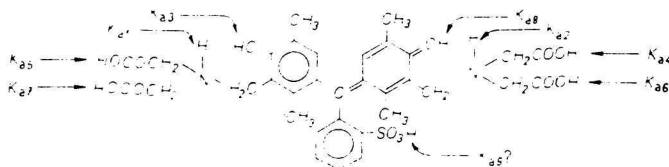
Scheme 1
Methylxylenol blue, cation H_9I^{3+}

Solutions of methylxylenol blue in concentrated sulfuric acid at $H_0 = -6.3$ to -2.8 are purple. The courses of the absorption spectra of such solutions differ slightly in the vicinity of the absorption maximum (550 nm). These spectral changes are probably connected with the proton dissociation from the $-SO_3H$ group and with the change of the charge from the ion H_9I^{3+} to H_8I^{2+}. However, it is very difficult to use these slight changes in absorbance values for the determination of the corresponding dissociation constant.
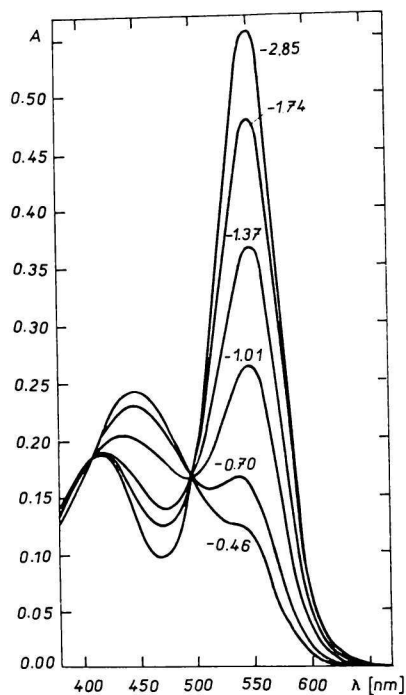

Fig. 1. Absorption spectra of methylxylenol blue in the range of $H_0 = -2.85$ to -0.46.
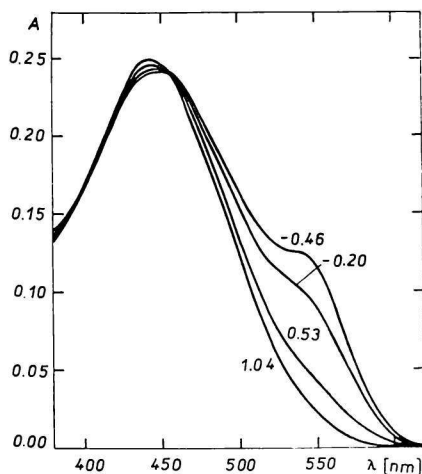$c_I = 3.14 \times 10^{-5}$ M, $d = 10.00$ mm, $t = 25°C$.

Fig. 2. Absorption spectra of methylxylenol blue in the range of $H_0 = -0.46$ to 1.04.
$c_I = 3.14 \times 10^{-5}$ M, $d = 10.00$ mm, $t = 25°C$.

Another two protolytic equilibria occur in the range of H_0 (pH) from -2.8 to 1. The proton bonded on the quinoide oxygen dissociates first ($H_8I^{2+} \rightarrow H_7I^+$). The symmetric structure of the molecule is thus disarranged and the intensive colour change takes place (Fig. 1). The colour change accompanying the dissociation of another proton is not so pronounced; it is seen from the course of the absorption spectra in Fig. 2. This change is usually ascribed to the proton dissociation from one of the carboxyl groups ($H_7I^+ \rightarrow H_6I$) in the case of the related dyes [21].

The stepwise dissociation of the protons from the remaining carboxyl groups ($H_6I \rightarrow H_5I^- \rightarrow H_4I^{2-} \rightarrow H_3I^{3-}$) occurs in the pH range $1-5$. The solutions of all the forms

of methylxylenol blue are yellow in this pH region and very small differences in the course of their electronic spectra cannot be utilized for the study of the protolytic equilibria.
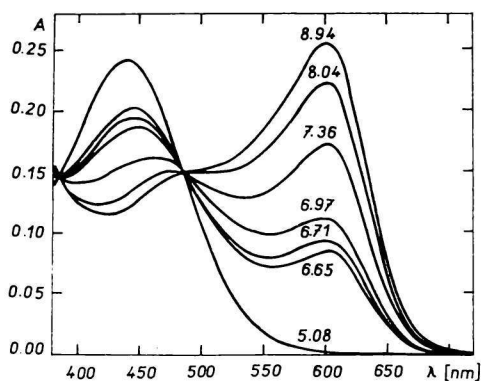

