

Effect of Dielectric Constant and Ionic Strength on the Fading of *N,N*-Dimethylaminophenolphthalein in Alkaline Medium

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Phenolphthalein (PP) is a well-known acid-base indicator for determination of the equivalence point in a titration. At pH 10 and higher the pink color fades as a tribasic salt of phenolphthalein acid forms. This reversible fading of PP in alkaline solution was recently used in an experiment illustrating pseudo-first-order kinetics (1). Moreover, this chemical reaction is a proper example for demonstrating the influence of ionic strength and the dielectric constant on the rate constant (2, 3).

At the University of Ulm every experiment in the Physical Chemistry Lab at the advanced level (seventh semester) is carried out by students working in pairs. One of these experiments deals with the study of the influence of the ionic strength of the solution on the rate of a reaction involving ions (salt effect) and the verification of the Brønsted-Bjerrum-Debye theory (4-6). The time needed to perform the experiment we are reporting in this paper is approximately 6 hours. Many schools do not have a 6-hour laboratory period. However, the experiment can be conducted in two 3-hour laboratory periods because it actually involves two separate experiments, one concerning the ionic strength effect and the second concerning the dielectric constant effect.

We ran this experiment using PP for two semesters. However, the results were ambiguous and often irreproducible. In a paper published in 1930, Lund reported that the use of *N,N*-dimethylaminophenolphthalein (DMAPP) instead of PP provides more pertinent and unequivocal results visualizing the salt effect on the rate constant in terms of the extended Debye-Hückel theory (7).

Solutions of DMAPP (Fig. 1, form 1) are colorless below pH = 9. In contrast to PP, the colored, chinoide form (2), of DMAPP is less negatively charged and consequently it fades considerably faster than PP. The absorption maximum, compared with PP ($\lambda_{\max} = 550$ nm), is shifted to higher wavelength ($\lambda_{\max} = 574$ nm).

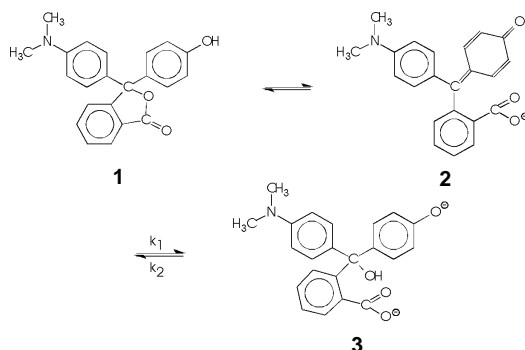


Figure 1. Structural forms of *N,N*-dimethylaminophenolphthalein.

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Calculation of Rate and Equilibrium Constants

The fading of DMAPP in basic solution can be represented by the reaction:



DMAPP⁻ is the colored form (2), k_1 is the molar rate constant for the formation of the carbinol DMAPPOH²⁻ (3), and k_2 is the corresponding constant for the reverse reaction. The differential expression describing the rate of the fading formulated in eq 1 is

$$-\frac{d[\text{DMAPP}^-]}{dt} = k_1[\text{OH}^-][\text{DMAPP}^-] - k_2[\text{DMAPPOH}^{2-}] \quad (2)$$

When an excess OH⁻ concentration is used the forward reaction obeys a pseudo-first-order rate law and in this case it is convenient to write

$$k'_1 = k_1[\text{OH}^-]$$

Integration of eq 2 gives

$$(k'_1 + k_2) = \frac{1}{t} \ln \left(\frac{[\text{DMAPPOH}^{2-}]_e}{[\text{DMAPPOH}^{2-}]_e - [\text{DMAPPOH}^{2-}]_t} \right) \quad (3)$$

where $[\text{DMAPPOH}^{2-}]_e$ and $[\text{DMAPPOH}^{2-}]_t$ are the concentrations of the carbinol at equilibrium and at time t , respectively.

According to Beer's law, the concentration of dye [DMAPP] is proportional to the logarithm of the transmittance T :

$$[\text{DMAPP}] \sim \ln T \quad (4)$$

Substitution of eq 4 in eq 3 gives

$$(k'_1 + k_2) = \frac{1}{t} \ln \left(\frac{\ln T_{t=0} - \ln T_e}{\ln T_t - \ln T_e} \right) \quad (5)$$

where $T_{t=0}$, T_t , and T_e are the transmittance at time zero, time t , and equilibrium, respectively.

