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The Direct Effects of Alkali Metal and Alkaline Earth Metal Perchlorates on the Equilibria of Acid–Base Indicators (Sulfonephthaleins) in Acetonitrile Solution

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With the addition of alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates, the cause of the color changes of several sulfonephthaleins of various pK_a values, i.e., Thymol Blue, Phenol Red, Bromothymol Blue, and Bromocresol Green, in acetonitrile solutions were examined by means of spectrophotometry and ^{1}H NMR. Upon the addition of ≥ 0.1 mol dm^{-3} $LiClO_4$ to 1.0×10^{-4} mol dm^{-3} Phenol Red, the γ-sultone ring of the sulfonephthalein was cleaved to give absorption bands at around 410 and 500 nm. The band at 500 nm was assigned to the acid form, and that around 410 nm to a quinonoid structure (the intermediate form) which would be formed by deprotonation from the acid form. The effects of $NaClO_4$ were much smaller than those of $LiClO_4$. Magnesium and barium perchlorates caused larger effects than $LiClO_4$; however, a nonmetallic salt, Et_4NClO_4, caused almost no effects. In addition, a purple-red colored species (λ_{max} = 563 nm), a basic form, was also produced from Phenol Red by the addition of ≥ 0.2 mol dm^{-3} $Mg(ClO_4)_2$. Interestingly, the metal ions assisted not only the acid effects of CH_3SO_3H, but also the base effects of Et_3N or 1,1,3,3-tetramethylguanidine on Phenol Red or Bromothymol Blue in acetonitrile. ^{1}H NMR spectra of the sulfonephthaleins confirmed the opening of the γ-sultone rings in the presence of the metal salts. The ring cleavage upon the addition of the metal ions was considered from the standpoint of not "medium effects", but a direct chemical interaction between the metal ions and the sulfonate ion (function) in the sulfonephthaleins.

Acid–base indicators are utilized for neutralization titration in nonaqueous as well as aqueous solution.[1] The equilibria of acid–base reactions in aprotic solvents are rather complicated[2] because of their poor solvating abilities. Alkali metal and alkaline earth metal salts of lower concentrations are regarded as being "indifferent" salts in aqueous media. The effects of "indifferent" salts can be evaluated by the Debye–Hückel theory or the extended theories, principally based on the electrostatic interaction between ions. However, we have demonstrated that even alkali metal (M^+) and alkaline earth metal (M^{2+}) ions take part directly in chemical equilibria in nonaqueous solutions.[3,4] For instance, the salt effects on the indicator acidity (or Hammett acidity function) with 4-(dimethylamino)azobenzene in acetonitrile were elucidated by chemical interactions with M^+, M^{2+}, and halide ions.[4] Even concentrated salt effects on the solvolysis reaction rates of aliphatic halides and related compounds (RX) in H_2O mixed solvents were explained by the change in the solvent character and a "chemical" interaction between anions (X^- = Cl^-, Br^-, or TsO^-) and M^+ or M^{2+}.[5] The Raman spectra of D_2O containing highly concentrated Et_4NBr have given concrete evidence for the breakdown of the water structure by hydrogen bonding.[6]

In previous papers,[7,8] we reported on the formation of stable carbocations from trityl and 4-methoxy-substituted trityl halides (R_3CX) by the addition of alkali metal or alkaline earth metal perchlorates in acetonitrile of a higher permittivity (ε_r = ca. 36). Very recently, we obtained conclusive evidence of triple ion formation from lithium β-diketonates (4-acyl-5-pyrazolonates) in acetonitrile by means of conductometry and UV-visible and ^{1}H or ^{7}Li NMR spectroscopy.[9] Thus, it is likely that alkali metal and alkaline earth metal ions in poor solvating media have a chemical reactivity, just as transition metal ions have in aqueous solution.

In the present study, we attempted to demonstrate by means of spectrophotometry and ^{1}H NMR that alkali metal or alkaline earth metal ions can affect directly the equilibria of common acid–base indicators (sulfonephthaleins) in acetonitrile solution. Kolthoff et al.[10] have investigated the acid–base properties of sulfonephthalein indicators in acetonitrile. Electrochemical studies on sulfonephthaleins have been performed in aqueous solutions.[11] Sulfonephthalein dyes entrapped within polymer matrixes have been utilized for an optical sensor of moisture and ammonia gas in ambient air.[12]

Experimental

Commercially obtained acetonitrile (Wako, GR grade) was distilled from CaH_2. Phenol Red (Phenolsulfonephthalein, Wako GR grade), Thymol Blue (Wako, GR grade), Bromothymol Blue (Wako, GR grade), and Bromocresol Green (TCI, GR grade) were used without further purification. Tetrabutylammonium hydroxide (10% aqueous solution, Wako, GR grade) was used as received. Magnesium perchlorate from Wako (for elemental analysis) was carefully dried in vacuo at 200 °C over P_2O_5. Another $Mg(ClO_4)_2$ from Aldrich was used as received. Other chemicals were used as mentioned previously.[3,4,7] Deionized and distilled water was decarbonated.

