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Basicity of Dimethyl Sulfoxide in an Aqueous Solution as Measured by the Spectrophotometric Indicator Method

Goro WADA

Department of Chemistry, Nara Women's University, Nara

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The basic nature of dimethyl sulfoxide (DMSO) has been known in water, and so has its pK_a value, which varies somewhat according to the measuring methods. In the present work, a spectrophotometric method employing thymol blue and *o*-nitroaniline as indicators was applied; the thermodynamical p$K_a{}^\circ$ value of DMSO was determined to be -1.04 at 25°C. Since there is no dependence of p$K_a{}^\circ$ upon the temperature, the proton transfer from water to DMSO in water is likely to be athermal.

The nature of dimethyl sulfoxide (DMSO) as a solvent for acid-base equilibria and for other chemical reactions has been well investigated, and the results have been well collected.[1,2] On the other hand, the quantitative basic strength of DMSO as a base itself in an aqueous solution was first found by potentiometric titration by Nylén[3] in 1941, who established that the p$K_a{}^\circ$ value of DMSO at 20°C was zero, where p$K_a{}^\circ$ was defined as the thermodynamical dissociation constant of the SH^+ acid, the protonated form of DMSO. Recently, Streuli[4] and Andersen *et al.*[5] determined the p$K_a{}^\circ$ value to be 1.0 and 0.911 respectively, by similar potentiometric titrations using perchloric acid as the titrant and acetic anhydride as the solvent. More recently, by measuring the chemical shifts of the methyl groups of DMSO as a function of the sulfuric acid concentration, Haake and Cook[6] determined the basicity of DMSO to be -2.7; this value shows a lower basicity than the values previously obtained.

The p$K_a{}^\circ$ values observed are thus widely scattered between -2.7 and $+1$. The present work was undertaken to estimate it by a method different from those previously adopted. A spectrophotometric method employing two acid-base indicators, thymol blue and *o*-nitroaniline, was applied; it gave -1.04 as p$K_a{}^\circ$ value, a value which lies nearly at the center between the two extreme values previously determined.

Experimental

Commercial DMSO was distilled twice under reduced pressure of oxygen-free nitrogen.[7] Anhydrous sodium perchlorate was prepared by recrystalizing a crude wet source from water and drying it to an anhydrous state at a temperature not higher than 300°C. The ionic strength of the solutions presently being investigated, μ, was controlled with this salt. The perchloric acid, thymol blue, and *o*-nitroaniline were used without further purification.

For the measurements of the optical densities of solutions, a Beckman spectrophotometer, Model DU, was used with a thermostated cell compartment and quartz cells with light paths of 1 cm and 10 cm.

Results with Thymol Blue

Ionization Constant and Molar Extinction Coefficients of Thymol Blue. The spectra of thymol blue (thymolsulfonephthalein) at various hydrogen ion concentrations in aqueous solutions are shown in Fig. 1. The figure indicates that the absorption peak at 544 mμ is due to the acid form of the indicator (represented by HIn), while the two absorption peaks at 433 and 335 mμ are due to the base form of the indicator (In^-). Another absorption of the acid form appearing with a peak at 395 mμ (shown by a broken line in Fig. 1) overlaps with the bottom part between the two absorption bands of the base form. Isosbestic points occur at 486 mμ and somewhere between 375 and 390 mμ.

Since the observed absorbance at 540 mμ can be approximately attributed only to the acid form of thymol blue, the molar extinction coefficient of

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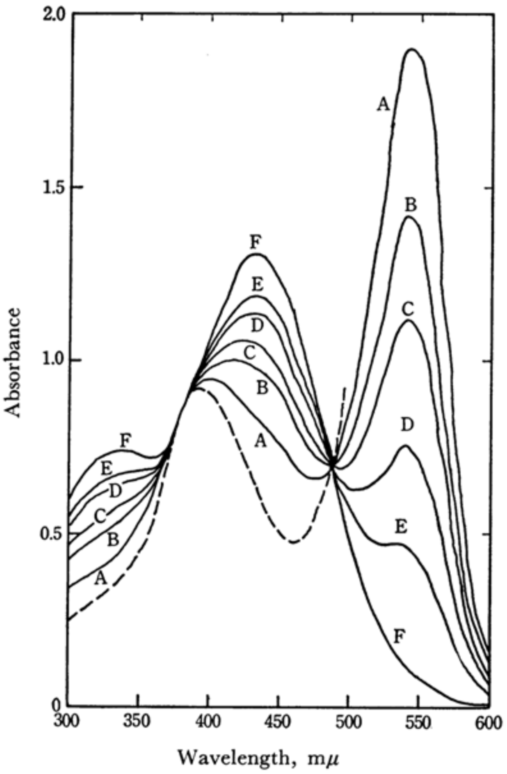

Fig. 1. Absorption spectra of thymol blue at various hydrogen ion concentrations, $[HIn]_0 = 1\times10^{-4}$ M.
A : $[H^+]=0.040$ M, B : 0.020 M, C : 0.013 M
D : 0.0067 M, E : 0.0033 M, F : 10^{-7} M
Broken line : acid from.

the acid form at 540 mμ, $\varepsilon_A{}^{540}$, can easily be estimated to be 3.13×10^4 $\text{M}^{-1}\text{cm}^{-1}$, by assuming that of the base form, $\varepsilon_B{}^{540}$, to be zero.