Fig. 3. Absorption spectra of methyl-
xylenol blue in the range of pH =
= 5—9.
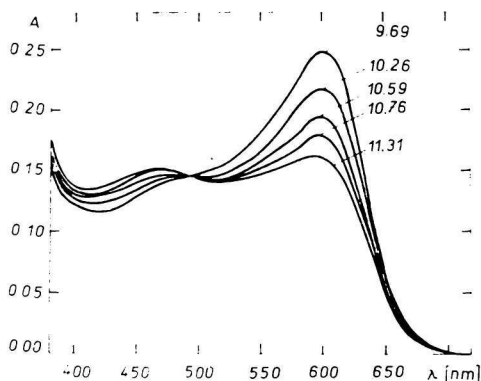$c_I = 3.14 \times 10^{-5}$ M, $d = 10.00$ mm, $I =$
= 0.2, $t = 25°C$.

Fig. 4. Absorption spectra of methyl-
xylenol blue in the range of pH = 9—11.
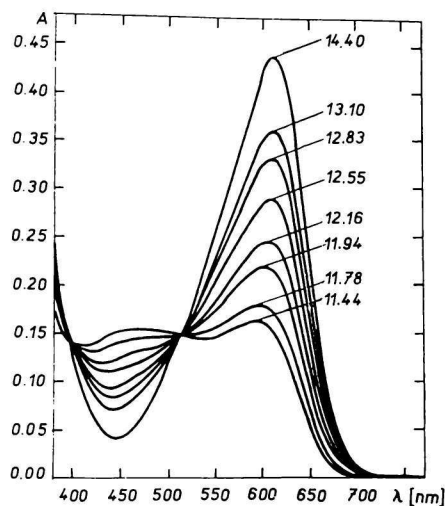$c_I = 3.14 \times 10^{-5}$ M, $d = 10.00$ mm, $I =$
= 0.2, $t = 25°C$.

Fig. 5. Absorption spectra of methyl-
xylenol blue in the range of pH (H_-)
11.3—14.4.
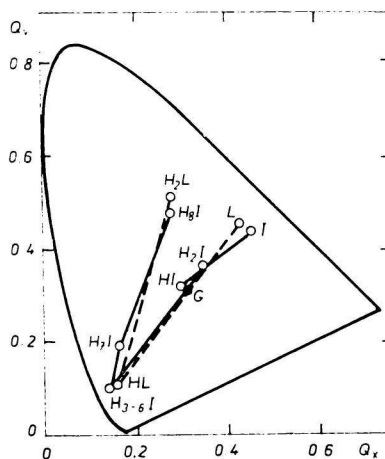$c_I = 3.14 \times 10^{-5}$ M, $d = 10.00$ mm, $t =$
= 25°C.

Fig. 6. Colour transitions of methyl-
xylenol blue (H_4I, full line) and *p*-xylenol
blue (H_4L, dashed line) in the complemen-
tary tristimulus diagram $Q_x Q_y$.

Another marked colour change is observed at pH 5—9 when the proton of the hydroxyl group dissociates and a symmetric molecule is thus formed again ($H_3I^{3-} \rightarrow H_2I^{4-}$, see Fig. 3). Further increase of pH is connected with the dissociation of the protons bonded on the nitrogen atoms linked with the oxygens in positions 4,4' by hydrogen bonds ($H_2I^{4-} \rightarrow HI^{5-} \rightarrow I^{6-}$). The considered equilibria are also accompanied by the colour changes of the solutions (Figs. 4 and 5) since the decoupling of the hydrogen bonds is connected with changes in the symmetry of the electron distribution in the dye molecule.

Colour changes of methylxylenol blue are compared with those of xylenol blue [19] in the complementary tristimulus diagram Q_xQ_y in Fig. 6. The colour changes of methylxylenol blue correspond in general to those of xylenol blue which is the parent compound for the synthesis. Furthermore, a bathochromic shift is seen in the absorption spectrum of the totally deprotonized molecule, owing to the effect of the two substituted di(carboxymethyl)aminomethyl groups.

