THE ACID DISSOCIATION CONSTANT OF METHYL RED

A Spectrophotometric Measurement

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THE partial dissociation of weak electrolytes is one of the most fundamental phenomena observed in solution chemistry. Calculations involving the dissociation constants of weak acids and bases are indispensable to any discussion of homogeneous equilibrium. However, many physical chemistry laboratory courses fail to include an experiment involving the determination of a dissociation constant of a weak acid or base. The experiment outlined below involves the direct spectrophotometric determination of the acid dissociation constant of methyl red (MR).

Figure 1 shows the acidic (HMR) and basic (MR^-) forms of methyl red. The acid form is a zwitterion in

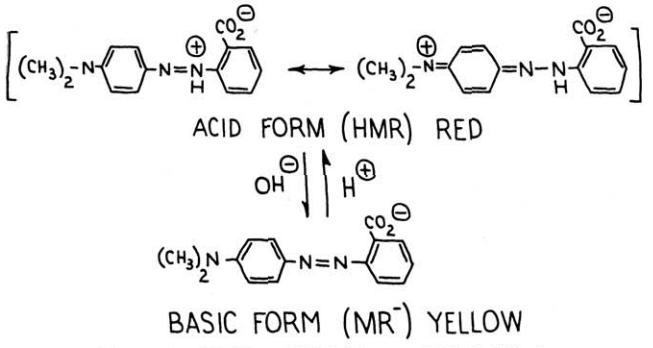

Figure 1. HMR and MR^- Forms of Methyl Red

solution. It is considered to be a resonating structure with an electronic configuration somewhere between the two extreme forms shown. Equation (1) defines the equilibrium constant to be measured. Equation (2), the familiar Henderson-Hasselbach statement of (1), is the form most readily tested by experiment.

$$K = \frac{(H^+)\,(MR^-)}{(HMR)} \qquad (1)$$

$$pK = p\mathrm{H} - \log_{10}\frac{(MR^-)}{(HMR)} \qquad (2)$$

Methyl red is a particularly good acid for study since both HMR and MR^- have strong absorption peaks in the visible portion of the spectrum, the acid dissociation constant is not greatly affected by changes in ionic strength, and the color change interval from *p*H 4–6 is conveniently obtained with a simple HOAc-NaOAc buffer system.[1]

EXPERIMENTAL PROCEDURE

A laboratory stock solution made by dissolving 1 g. of crystalline methyl red[2] in 300 ml. of 95% ethanol and diluting to 500 ml. with distilled water is convenient. The standard solution of methyl red for use in the actual experiment is made by adding 4 ml. of the stock solution to 50 ml. of 95% ethanol and diluting to 100 ml. with water. In addition to this standard solution, the following solutions are required: 250 ml. 0.04 *M* NaOAc, 100 ml. 0.01 *M* NaOAc, 100 ml. 0.02 *M* HOAc, 25 ml. 0.1 *M* HCl, and 100 ml. 0.01 *M* HCl. The concentrations of these latter solutions are not critical and they can be prepared by diluting laboratory stock solutions.

The first step in the experiment involves determining the wave lengths at which HMR and MR^- exhibit absorption maxima. This is done by investigating the absorbancy versus wave length of the two solutions described below, both of which contain the same total concentration of methyl red. The first solution (A) is prepared by diluting a mixture of 10 ml. of the standard MR solution and 10 ml. 0.1 *M* HCl to 100 ml. The *p*H of this solution is about 2, so the MR is present entirely as HMR. The second solution (B) is prepared by diluting a mixture of 10 ml. of the standard MR solution and 25 ml. of 0.04 *M* NaOAc to 100 ml. The *p*H of this latter solution is about 8 so the MR is present entirely as MR^-. Portions of solutions A and B are placed in matched 1-cm. Pyrex cells and the absorbancy versus water measured between 350 and 600 mμ. Figure 2 illustrates the type of plots obtained. A Beckman Model B spectrophotometer was used in taking all absorbancy readings. The absorption peak for HMR (λ_A) is at 520 mμ. The absorption peak for MR^- (λ_B) is at 425 mμ. As can be seen from the figure the absorption peaks are not completely separated but cross at a wave length of 460 mμ. At this point the absorbancy indexes of HMR and MR^- are identical, and the spectral curves are said to be at the isobestic point. If the absorbancy of a solution containing both HMR and MR^- is measured at this particular wave length, the observed absorbancy is independent of the relative amounts of HMR and MR^- present, and depends solely on the total amount of MR in the solution.

[1] KOLTHOFF, I. M., "Acid-Base Indicators," 2nd. ed., The Macmillan Company, New York, **1953,** pp. 145–46.

[2] Methyl red (Cryst.) m.p. 178°–179° can be obtained from Eastman Organic Chemicals, Rochester 3, New York.