UV-visible spectra were measured using a Hitachi double-beam spectrophotometer (Model U-2000) in 0.1 and 1.0 cm quartz cuvettes at ca. 25 °C. ^{1}H NMR measurements were carried out with a JEOL FT-NMR spectrometer (Model JNM-LA400) in 5 mm sample tubes at room temperature. Acetonitrile-d_3 (99.6 atom% D, containing 0.03% TMS) and CF_3SO_3D (98 atom% D) from Aldrich were used for the NMR measurements. The glassware was carefully dried at 120 °C in a dry-oven as well as by blowing nitrogen gas.

Results and Discussion

UV-visible Absorption Spectra. In an aqueous solution at 20 °C, Thymol Blue and Phenol Red have two distinct pK_a values of 1.65 and 9.20 and ca. 1.5 and 8.0, respectively, while only single pK_a values are reported for Bromothymol Blue (7.30) and Bromocresol Green (4.90).[13] The structures of the sulfonephthaleins are shown in Chart 1. The color change intervals of Phenol Red are pH < 1.5 (orange-red); 1.5 < pH < 7.9 (yellow); and 7.9 < pH (purple-red). In acetonitrile, however, the pK_a values of these indicators shift by much larger values than in H_2O, roughly speaking, $\Delta pK_a \approx +10$.[10,14] Note that the basicities of the amines also increase much in acetonitrile, $\Delta pK_{BH^+} \approx +10$.[14]

First of all, we would like to discuss the effects of Brønsted acids and bases on Phenol Red in acetonitrile. In dried acetonitrile, Phenol Red exists as the colorless γ-sultone form, accompanied by a small amount of the yellow form (cf. Scheme 1). The addition of a strong base, 1,1,3,3-tetramethylguanidine (TMG, cf. Chart 1) of ≥ 0.1 mol dm^{-3}, in acetonitrile caused the maximum absorbance of 6.78 (for 1.0 cm path-length, converted from 0.1 cm) at $\lambda_{max} = 578$ nm: the basic form (cf. Scheme 1). However, only the yellow color and no purple-red color was observed upon the addition of 1.0×10^{-4}—1.0 mol dm^{-3} triethylamine (Et_3N, a weaker base than 1,1,3,3-TMG) to the Phenol Red solution, cf. Table 1.

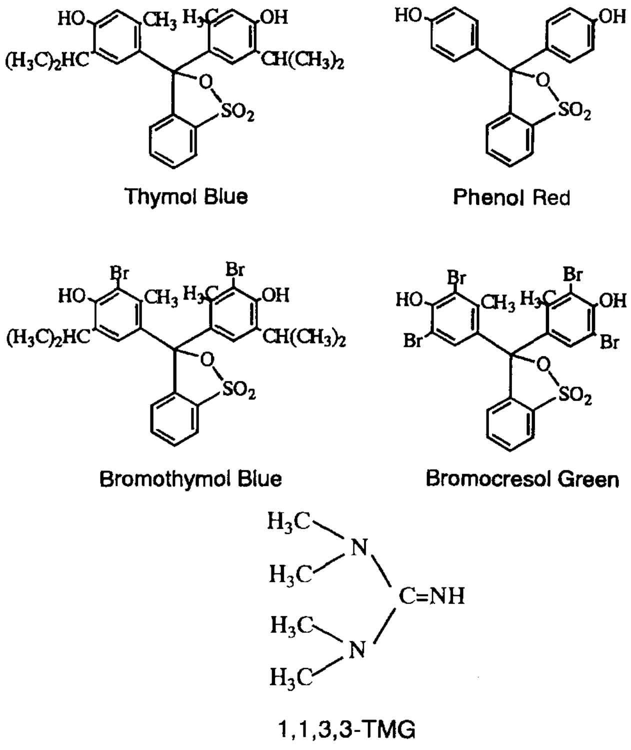
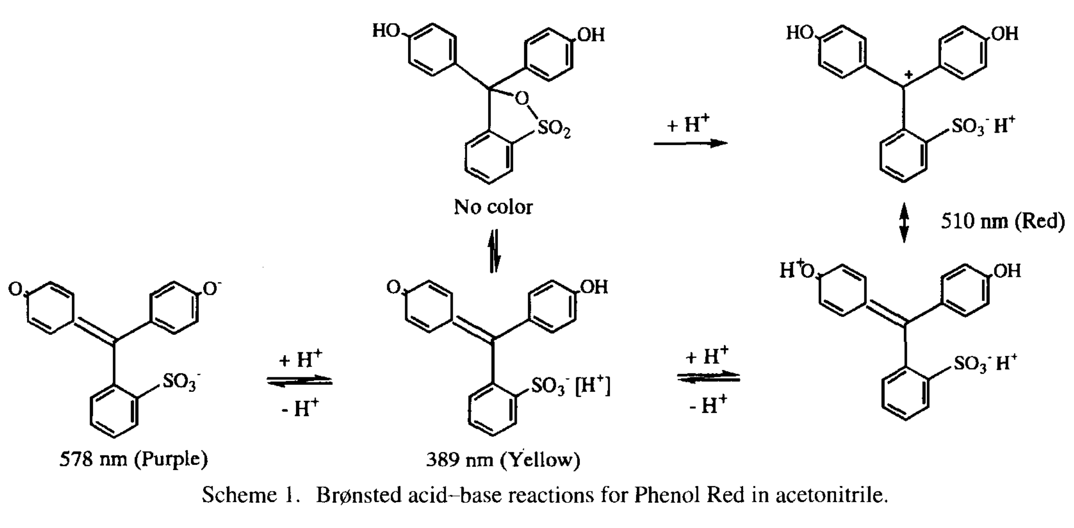


Chart 1.