The equilibrium constant is given by

$$K_c = \frac{[\text{DMAPPOH}^{2-}]}{[\text{DMAPP}^-] \cdot [\text{OH}^-]} = \frac{\ln T_{t=0} - \ln T_e}{[\ln T_e][\text{OH}^-]} = \frac{k_1}{k_2} \quad (6)$$

Values of the molar rate constant are calculated from

$$k_1 = \frac{(K'_1 + k_2)}{[\text{OH}^-] + 1/K_c} \quad (7)$$

Salt Effect

The kinetics of the reaction 1 may be formulated as $\text{DMAPP}^- + \text{OH}^- \rightleftharpoons \text{X}^{2-} \rightarrow \text{DMPPOH}^{2-}$ where X^{2-} is the transition state, which is in equilibrium with the reactants but not with the product. The variation of the rate constant of a reaction between ions with the ionic strength I of the solution, which is known as the kinetic salt effect, is given by the Brønsted-Bjerrum-Debye limiting law (4-6):

$$\log k_1 = \log k_0 + 2A \cdot z_{\text{DMAPP}^-} \cdot z_{\text{OH}^-} \cdot I^{1/2} \quad (8)$$

where k_0 is the extrapolated molar rate constant for zero ionic strength, z is the charge of the corresponding ion, and A is equal to $0.509 \text{ kg}^{1/2} / \text{mol}^{1/2}$ for aqueous solutions at 25°C .

Solvent Effect

As expected, the rate of an ionic reaction is affected by the solvent. This effect is characterized by the permittivity ϵ (dielectric constant) of the solvent and its ionic strength I . The rate constant in this case is given by the Brønsted-Christiansen-Scatchard (8-10) equation, which is valid for dilute solutions:

$$\log k = \log k_{\kappa=0}^{\infty} - \frac{z_A z_B e^2 N_A}{2.303 \cdot 4\pi\epsilon_0 \epsilon R T} \cdot \frac{1}{r_A + r_B} + \frac{z_A z_B e^2 N_A}{2.303 \cdot 4\pi\epsilon_0 \epsilon R T} \cdot \Omega \quad (9)$$

where $\Omega = \kappa / (1 + \kappa a_i)$; κ is the Debye kappa and is proportional to $I^{1/2}$; and a_i is a qualitative measure for ionic interaction, which accounts to a large extent for solvation effects. For small values of I the term κa_i becomes negligible. $k_{\kappa=0}^{\infty}$ is the molar rate constant extrapolated to a medium of infinite dielectric constant and all electrostatic effects (Coulombic forces) are considered to vanish. κ under these conditions represents a reference state. $r_A + r_B$ is the distance between the centers of the reacting ions A and B , approaching each other when forming the activated complex in the transition state.

The second term on the right side of eq 9 expresses the dependence of the rate constant on the dielectric constant ϵ of the reaction media. Accordingly, as ϵ increases, the rate constant increases for reactant ions of the same charge signs and decreases for ions of different charge signs. However, as it is shown by eq 9, the overall variation of k depends also on the contribution of the last term in this equation, and therefore on the ionic strength (Brønsted primary salt effect). This term basically accounts for the ionic interaction and predicts an increase of the rate constant k with $I^{1/2}$ when the reactants A and B have the same charges, and a decrease of k with $I^{1/2}$ if A and B have opposite signs. For instance, the increase of the ionic strength due to the solvent reduces the effective rate constant because the ions are shielded from each other to a larger extent. The last term in eq 9 represents the contribution to the rate constant arising from the reduction of repulsive forces between the reacting ions as the result of the presence of an ionic atmosphere around each reactant ion.

With $r = r_A + r_B$ and $\kappa = [(2e^2 N_A^2 I) / (1000 \epsilon_0 \epsilon R T)]^{1/2}$ one obtains

$$\log k = \log k_{\kappa=0}^{\infty} - \frac{z_A z_B e^2 N_A}{2.303 \cdot R T} \times \left[\frac{1}{4\pi\epsilon_0 \epsilon r} - \frac{2 N_A e}{(4\pi\epsilon_0 \epsilon)^{3/2}} \cdot \left(\frac{2 I \pi}{1000 R T} \right)^{1/2} \right] \quad (10)$$

Experimental Procedure

Synthesis

N,N-Dimethylaminophenolphthalein (**1**) was prepared in a two-step reaction according to a modified synthesis has been described in the literature (11-13) and as demonstrated in Figure 2.