Potentiometric titrations

Since the preparation containing prevailingly the tetrasodium salt was obtained by purification of methylxylenol blue, it was not possible to carry out a direct alkalimetric titration. An exchange of sodium for hydrogen ions on the cation exchanger in the H⁺ cycle was unsuccessful as the dye was also strongly adsorbed. Therefore we decided for the indirect titration.

A sample (215 mg) of the purified preparation of methylxylenol blue was mixed with 0.09966 M-NaOH (2 ml). Sodium perchlorate was added in such an amount so as to adjust the ionic strength of the solution to the final value $I = 0.2$ after addition of water
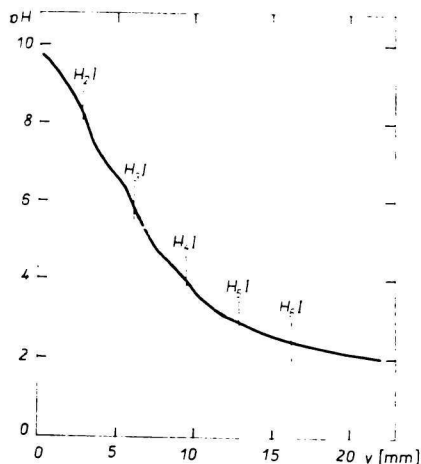

Fig. 7. Potentiometric titration curve of methylxylenol blue.
$I = 0.2$, $t = 25°C$, 1 mm shift of the microburette screw corresponds to 0.05869 ml addition of titrant.
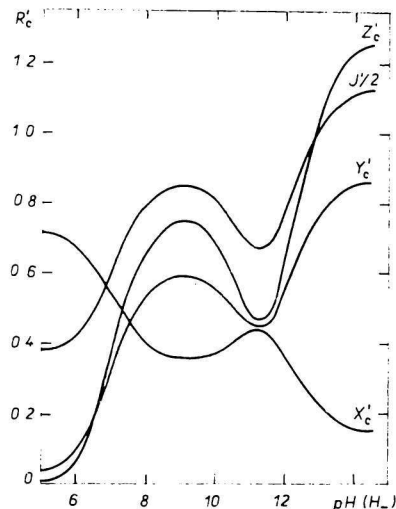
Fig. 8. R_c'—pH curves of methylxylenol blue in alkaline region.

up to the initial volume (25 or 30 ml). The titrant was 1.079 M-HCl and the titrations were carried out with the piston microburette at 25°C. One of the titration curves is recorded in Fig. 7.

When the excess of hydroxide is titrated and the first point of the half equivalence is reached, the shape of the potentiometric titration curve is determined by the four following dissociation constants together with the ionic product of water (K_w)

$$K_{a3} = \frac{[H_2I^{4-}][H^+]}{[H_3I^{3-}]}, \qquad K_{a4} = \frac{[H_3I^{3-}][H^+]}{[H_4I^{2-}]},$$

$$K_{a5} = \frac{[H_4I^{2-}][H^+]}{[H_5I^-]}, \qquad K_{a6} = \frac{[H_5I^-][H^+]}{[H_6I]}; \tag{1}$$

$$K_w = [H^+][OH^-] = 1.27 \times 10^{-14}. \tag{2}$$

The total analytical concentrations are given by relations

$$\left.\begin{array}{c} c_I = [H_6I] + [H_5I^-] + [H_4I^{2-}] + [H_3I^{3-}] + [H_2I^{4-}], \\ c_{HCl} = [Cl^-], \\ c_{NaOH} = [Na^+] - 4c_I. \end{array}\right\} \tag{3}$$

The condition of electroneutrality is expressed by equation

$$[Na^+] + [H^+] = 4[H_2I^{4-}] + 3[H_3I^{3-}] + 2[H_4I^{2-}] + [H_5I^-] + [Cl^-] + [OH^-]. \tag{4}$$

Rearranging (1—4) we obtain the final equation in the polynomial form

$$[H^+]^4 GF_1 + [H^+]^3 (G - c_I) F_2 + [H^+]^2 (G - 2c_I) F_3 + [H^+] (G - 3c_I) F_4 + + (G - 4c_I) = 0. \tag{5}$$