From the absorbances at 540 mμ at various hydrogen ion concentrations, the respective concentrations of HIn and In^- can be ascertained. Therefore, the ionization constant of the indicator, defined as $K_{HIn}=[H^+][In^-]/[HIn]$, at 25°C is calculated to be $(2.21\pm0.12)\times10^{-2}$ M.

At 540 mμ, $\varepsilon_A{}^{540}$ is so complicatedly affected by the addition of even a small amount of DMSO to the aqueous solution that this wavelength seems less suitable than 433 and 335 mμ for the present purpose of measuring the K_a of the protonated DMSO.

When the solution is neutral, thymol blue may be considered to be completely in the base form.[*1] This fact enables us easily to obtain the molar extinction coefficients of the base form, ε_B's. At some acid concentrations, on the other hand, the apparent absorbance of the solution, A, is the sum of those due to the two forms, as is expressed by:

$$A = \varepsilon_A[HIn] + \varepsilon_B[In^-] \tag{1}$$

when either 433 mμ or 335 mμ is employed for the measurement. With the help of the K_{HIn} value, the following data were obtained on the extinction coefficients:

$$\left.\begin{aligned}\varepsilon_A{}^{433} &= 6.11\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}\\ \varepsilon_A{}^{335} &= 2.71\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}\\ \varepsilon_B{}^{433} &= 1.31\times10^4\ \text{M}^{-1}\,\text{cm}^{-1}\\ \varepsilon_B{}^{335} &= 7.36\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}\end{aligned}\right\} \tag{2}$$

The ε_A's of thymol blue in an aqueous solution at both 433 and 335 mμ are indifferent to the presence of DMSO at concentrations as high as $[S]_0=0.6$ M within the limits of experimental error, while it was found that the absorption spectrum of the base form of thymol blue has a slight tendency to be lowered in the 350—480 mμ region and raised in that of 300—350 mμ with an increase in the concentration of DMSO at the rates expressed empirically as:

$$\left.\begin{aligned}\varepsilon_B{}^{433} &= (1.31-0.029[S]_0)\times10^4\ \text{M}^{-1}\,\text{cm}^{-1}\\ \varepsilon_B{}^{335} &= (7.36+0.114[S]_0)\times10^3\ \text{M}^{-1}\,\text{cm}^{-1}\end{aligned}\right\} \tag{3}$$

Calculation of K_a of Protonated DMSO. Since the total concentration of the indicator, $[HIn]_0$, is represented by:

$$[HIn]_0 = [HIn] + [In^-] \tag{4}$$

the following expression can be obtained by combination with Eq. (1):

$$A = \frac{\varepsilon_A[H^+]+\varepsilon_B K_{HIn}}{[H^+]+K_{HIn}}[HIn]_0 \tag{5}$$

When DMSO is added to water to make its total concentration $[S]_0$, with $[HIn]_0$ and $[HClO_4]_0$ kept constant, $[H^+]$ will decrease to $[H^+]'$ due to the protonation of DMSO and, at the same time, ε_B will vary according to Eq. (3). Consequently, A will also alter to A'. By putting the observed A' and calculated ε_B values into Eq. (5), the decrease in the hydrogen ion concentration can be obtained; it is equivalent to the concentration of the protonated DMSO, $[SH^+]$. Since $[S]=[S]_0-[SH^+]$, the value of K_a can easily be calculated. The change in the absorbance caused by the addition of DMSO, $A'-A$, was generally so small compared with A itself that differential spectrophotometry had better be adopted, taking a solution of the indicator in the absence of DMSO as the reference solution.

At comparatively high $[S]_0$ values, the activity of water in the system, a_{H_2O}, is no longer equal to unity but is, rather, reduced to an extent which is assumed to be approximately proportional to its mole fraction in the system. Such a consideration was taken into account in the course of the calculation of K_a.

The values of K_a calculated at various acid and DMSO concentrations at $\mu=0.55$ M and 25°C are listed in Table 1; they give an averaged value

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[*1] Since thymol blue is dibasic, "the base form" used here must be "the neutral form".