Preparation of 2-[4-Dimethylaminophenyl]-benzoic acid (**4**)

Eighty-four grams (0.63 mol) of AlCl_3 was added portionwise under magnetic stirring to a mixture of 44.4 g (0.3 mol) of phthalic anhydride and 38 mL (0.3 mol) of dimethylaniline dissolved in 160 mL of dichloromethane. Dichloromethane was preferable to CS_2 because of the toxicity of CS_2 , even if CH_2Cl_2 caused some problems in the separation of **4**. Because of the expected vigorous exothermic reaction, the temperature of the mixture was maintained at about 35°C by using ice bath. After the addition was complete (ca. 1 h) the ice bath was removed and the mixture stirred under reflux for about 3 h. The mixture was then cooled to room temperature and poured slowly onto 250 g of crushed ice. The organic layer was removed and the strong acidic aqueous layer was treated with a solution of NaHCO_3 and extracted with CH_2Cl_2 several times. When $\text{pH} = 3$ was reached a heavy white precipitate of $\text{Al}(\text{OH})_3$ was formed, which made the phase separation very difficult. The extracts were combined, washed once with water, and dried over anhydrous Na_2SO_4 . Removal of the solvent left a black toffee-like gum. The residue was then redissolved in 50 mL of hot methanol, the precipitate (aluminum hydroxide) was removed by filtration, and the filtrate was treated with about 20 mL of water, affording dark-green crystals. This crude solid was then dissolved in 50 mL of ethyl acetate. Treatment of the resulting greenish solution with charcoal, filtration, and concentration yielded 19.5 g (20%) of **4** as yellow crystals; mp $200\text{--}201^\circ\text{C}$.

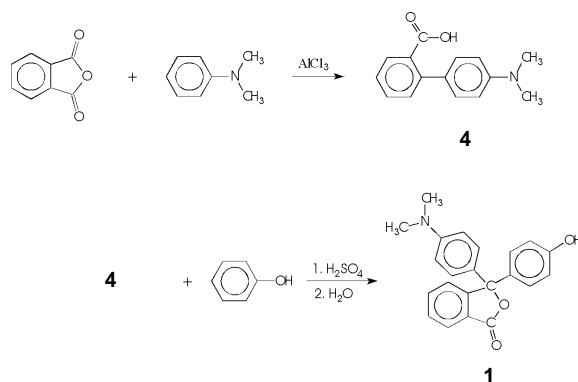


Figure 2. Synthesis of *N,N*-dimethylaminophenolphthalein.

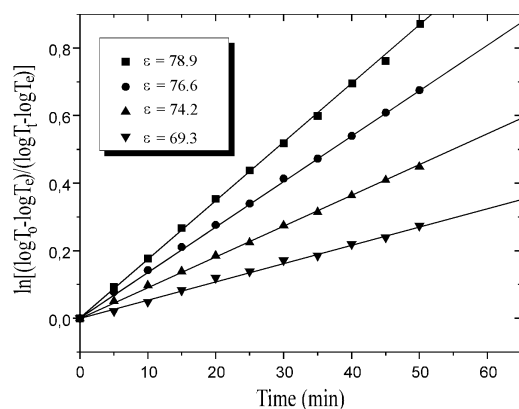


Figure 3. Relative transmittance vs. time, each at constant $[\text{OH}^-] = 0.01 \text{ M}$. In all graphs, the points are data, and each line is drawn using least-squares analysis.

Preparation of *N,N*-Dimethylaminophenolphthalein (**1**)

To a vigorously stirred dark yellow solution of 7.3 g (27.1 mmol) of powdered 2-[4-dimethylaminophenyl]-benzoic acid in 110 mL of 90% sulfuric acid was added 2.6 g of phenol. The reaction mixture was allowed to stir overnight at room temperature. The orange mixture was then poured on 300 g of crushed ice and filtered, and the toffee-like gum residue was transferred into a diluted solution of NaOH (10%). The color of the suspension turned to violet. After filtration the filtrate was neutralized by dropwise addition of a diluted solution of hydrochloric acid. A grey-white precipitate was formed. Removal of the precipitate by filtration and further treatment of the filtrate with diluted hydrochloric acid led to formation of a brown precipitate. This operation was repeated several times until no more precipitate formed. The combined precipitates were dried in a desiccator over CaCl_2 . The crude product, 7.4 g (79%) of **1**, showed no definite melting point, but sintered and turned brown (decomposition) on heating. Many attempts to purify