Solutions of eqn (5) with four mutually different $[H^+]$ values yield the four unknown $F_1 - F_4$ defined as

$$\left.\begin{array}{ll} F_1 = (K_{a3} K_{a4} K_{a5} K_{a6})^{-1}, & F_2 = (K_{a3} K_{a4} K_{a5})^{-1}, \\ F_3 = (K_{a3} K_{a4})^{-1}, & F_4 = K_{a3}^{-1} \end{array}\right\} \tag{6}$$

and the quantity G as

$$G = [Na^+] + [H^+] - [Cl^-] - K_w/[H^+]. \tag{7}$$

When calculating G by eqn (7), the equilibrium concentration of Cl^- ions was enumerated from the consumption of the volumetric solution of hydrochloric acid, and the equilibrium concentration of H^+ ions from the measured pH values. Since the measuring cell was calibrated by the standard solutions of the conventional pH scale, the calculations were laden by a systematic deviation following from the approximate validity $pa_H^{\bullet} \approx \approx -\log[H^+]$. The systematic deviation is however lower than the variance of results obtained from potentiometric measurements. Corrections for the volume changes of the titrated solutions were taken into account.

Evaluation of dissociation constants

The dissociation constants K_{a8} and K_{a7} were evaluated from the calculated values of the complementary tristimulus coordinates Q_x, Q_y. By multiplying the coordinates by

corresponding values of the optical concentration, J, we obtained a linear relationship between the position of a point with coordinates $Q_x J$, $Q_y J$ and the concentration ratio of the components in the given equilibrium [23]. Two straight lines were obtained for the two consecutive equilibria, $H_8 I^{2+} \rightarrow H_7 I^+ \rightarrow H_6 I$, the coordinates of their intersect corresponding to the middle form $H_7 I^+$. The dissociation constants K_{a8} and K_{a7} were then calculated, using the H_0 values and products $Q_y J$ from the linearized relationship

$$pK_{ai} = H_0 - \log \frac{Q_y J - (Q_y J)_{H_i I}}{(Q_y J)_{H_{i-1} I} - Q_y J} . \qquad (8)$$

The evaluation of the dissociation constants K_{a6}, K_{a5}, K_{a4}, and K_{a3} from the course of potentiometric titration curves was carried out without difficulties. The calculations and processing of a large number of experimental data were facilitated by a program we set up for a computer Odra 1013. Negative logarithms of the stepwise dissociation constants were calculated by solving a set of equations following from eqn (5):

$$\begin{aligned} pK_{a3} &= \log F_4, & pK_{a4} &= \log F_3 - \log F_4, \\ pK_{a5} &= \log F_2 - \log F_3, & pK_{a6} &= \log F_1 - \log F_2. \end{aligned} \qquad (9)$$

The constant K_{a6} has, however, been determined with low precision.

The dissociation constant K_{a3} was calculated from the spectrophotometric data by eqn (8) where, instead of H_0 values, the pH values of the conventional activity scale were inserted.

The evaluation of the constants K_{a2} and K_{a1} was complicated owing to a slight difference of their logarithms. Consequently, the middle form HI^{5-} of methylxylenol blue is not present exclusively at any pH value of the solution. Since the lines marking the colour transitions $H_2 I^{4-} \rightarrow HI^{5-}$ and $HI^{5-} \rightarrow I^{6-}$ are at a very acute angle, neither the conversion of the absorption spectra into the chromaticity coordinates, Q_x, Q_y enabled to read off exactly the coordinates of the form HI^{5-} (Fig. 6). A partial improvement was achieved by reading the absorbance values A_λ at several wavelengths [23] and using the modified chromaticity components

$$\begin{aligned} X_c' &= A_{430} + A_{440} + A_{450}, \\ Y_c' &= A_{550} + A_{560} + A_{570}, \\ Z_c' &= A_{590} + A_{600} + A_{610}, \\ J' &= X_c' + Y_c' + Z_c'. \end{aligned} \qquad (10)$$

The pH dependence of these components is seen in Fig. 8. But the estimate of the coordinates of the middle form was not quite reliable even by such a procedure.

The last two dissociation constants of methylxylenol blue were therefore evaluated using a method recommended by *Stearns* and *Wheland* [24] for the case where the spectrophotometric data of one of the limiting forms of the equilibrium are not available. The relationship for the constant K_{a2} can be rearranged into equation

$$\frac{1}{A - A_{H_2 I}} = a_H \frac{1}{K_{a2}(A_{HI} - A_{H_2 I})} + \frac{1}{(A_{HI} - A_{H_2 I})} . \qquad (11)$$

When the $1/(A - A_{H_2 I})$ values (y axis) are plotted against a_H (x axis), the reciprocal value of the difference $(A_{HI} - A_{H_2 I})$ can be read off as an intercept on the y axis. For its twofold value, the equality $K_{a2} = a_H$ is valid.

