The Electrical Conductivities of the Sodium Salts of Methyl Orange, *o*-Methyl Red and *p*-Methyl Red in Aqueous Solutions

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ABSTRACT

The electrical conductivities of the sodium salts of methyl orange, o-methyl red and p-methyl red were measured in water at 25°C in the concentration range $1\cdot0 \times 10^{-4}$–$1\cdot0 \times 10^{-3}$ mol dm^{-3}. The molar conductivity data were found to fit the Debye–Hückel–Onsager equation for a symmetrical electrolyte. The values of the molar conductivities of the three electrolytes at infinite dilution are $80\cdot05 \pm 0\cdot71$, $80\cdot47 \pm 0\cdot43$ and $81\cdot30 \pm 0\cdot38$ S cm^2 mol^{-1} for the sodium salts of methyl orange, o-methyl red and p-methyl red, respectively. The ionic conductivities at infinite dilution were calculated as $29\cdot94$, $30\cdot36$ and $31\cdot19$ S cm^2 mol^{-1} for the anions of methyl orange, o-methyl red and p-methyl red, respectively. The significance of these results with respect to dye aggregation and its inclusion by cyclodextrins is discussed.

1 INTRODUCTION

The state of aggregation of dyes in solution is important to those working in the dye and photographic industry and to those using lasers.[1] The large changes in the UV–visible spectra that occur as the dye concentration is increased were utilized for studying the stacking behavior of cationic dyes such as methylene blue[2] for concentrations above 10^{-5} molal. However the aggregation of the anionic dyes is not accompanied by large changes in the absorbance, which makes it difficult to use the spectrophotometric method for studying the aggregation processes of
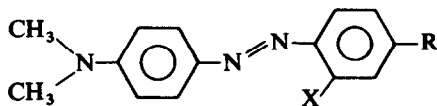
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Fig. 1. The structural formulas of the anions of methyl orange (X = H, R = SO_3^-), *o*-methyl red (X = COO^-, R = H) and *p*-methyl red (X = H, R = COO^-).

such dyes.[3] Kendrick and Gilkerson[4] have studied the aggregation of methyl orange by measuring the electrical conductances, the UV–visible absorbances and the osmotic coefficients of aqueous solutions of the sodium salt of methyl orange. These authors have concluded that the methyl orange anion is almost completely dimerized above 2×10^{-4} mol dm^{-3} and undergoes further aggregation above 1×10^{-3} mol dm^{-3}. On the other hand, Robinson and Garrett[5] reported that the anion of methyl orange is monomeric in the submillimolar region, as indicated by their conductance data. Deviations from Beer's law were reported to be quite small for methyl orange at concentrations below 1×10^{-3} mol dm^{-3}, with indications of aggregation occurring above this concentration.[6] With the exception of methyl yellow, which gave significant deviations from Beer's law,[7] the anions of methyl orange,[7] *o*-methyl red[8] and *p*-methyl red[9] gave no deviations from Beer's law in aqueous solutions for concentrations $\leq 1.5 \times 10^{-4}$ mol dm^{-3}, indicating that these ionic dyes are in the monomer form.

The present study is concerned with measuring the conductances of the sodium salts of methyl orange, *o*-methyl red and *p*-methyl red in water at 25°C in the concentration range 1×10^{-4}–1×10^{-3} mol dm^{-3}. An attempt is made to report the molar ionic conductivities of the anions of these dyes at infinite dilution. Such information is not available in the literature. The structural formulas of the anions of the investigated dyes are given in Fig. 1.

2 EXPERIMENTAL

The sodium salt of methyl orange ($C_{14}H_{14}N_3SO_3Na$) was purchased from Sigma (St Louis, Missouri, USA) and was used without additional purification. The acid form of *o*-methyl red ($C_{15}H_{15}N_3O_2$) was also purchased from Sigma. Preparation of the acid form of *p*-methyl red ($C_{15}H_{15}N_3O_2$) was described previously.[9] KCl (Fisher Scientific, Fair Lawn, NJ, USA) was used for determining the cell constant. NaOH (J. T. Baker Inc., Phillipsburg, NJ, USA) was used to convert the acid forms of the isomers of methyl red into their sodium salts. NaCl (Riedel-De Haën Ag, Seelze-Hannover, Germany) was used for checking the accuracy of the conductance measurements. The buffer materials used in calibrating the pH meter were described previously.[7]