Table 1. K_a values at various acid and DMSO concentrations at $\mu=0.55$ M and 25°C by use of Thymol Blue as an indicator

$[HClO_4]_0$ M	λ mμ	$[S]_0$ M				
		0.3	0.4	0.5	0.6	0.7
0.06	433	4.3	4.5	3.7	4.8	4.5
	335	5.0	3.7	4.3	4.2	4.5
0.08	433	4.3	4.2	4.8	4.5	4.5
	335	4.8	4.5	4.8	4.8	4.5
0.10	433	4.8	4.2	5.6	4.2	4.3
	335	5.9	4.3	4.8	5.0	4.8
0.12	433	3.9	4.8	5.6	5.6	5.3
	335	4.3	4.8	4.5	5.0	4.5
0.14	433	3.9	4.8	4.3	3.7	4.8
	335	4.5	4.3	4.8	4.5	5.0
0.16	433	—	5.9	5.6	4.3	5.3
	335	5.9	4.5	4.8	4.5	4.0

Mean 4.7±0.5

Table 2. K_a values measured with Thymo Bllue at various temperatures at $[S]_0=0.3-0.7$ M, $[HClO_4]_0=0.06-0.12$ M and $\mu=0.55$ M

T, °C	K_a, M
15	4.5±0.6
25	4.7±0.5
35	4.5±0.6

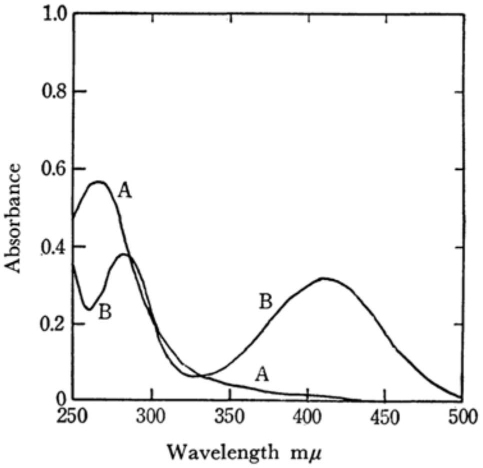

Fig. 2. Absorption spectra of *o*-nitroaniline at $[In]_0=1\times10^{-4}$ M.
A : acid form, B : base form

$K_a=4.7\pm0.5$ M. Table 2 summarizes the averaged K_a values measured in the same way as before at various temperatures; this table indicates that there is almost no variation in K_a with a change in the temperature.

Results with *o*-Nitroaniline

Ionization Constant and Molar Extinction Coefficients of *o*-Nitroaniline. The spectra of *o*-nitroaniline in both the acid and base forms are shown in Fig. 2. Only the base form exhibits a broad absorption band, with a peak at 410 mμ, while the acid form has a maximum absorption at 265 mμ in the ultraviolet region, where the base form has a considerable absorption, too.

Since molecular *o*-nitroaniline is a kind of base, the acid and base forms may be better represented by HIn^+ and In respectively. Then, the ionization constant of the indicator is defined as $K_{In}=[H^+][In]/[HIn^+]$. As to the mass and absorption balances with respect to the indicator, the following two equations are maintained:

$$[In]_0=[HIn^+]+[In] \tag{6}$$

$$A=\varepsilon[In]_0=\varepsilon_A[HIn^+]+\varepsilon_B[In] \tag{7}$$

where ε stands for the apparent molar extinction coefficient of the indicator. From these relations, ε is expressed as a function of $[H^+]$:

$$\frac{1}{\varepsilon-\varepsilon_A}=\frac{1}{\varepsilon_B-\varepsilon_A}\left(1+\frac{[H^+]}{K_{In}}\right) \tag{8}$$

If ε_A is negligibly small as compared with ε_B, Eq. (8) is reduced to:

$$\frac{1}{\varepsilon}=\frac{1}{\varepsilon_B}+\frac{[H^+]}{\varepsilon_B K_{In}} \tag{9}$$

This is clearly the case when 380, 410, or 440 mμ is employed for the measurement. The plots of $1/\varepsilon$ *versus* $[H^+]$ at $\mu=0.55$ M and 25°C yield good straight lines at the respective wavelengths, as is shown in Fig. 3, which reveal $\varepsilon_B^{440}=3.48\times10^3$, $\varepsilon_B^{410}=4.47\times10^3$, $\varepsilon_B^{380}=3.16\times10^3$ M^{-1} cm^{-1}, and $K_{In}=1.27$ M on the average. The latter value