The relationship for the last dissociation constant K_{a1} can be analogously arranged as follows

$$\frac{1}{A_I - A} = \frac{1}{a_H} \cdot \frac{K_{a1}}{(A_I - A_{HI})} + \frac{1}{(A_I - A_{HI})} . \tag{12}$$

If we put $y = 1/(A_I - A)$ and $x = 1/a_H$, eqn (12) can also be replaced by a regression straight line that enables similar evaluation of K_{a1}.

For the purpose of the linear regression analysis we used the Z'_c values in eqns (11) and (12) as additive quantities instead of absorbance values. Estimates of the standard deviations of the determined values of K_{a2} and K_{a1} were evaluated from the estimates of the standard deviations of the shifts of regression lines.

All the calculated dissociation constants are summarized in Table 1.

Table 1

Dissociation constants of methylxylenol blue

Equilibrium	pK_{ai} ($\bar{x} \pm s$) determined	
	spectrophotometrically	potentiometrically
$H_9I^{3+} \rightleftharpoons H_8I^{2+} + H^+$	< -2.8	—
$H_8I^{2+} \rightleftharpoons H_7I^+ + H^+$	-1.90 ± 0.08	—
$H_7I^+ \rightleftharpoons H_6I + H^+$	0.08 ± 0.02	—
$H_6I \rightleftharpoons H_5I^- + H^+$	—	2.0 ± 0.8
$H_5I^- \rightleftharpoons H_4I^{2-} + H^+$	—	3.4 ± 0.2
$H_4I^{2-} \rightleftharpoons H_3I^{3-} + H^+$	—	4.3 ± 0.1
$H_3I^{3-} \rightleftharpoons H_2I^{4-} + H^+$	7.00 ± 0.01	6.95 ± 0.02
$H_2I^{4-} \rightleftharpoons HI^{5-} + H^+$	10.61 ± 0.03	—
$HI^{5-} \rightleftharpoons I^{6-} + H^+$	12.47 ± 0.06	—

Verification of metallochromic properties of methylxylenol blue

Methylxylenol blue forms blue coloured complex compounds with a number of metal ions in mild acidic media. The complex formation depends strongly upon the acidity of the medium. Polyvalent ions react with the dye already at pH $1-3$, for bivalent cations the optimum pH is usually $5-6$. We verified the metallochromic properties of the dye in the preliminary tests with solutions of cations listed in Table 2. Some of the tested reactions cannot be utilized in chelatometric titrations because *e.g.* the ions Al^{3+}, Ni^{2+}, and also Cu^{2+} form more stable complexes with methylxylenol blue than with ethylenediaminetetraacetic acid. In alkaline medium, at pH about 11.5, methylxylenol blue reacts also with Mg^{2+} ions and cations of alkaline earths. As solutions of methylxylenol blue are grey in colour in the alkaline medium, the colour transitions are not so distinguishable in chelatometric titrations of those metals.

Discussion

The detailed study of the behaviour of methylxylenol blue in solutions showed that its protolytic equilibria can be interpreted analogously to the equilibria of xylenol orange and methylthymol blue. The analogy follows especially from the comparison of electronic absorption spectra of xylenol orange [21, 22] or methylthymol blue [20] with those of methylxylenol blue in the course of colour changes described in this communication.

With respect to the acid-base equilibria and the colour reactions with metal ions, methylxylenol blue is more related with methylthymol blue than with xylenol orange. In comparison with xylenol orange, methylxylenol blue has another two CH_3 groups, located in positions 2,2′. It brings about far more conspicuous changes in colour reactions

Table 2

Reactions of methylxylenol blue with metal ions

Cation M^{n+}	pH	Colour of solution of	
		free dye	metal complex
Al^{3+}	5	Yellow	Violet
Ba^{2+}	11.5	Grey	Blue
Bi^{3+}	1—3	Yellow	Blue-violet
Ca^{2+}	11.5	Grey	Blue
Cd^{2+}	5—6	Yellow	Light blue
Co^{2+}	5—6	Yellow	Blue
Cu^{2+}	5—6	Yellow	Violet
Fe^{3+}	5	Yellow	Blue-green
Hg^{2+}	6	Yellow	Blue
In^{3+}	5	Yellow	Blue
La^{3+}	5—6	Yellow	Blue
Mg^{2+}	11.5	Grey	Blue
Mn^{2+}	6	Yellow	Blue
Ni^{2+}	5—6	Yellow	Greenish-blue
Pb^{2+}	5—6	Yellow	Blue
Sc^{3+}	5—6	Yellow	Light blue
Sn^{2+}	5—6	Yellow	Intensive blue
Th^{4+}	3	Yellow	Blue
Zn^{2+}	5—6	Yellow	Light blue
Zr^{4+}	1—2	Yellow	Blue