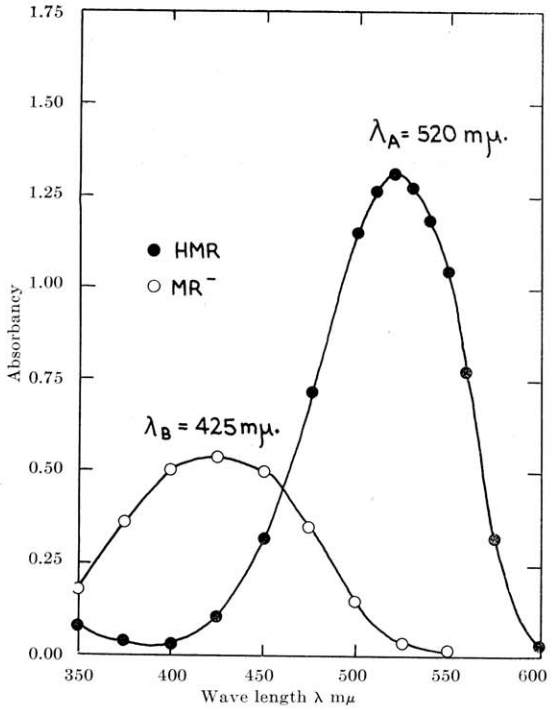

Figure 2. Absorbancies of HMR and MR^- versus λ

The second step in the experiment involves verifying Beer's law for both HMR and MR^-, and determining their absorbancy indexes at λ_A and λ_B. Portions of solutions A and B are diluted to 0.75, 0.50, and 0.25 times their initial concentrations using 0.01 *M* HCl and 0.01 *M* NaOAc respectively. The absorbancies of these solutions versus water are measured at λ_A and λ_B. Figure 3 shows the type of data obtained. It is important in taking these and all subsequent absorbancy data to be sure that all measurements are made at a constant temperature. The easiest way to do this is to have all the solutions at room temperature and insert the filled cells in the spectrophotometer just prior to taking measurements.

The third step in the experiment is to determine the relative amounts of HMR and MR^- present in solution as a function of *p*H. A series of solutions is prepared by adding varying amounts of 0.02 *M* acetic acid to constant amounts of standard indicator solution buffered with 0.04 *M* NaOAc solution. The absorbancies (A_A and A_B) of the solutions at λ_A and λ_B are measured, and the *p*H values determined. A Beckman Model H *p*H meter with glass electrode standardized at *p*H 6.00 was used in these determinations.

STUDENT RESULTS

Table 1 shows the results of a typical student experiment.

From the data in Table 1 and the absorbancy indexes of HMR and MR^- calculated from Figure 3, the relative amounts of HMR and MR^- in solution can be calculated using equations (3) and (4). These equations imply that the observed absorbancies at λ_A and λ_B are the simple additive sums of the absorbancies due to HMR and MR^-.

$$A_A = a_{A,HMR}(HMR) + a_{A,MR^-}(MR^-) \quad (3)$$

$$A_B = a_{B,HMR}(HMR) + a_{B,MR^-}(MR^-) \quad (4)$$

TABLE 1
Experimental Data

Solution no.	*Vol.[a] HOAc (ml.)*	A_A	A_B	*pH*
1	50	0.852 ± 0.001	0.280 ± 0.001	4.85 ± 0.02
2	25	0.640	0.352	5.09
3	10	0.366	0.441	5.50
4	5	0.224	0.490	5.82

Temp. = 27.2 ± 0.2° C.

[a] This column gives the volume of 0.02 *M* HOAc to be added to 10 ml. standard MR solution plus 25 ml. 0.04 *M* NaOAc solution before dilution with water to 100 ml. total volume.

TABLE 2
Summary of Results

Solution no.	$\frac{(MR^-)}{(HMR)}$	$log_{10}\frac{(MR^-)}{(HMR)}$	*pH*	*pK*
1	0.62	−0.21	4.85	5.06
2	1.21	+0.08	5.09	5.01
3	3.12	+0.49	5.50	5.01
4	6.52	+0.82	5.82	5.00

From the relative amounts of HMR and MR^- present as a function of *p*H the value of *pK* for methyl red can be calculated using equation (1). These calculations are summarized in Table 2. The value for *pK* is constant within the limits of experimental error.

The average value for *pK* of 5.02 ± 0.02 at 27.2°C. taken from Table 2 agrees very well with an over-all average for the *pK* of methyl red of 5.05 ± 0.05 determined in the range 25–30°C. by a number of workers,[3] using both colorimetric and spectrophotometric methods.

[3] KOLTHOFF, I. M., *loc. cit.*, pp. 290–91.

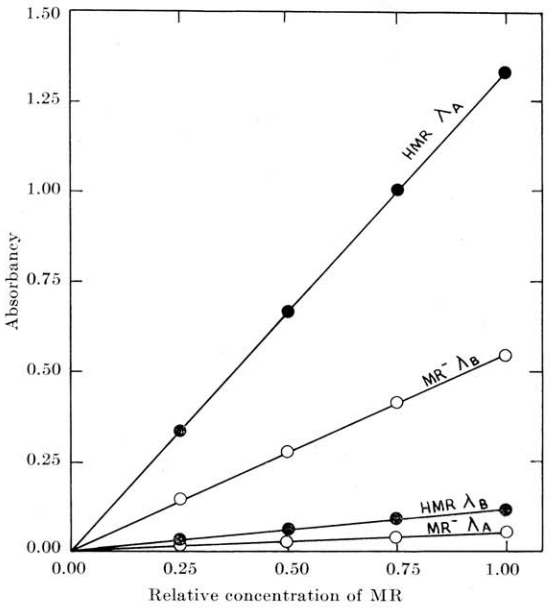

Figure 3. Absorbancies of HMR and MR^- at λ_A and λ_B versus Concentration