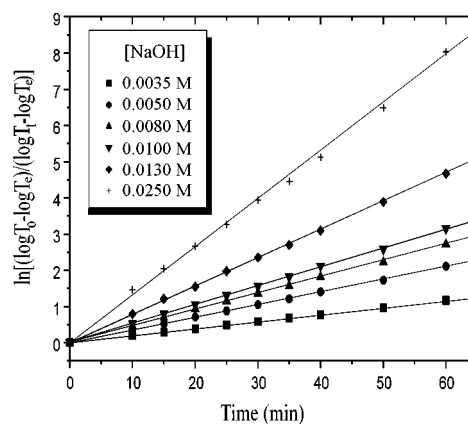


Figure 4. Relative transmittance vs. time, each at constant $[\text{OH}^-]$. In all graphs, the points are data, and each line is drawn using least-squares analysis.

the sample by recrystallization failed. Finally, purification by column chromatography on silica gel column B Si60 afforded the pure product. For this purpose 1 g of the crude product was dissolved in 10 mL of a mixture of ethyl acetate–alcohol–water (5:5:1), filtered, and added into the column portionwise (1 mL). The flow rate was 33 mL/10 min under reduced pressure. The chromatographic purification provided the pure amorphous product **1**, which started to decompose at about 250 °C.

Electrolyte Solutions and Equipment

The stock solution for the fading runs consisted of a 34.54 mg of DMAPP in 100 mL of 50% aqueous ethanol solution. For the regeneration reactions, 34.54 mg of DMAPP was dissolved in 100 mL of 0.2 M NaOH. It was used after standing for at least one hour but not more than eight hours. Two Metrohm single-beam colorimeters Type E 1009 were used to measure the transmittance of the colored solutions. We would like to emphasize that the accuracy of the results depends on the quality of the spectrometer used

Table 1. Dependence of k_1 , k_2 , and K_c on Ionic Strength, I^a

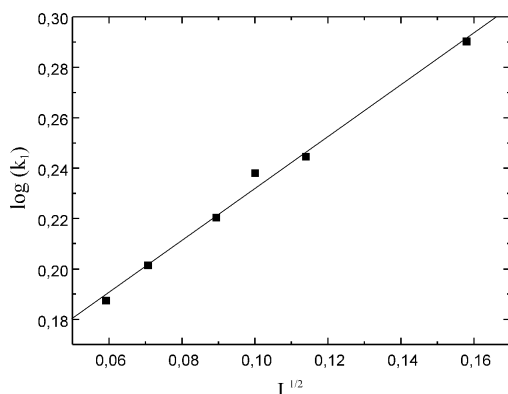
Sol.	$[\text{OH}^-]$ (M)	$I^{1/2} \cdot 10^{-2}$ (M)	$(k_1 + k_2) \cdot 10^{-2}$ [1/(M · min)]	K_c (1/M)	k_1 [1/(M · min)]	$k_2 \cdot 10^{-3}$ (1/min)	T_0	T_e
1	0.0035	5.92	0.756	710.457	1.540	2.168	0.192	0.623
2	0.0050	7.07	0.999	777.555	1.590	2.295	0.231	0.741
3	0.0080	8.94	1.540	788.918	1.661	2.106	0.245	0.825
4	0.0100	10.0	1.939	828.167	1.730	2.089	0.252	0.862
5	0.0130	11.4	2.508	780.089	1.756	2.251	0.217	0.872
6	0.0250	15.8	5.111	836.539	1.951	2.332	0.270	0.942

^a[*N,N*-Dimethylaminophenolphthalein] = $5 \times 10^{-5} \text{ M}$.

Table 2. Dependence of k_1 on Dielectric Constant, ϵ^a

Sol.	EtOH (vol. %)	EtOH (wt. %)	ϵ at 21 °C	k_1 [1/(M · min)]	$\log k_1$	$\frac{\sqrt{4\pi\epsilon_0\epsilon} - 2N_A e r \sqrt{\frac{2I\pi}{1000RT}}}{(4\pi\epsilon_0\epsilon)^{3/2} \cdot r} \cdot 10^{-17}$
7	2.5	2	78.86	2.398	0.380	2.849
8	7.5	6	76.56	1.812	0.258	2.934
9	12.5	10.083	74.22	0.812	-0.090	3.027
10	22.5	18.167	69.33	0.331	-0.480	3.240

^a[*N,N*-Dimethylaminophenolphthalein] = $5 \times 10^{-5} \text{ M}$; $[\text{NaOH}] = 0.01 \text{ M}$.

Figure 5. Plot of $\log k_1$ vs. $I^{1/2}$.

to perform the experiment. Therefore, a better spectrometer than that we used would give more accurate results. Each spectrometer was connected to an x/y -plotter and the paper feed was 300 mm/h. We used thermostable cuvettes with a path length of 20 mm.