Observed at $c_M \approx 10^{-3}$ M, $c_I \approx 5 \times 10^{-5}$ M, $d \approx 10$ mm.

than the replacement of CH_3 groups by $(CH_3)_2CH$ groups in positions 5,5′ when comparing methylxylenol blue and methylthymol blue. Alkaline solutions of xylenol orange and also its chelates with metal ions are purple in colour. Methylxylenol blue and methylthymol blue form mostly the blue coloured chelates and the protolytic equilibria of both the dyes in alkaline solutions ($H_2I \rightarrow HI \rightarrow I$) find better colour expression than those of xylenol orange.

The results of the presented work indicate the applicability of methylxylenol blue. It can be used not only as a reagent for spectrophotometric determination of microgram concentrations of metals, but, in the media with convenient acidity, also as a metallochromic indicator in chelatometric microtitrations. Some advances in the mentioned course of studies of methylxylenol blue have been made in our laboratory [25, 26] and the results will soon be published in this series of communications.

References

1. Körbl, J. and Přibil, R., *Chem. Ind.* (London) *1957*, 233.
2. Cherkesov, A. I., Astakhova, N. K., and Cherkesov, A. A., *Ftaleksony 1970*, 19.
3. Deguchi, M., Yamabuki, S., and Yashiki, M., *Bunseki Kagaku 20*, 891 (1971).
4. Deguchi, M., Okumura, I., and Sakai, K., *Bunseki Kagaku 19*, 836 (1970).
5. Enoki, T., Mori, I., Yamazaki, M., and Inouem, M., *Bunseki Kagaku 21*, 31 (1972).
6. Deguchi, M. and Sakai, K., *Bunseki Kagaku 19*, 241 (1970).
7. Kitano, M. and Ueda, J., *Nippon Kagaku Zasshi 92*, 168 (1971).
8. Ueda, J., *Nippon Kagaku Kaishi 1972*, 1422.
9. Ueda, J., *Nippon Kagaku Kaishi 1972*, 584.
10. Deguchi, M. and Kunishige, T., *Bunseki Kagaku 21*, 392 (1972).
11. Deguchi, M., Kunishige, T., and Yashiki, M., *Yakugaku Zasshi 92*, 1055 (1972).
12. Cherkesov, A. I., Argisheva, A. I., Astakhova, N. K., and Konyakhina, A. A., *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 14*, 999 (1971).
13. Mori, I. and Enoki, T., *Yakugaku Zasshi 90*, 494 (1970).
14. Ueda, J., *Nippon Kagaku Kaishi 1973*, 724.
15. Ueda, J., *Nippon Kagaku Kaishi 1973*, 1467.
16. Macejunas, A. G., *J. Amer. Water Works Ass. 61*, 311 (1969).
17. Boyd, R. H., *Solute-Solvent Interactions 1969*, 97.
18. Schwarzenbach, G., *Helv. Chim. Acta 20*, 490 (1937).
19. Vytřas, K., *Chem. Zvesti 28*, 252 (1974).
20. Körbl, J. and Kakáč, B., *Chem. Listy 51*, 1680 (1957).
21. Řehák, B. and Körbl, J., *Collect. Czech. Chem. Commun. 25*, 797 (1960).
22. Murakami, M., Yoshino, T., and Harasawa, S., *Talanta 14*, 1293 (1968).
23. Reilley, C. N. and Smith, E. M., *Anal. Chem. 32*, 1233 (1960).
24. Stearns, R. S. and Wheland, G. W., *J. Amer. Chem. Soc. 69*, 2025 (1947).
25. Mach, V., *Thesis.* Institute of Chemical Technology, Pardubice, 1971.
26. Malcová, M., *Thesis.* Institute of Chemical Technology, Pardubice, 1973.
27. Grunin, A. V., *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 16*, 1486 (1973).
28. Ueda, J., *Nippon Kagaku Kaishi 1974*, 273.

Translated by F. Kopecký