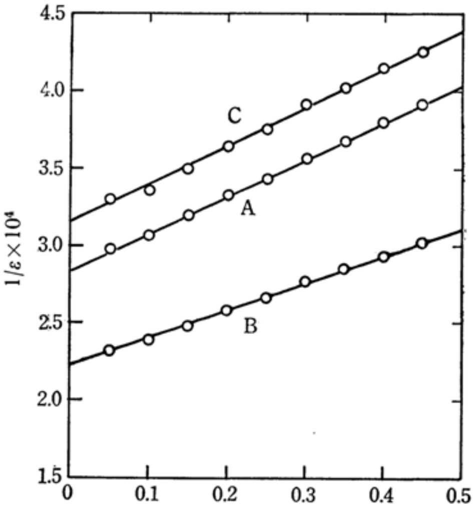

Fig. 3. Linearities of $1/\varepsilon$ of *o*-nitroaniline solution against $[H^+]$ at $\mu=0.55$ M, 25°C.
$[In]_0=1\times10^{-4}$ M, A: 440 mμ, B : 410 mμ, C : 380 mμ

agrees fairly well with the $K_{\mathrm{In}}=1.55$ M measured in very concentrated perchloric acid.[8]

In a way quite similar to the case of thymol blue, the ε_{B}'s of *o*-nitroaniline at 440 and 410 mμ were found to be affected by the addition of DMSO, thus:

$$\left.\begin{aligned}\varepsilon_{\mathrm{B}}{}^{440} &= (3.48+0.138[\mathrm{S}]_0)\times 10^3\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}\\ \varepsilon_{\mathrm{B}}{}^{410} &= (4.47+0.113[\mathrm{S}]_0)\times 10^3\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}\end{aligned}\right\} \quad (10)$$

although $\varepsilon_{\mathrm{B}}{}^{380}$ is almost independent of $[\mathrm{S}]_0$.

Calculation of K_a of Protonated DMSO. As in the case of thymol blue, a slight change in A, and, therefore, in ε, upon the addition of DMSO at constant $[\mathrm{HClO_4}]_0$ and $[\mathrm{In}]_0$ values, observed by means of the differential spectrophotometry, results from the changes in $[\mathrm{H^+}]$ and in ε_{B} (in the case of 440 or 410 mμ) according to Eq. (9). The decrease in $[\mathrm{H^+}]$ corresponds to the occurrence of $\mathrm{SH^+}$; this enables us to determine K_a. The calculated results of K_a are summarized in Table 3. The averaged value of K_a at $\mu=0.55$ M and 25°C is found to be 4.6 ± 0.5 M; this value is in good agreement with the results obtained with thymol blue.

TABLE 3. K_a VALUES AT VARIOUS ACID AND DMSO CONCENTRATIONS AT $\mu=0.55$ M AND 25°C BY USE OF *o*-NITROANILINE AS AN INDICATOR

$[\mathrm{HClO_4}]_0$ M	λ mμ	$[\mathrm{S}]_0$ M					
		0.2	0.3	0.4	0.5	0.6	0.7
0.3	440	—	4.5	4.8	5.0	5.0	4.8
	410	—	5.3	5.3	5.9	5.6	5.3
	380	—	4.5	4.3	5.3	4.8	4.3
0.4	440	4.8	4.2	4.0	4.5	4.3	4.3
	410	5.0	4.3	4.2	4.8	4.3	4.5
	380	4.8	4.0	3.7	4.0	3.9	3.9

Mean 4.6±0.5

Discussion

The averaged value of K_a as measured by both indicators is 4.7 ± 0.5 M; namely, $\mathrm{p}K_a=-0.67$ at $\mu=0.55$ M and 25°C. Through the approximate Debye-Hückel relation:

$$\mathrm{p}K_a{}^{\circ} = \mathrm{p}K_a - 0.5\sqrt{\mu} \qquad (11)$$

the thermodynamical basicity strength of DMSO is estimated to be $\mathrm{p}K_a{}^{\circ}=-1.04$. This $\mathrm{p}K_a{}^{\circ}$ value is less basic than the values found by the potentiometric titration[4,5] and more basic than that found by the chemical-shifts method.[6] As to the acidic nature, on the other hand, DMSO is an extremely weak acid which yields the $\mathrm{CH_3\text{-}SO\text{-}CH_2{}^-}$ anion, with a supposed acid dissociation constant of 10^{-31}.[2] In fact, the practical preparation of this anion (methylsulfinyl carbanion) is possible only under very severe conditions.[9]

The fact that the $\mathrm{p}K_a$ values of DMSO vary according to the alteration of the measuring methods, namely, about 1 by the potentiometric titration, −1 by the spectrophotometric method and −2.7 by the chemical shifts of the protons, indicates that there may be some variation in the extent of the association between a proton and a DMSO molecule in water. The method of the chemical shifts measures only the closest combination between them, while the electrochemical method finds more associated molecules of DMSO with protons, including those in looser combination. The spectrophotometry discriminates the protonated DMSO from the unprotonated by a way intermediate between the two other methods.

According to the values in Table 2, there is no dependence of K_a upon the temperature; therefore, the enthalpy change associated with the $\mathrm{S+H_3O^+ \rightleftharpoons SH^+ + H_2O}$ reaction seems to be zero. This means that the protonation energies of water and DMSO are nearly equal to each other in water.

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