Procedure

In a typical color-fading experiment, 5 mL of *N,N*-dimethylaminophenolphthalein stock solution was diluted with double-distilled water to about 80 mL. Then a sodium hydroxide solution was added to give concentrations of 0.0035 to 0.025 M sodium hydroxide (Table 1). At this point the plotter was started. The solution was mixed rapidly, water was added to give 100 mL, and an absorption cell filled with solution for measurement of the transmittance spectrum. The remaining solution was placed in a thermostated box at 21 °C, and the transmittance (T_0) was measured the next day. T_0 was determined by extrapolation. In a further experiment we added solutions of sodium chloride as an extraneous salt, but the results in this case did not clearly show the expected salt effect.

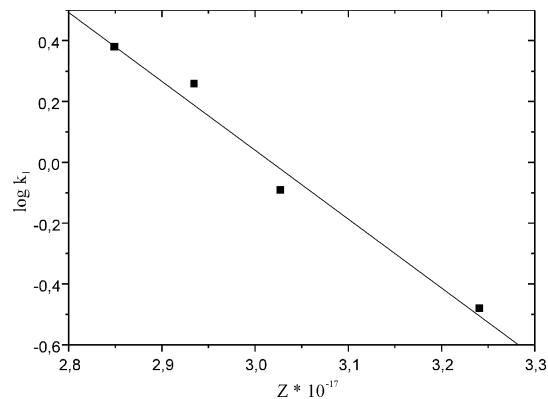
We also performed regeneration runs by diluting 5 mL of stock solution (1×10^{-5} M dye in 0.1 M NaOH) with dilute sodium hydroxide of such strength, that concentrations of 0.005 to 0.020 M were obtained.

To study the dependence of k_1 on the dielectric constant ϵ , the dielectric constant was varied by addition of appropriate amounts of ethanol and calculated (Table 2) according to the data published by Åkerlöf (14). The amount of ethanol in the stock solution was thereby taken into account. The results provided by varying the dielectric constant are shown in Figure 3.

The fading experiment described in this work can be modified. For example, only four or five concentrations of NaOH can be used instead of six. Furthermore, fewer runs to demonstrate the dependence of the rate constant on the dielectric constant can be applied. Another possibility to shorten the time needed for carrying out this experiment is to skip that part of the experiment related to the dependence of k_1 on the dielectric constant ϵ . In this case the experiment will take only about 4 hours.

Results

Some typical fading runs with various OH^- concentration are illustrated in Figure 4. The pseudo-first-order rate

Figure 6. Plot of $\log k_1$ vs. $Z = \frac{\sqrt{4\pi\epsilon_0\epsilon} - 2N_A e r \sqrt{\frac{2I\pi}{1000RT}}}{(4\pi\epsilon_0\epsilon)^{3/2} \cdot r}$.

constant $k'_1 + k_2$ for each NaOH concentration is determined from the slope of the corresponding graph. The values for k_1 and K_c derived from eqs 6 and 7 are summarized in Table 1. Figure 5 shows a plot of $\log k_1$ vs. $I^{1/2}$. The ionic strength is varied by increasing the concentration of sodium hydroxide. From the slope we obtain an experimental value for the Debye–Hückel constant A (eq 8) of $A = 0.516 \pm 0.22 \text{ kg}^{1/2} / \text{mol}^{1/2}$, which is in good agreement with the theoretical value of $A = 0.517 \text{ kg}^{1/2} / \text{mol}^{1/2}$.

Typical results of the fading reaction in water–ethanol mixtures possessing different dielectric constants are listed in Table 2 and shown in Figure 6. When $\log k_1$ is plotted vs.

$$\frac{\sqrt{4\pi\epsilon_0\epsilon} - 2N_A e r \sqrt{\frac{2I\pi}{1000RT}}}{(4\pi\epsilon_0\epsilon)^{3/2} \cdot r}$$

one obtains a straight line with the slope equal to $-2.26 \times 10^{-17} \pm 0.26 \times 10^{-17}$, demonstrating the lowering of the molar rate constant k_1 with diminishing dielectric constant ϵ of the solvent. It is worth noting that the values of the slopes obtained from the student's experiment were generally higher than the theoretically determined value of $-(e^2 N_A) / (2.303 RT) = 2.745 \times 10^{-18}$. This finding may be attributed to a probable reaction between the solvent and DMAPP or its intermediates.

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