The acid forms of *o*- and *p*-methyl red were converted into the sodium salt by reacting carbonate-free aqueous NaOH with the acid form in toluene, followed by filtration of the toluene layer. The filtrate was washed with methanol. The product was recrystallised twice from methanol and dried for several hours at 200°C before use. The purity of these preparations was checked by performing elemental analysis (MHW Laboratories, Phoenix, Arizona, USA). The analysis of the sodium salt of *o*-methyl red (average of duplicate analysis) was 62·60% for C, 4·71% for H, 13·95% for N and 7·88% for Na. The analysis of the sodium salt of *p*-methyl red (average of four analyses, except for Na which is based on duplicate analysis) was 58·74% for C, 4·73% for H, 13·84% for N and 8·67% for Na. The formula $C_{15}H_{14}N_3O_2Na$, which represents the sodium salt of the two isomers of methyl red, requires 61·84% for C, 4·84% for H, 14·42% for N and 7·89% for Na. The elemental analysis of the sodium salt of *o*-methyl red was considered acceptable. The largest deviation in the elemental analysis of the *p*-methyl red salt is in the carbon content. If we assume that the deviation arises from coprecipitation of NaOH with the sodium salt of *p*-methyl red sample, the purity of the sample would be 98·43% based on the Na percentage reported in the analysis. The effect of this suspected impurity on the conductivity of the sodium salt of *p*-methyl red was assessed to be about 3%. The molar absorptivity at 464 nm (λ_{max}) in water at 25°C and pH of about 8 was found to be $2·72 \times 10^4$ cm^{-1} mol^{-1} dm^3 when using the sodium salt and $2·74 \times 10^4$ cm^{-1} mol^{-1} dm^3 when using the acid form of *p*-methyl red. This result indicates that the purity of *p*-methyl red salt is higher than suspected, and that the deviation in the carbon analysis is probably due to incomplete combustion.

The water used in the conductance measurements was double distilled, deionized and freshly boiled, with specific conductivity in the range $1·6–2·0 \times 10^{-6}$ S cm^{-1} and pH 6·7 at 25°C. The required concentration of a test solution was obtained by diluting a specific volume of a stock solution having a concentration of about $4·0 \times 10^{-3}$ mol dm^{-3}. The pH values of these stock solutions were 8·58, 7·80 and 8·00 for the sodium salts of methyl orange, *o*-methyl red and *p*-methyl red, respectively. The description of the conductimeter has been given in a previous publication.[10] The conductivity cell had a cell constant of 2·14 cm^{-1}.

3 RESULTS AND DISCUSSION

The molar conductivities of the sodium salt of methyl orange in water at 25°C are given in Table 1 in the concentration range $2·113 \times 10^{-4}$–

TABLE 1

The Molar Conductivities of the Sodium Salt of Methyl
Orange in Water at 25°C

[Methyl orange]/M^a	Λ/S cm^2 mol^{-1}
2.113×10^{-4}	79.24
2.255×10^{-4}	78.94
3.494×10^{-4}	78.70
3.521×10^{-4}	78.67
4.225×10^{-4}	77.87
4.929×10^{-4}	78.92
5.633×10^{-4}	78.47
6.338×10^{-4}	77.47
7.042×10^{-4}	77.25
7.746×10^{-4}	78.88
8.450×10^{-4}	77.87
9.154×10^{-4}	78.00

^{a} M = 1 mol dm^{-3}.

9.154×10^{-4} mol dm^{-3}. The molar conductivity of a test solution, Λ, was calculated according to the following equation

$$\Lambda = 10^3 k/C \quad \text{S } cm^2 \text{ mol}^{-1} \tag{1}$$

where k is the specific conductivity of the test solution (obtained from the conductimeter reading) and C is its stoichiometric concentration in mol dm^{-3}.

Tables 2 and 3 show the molar conductivities of the sodium salts of *o*- and *p*-methyl red, respectively, in water at 25°C in the concentration ranges indicated in the two Tables. The general trend in the data of Tables 1–3 is that the molar conductivity slightly decreases as the concentration of the electrolyte increases. However, exceptions are present in all Tables, which reflect a scatter caused by errors arising from working with dilute solutions.

The data in Tables 1–3 were evaluated according to the Debye–Hückel–Onsager limiting law

$$\Lambda = \Lambda_o - (a + b\Lambda_o)\sqrt{C} \tag{2}$$

where Λ_o is the molar conductivity of the test electrolyte at infinite dilution, while a and b are constants for a given solvent and temperature. For H_2O at 25°C the constants a and b are 60.6 and 0.230, respectively.[11] Equation (2) assumes a linear relationship between Λ and $\sqrt{C}$. The data in Tables 1–3 were subjected to a linear least squares analysis. The values of Λ_o obtained from such analysis were found to be 80.05 ± 0.71, 80.47 ± 0.43 and 81.30 ± 0.38 S cm^2 mol^{-1} for the sodium salts of methyl orange, *o*-methyl red and *p*-methyl red, respectively.

TABLE 2

The Molar Conductivities of the Sodium Salt of *o*-Methyl
Red in Water at 25°C

[*o*-Methyl red]/M	Λ/S cm^2 mol^{-1}
1.006×10^{-4}	79.52
2.012×10^{-4}	79.22
3.019×10^{-4}	79.50
4.025×10^{-4}	78.76
5.031×10^{-4}	78.51
6.037×10^{-4}	78.35
7.043×10^{-4}	77.80
8.050×10^{-4}	77.39
9.056×10^{-4}	78.40
9.988×10^{-4}	78.10

By using these values of Λ_0, together with the values of the constants a
and b, the calculated slope of eqn (2) is -79 for each salt. This value is in
agreement with the values usually cited for 1:1 electrolytes.[12] The slopes
of the linear regression analysis were -75, -85 and -79 for the data in
Tables 1, 2 and 3, respectively. The corresponding correlation coefficients
were -0.61, -0.85 and -0.87. The significant deviation from unity,
especially for methyl orange, reflects the scatter in the data caused by
dealing with dilute solutions. The conclusion to be drawn from these
results is that the three salts are strong electrolytes and the anion of each
dye is present in the monomer form in the concentration ranges reported in
Tables 1–3. This conclusion is in agreement with that given by Robinson
and Garrett[5] concerning the sodium salt of methyl orange. Re-analysis of
the conductance data reported by Kendrick and Gilkerson[4] for concen-

TABLE 3

The Molar Conductivities of the Sodium Salt of *p*-Methyl
Red in Water at 25°C

[*p*-Methyl red]/M	Λ/S cm^2 mol^{-1}
1.044×10^{-4}	80.46
2.089×10^{-4}	80.42
3.133×10^{-4}	79.80
4.177×10^{-4}	79.48
5.221×10^{-4}	78.91
6.266×10^{-4}	79.80
7.310×10^{-4}	79.34
8.354×10^{-4}	79.00
9.398×10^{-4}	78.74

trations below 1.6×10^{-3} mol dm^{-3} methyl orange gave Λ_o of 75.1 S cm^2 mol^{-1} with a slope of -141 and a correlation coefficient of -0.95. The adherence of these data to a straight line is better than our data for methyl orange. However, the conflicting conclusions, especially those concerning the ionic conductances of the monomer and dimer forms of the anion of methyl orange given by Kendrick and Gilkerson[4] are probably caused by considering the conductance data over a relatively large range of concentration (1.0×10^{-4}–1.0×10^{-2} mol dm^{-3}). These authors have assumed a value of 75 S cm^2 mol^{-1} for Λ_o of the sodium salt of methyl orange, while Robinson and Garrett[5] have speculated a value not more than 82 S cm^2 mol^{-1}. No literature information is available on Λ_o for the sodium salts of the isomers of methyl red. Our results indicate that the values of Λ_o are nearly equal for the three dyes.

By using the literature value[13] of the ionic conductivity of Na$^+$ at infinite dilution, which is given as 50.11 S cm^2 mol^{-1}, the ionic conductivities of the anions at infinite dilution were calculated as 29.94, 30.36 and 31.19 S cm^2 mol^{-1} for the anions of methyl orange, *o*-methyl red and *p*-methyl red, respectively.

The accuracy of the conductimeter was checked by measuring the molar conductivity of NaCl in water at 25°C. The measured value for 6.742×10^{-4} mol dm^{-3} NaCl was 125.3 S cm^2 mol^{-1}, while the value calculated according to the following empirical equation[14]

$$\Lambda = 126.42 - 88.53\sqrt{C} + 89.5C(1 - 0.2274\sqrt{C}) \tag{3}$$

is 124.2 S cm^2 mol^{-1}. The agreement between these two values indicates that the conductimeter was sufficiently accurate for the studies reported in this paper.

The main conclusion to be drawn from this present study is that aggregation of the anions of the investigated dyes is not detectable in the submillimolar range, as deduced from conductivity measurements. An interesting extension of the present study is to use the conductimetric method for calculating the stability constants of the inclusion complexes of these dyes with cyclodextrins at relatively very low cyclodextrin concentrations, which are normally not practical for the spectrophotometric method of obtaining such stability constants. Our results concerning this application will be reported separately.

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