Also, a 1.0×10^{-4} mol dm^{-3} Thymol Blue solution showed interesting changes in the absorption spectra with increasing concentration (5.0×10^{-5}—0.1 mol dm^{-3}) of 1,1,3,3-TMG: at 1.0×10^{-4} mol dm^{-3}, the absorbance of the peak at 391 nm reached the maximum value of 1.63 ($\varepsilon = 1.6\times10^4$ at 391 nm, cf. Ref. 10: $\varepsilon = 1.65\times10^4$ at 395 nm), and the peak showed bathochromic effects, giving isosbestic points at 341 and 410 nm. A new peak at 614 nm, due to the basic form, was clearly observed for $\geq 1.0\times10^{-2}$ mol dm^{-3} 1,1,3,3-TMG. Phenol Red gave similar absorption changes with the addition of 1,1,3,3-TMG. Thus, the sulfonephthaleins gave the most intense yellow color of the quinonoid structure (the intermediate form) upon the addition of an equivalent amount of an appropriate base (B) as

$$HO\text{–}R\text{–}OH + B \rightleftharpoons O{=}R(\text{–}SO_3^-)\text{–}OH + BH^+. \quad (1)$$

Upon the addition of an acid, CH_3SO_3H, of $(0.1—1.0)\times10^{-3}$ mol dm^{-3}, the pale-yellow color of Phenol Red in acetonitrile disappeared completely (Table 1).



Scheme 1. Brønsted acid–base reactions for Phenol Red in acetonitrile.

Table 1. UV-visible Absorption Data of 1.0×10^{-4} mol dm^{-3} Thymol Blue and Phenol Red in the presence of Various Acids, Bases, and Salts in Acetonitrile at ca. 25 °C

Brønsted acids and bases or salts	Concn mol dm^{-3}	λ_{max} nm (Abs.)[a]	ε cm^{-1} mol^{-1} dm^3
	[Thymol Blue] = 1.0×10^{-4} mol dm^{-3}		
None		391 (0.10), 534 (0.03)	
CH_3SO_3H	0.10	387 (0.24),[b] 547 (0.85)[b]	
	1.0	385 (1.17),[b] 551 (4.19)[b]	
CF_3SO_3H	1.0×10^{-4}	539 (0.05)	
	1.0×10^{-3}	384 (0.73),[c] 553 (2.83)[c]	
	1.0×10^{-2}	384 (1.25),[c] 554 (4.73)[c]	
	0.10	384 (1.41),[c] 554 (5.04)[c]	5.0×10^4 at 554 nm
1,1,3,3-TMG[d]	1.0×10^{-4}	391 (1.63)	1.6×10^4 at 391 nm
	1.0×10^{-3}	392 (1.61), 613 (0.03)	
	1.0×10^{-2}	396 (1.50), 614 (0.22)	
	0.10	405 (1.40), 614 (0.49)	
[n-Bu_4N]OH	0.8×10^{-3}	384 (0.82),[c] 614 (5.17)[c]	5.2×10^4 at 614 nm
	1.6×10^{-3}	380 (0.82),[c] 612 (5.02)[c]	
$LiClO_4$	1.0	421 (1.21), 541 (1.50)	
$NaClO_4$	1.0	405 (1.42), 540 (0.41)	
$Mg(ClO_4)_2$	1.0×10^{-2}	399 (0.74), 541 (1.03)	
	0.10	468 (1.98)[e]	
	0.20	468 (2.19)[e]	
$Ba(ClO_4)_2$	0.10	409 (0.89), 542 (1.15)	
Et_4NClO_4	1.0	394 (0.15), 536 (0.09)	
	[Phenol Red] = 1.0×10^{-4} mol dm^{-3}		
None		388 (0.29)	
H_2O	(1.0 vol%)	390 (0.26)	
	(5.0 vol%)	396 (0.32), 502 (0.11)	
	(10.0 vol%)	405 (0.88), 502 (0.20)	
	(20.0 vol%)	419 (1.63)	
	(50.0 vol%)	427 (2.02)	
CH_3SO_3H	$(0.1-1.0)\times10^{-3}$	No absorbance for > 300 nm[f]	
	1.0×10^{-2}	498 (0.01)[b]	
	0.1	504 (0.06)[b]	
CF_3SO_3H	1.0×10^{-4}	509 (0.06)	
	1.0×10^{-3}	373 (0.10), 510 (0.97)	
	1.0×10^{-2}	371 (0.75),[c] 510 (6.38)[c]	
	≥ 0.1	370 (0.96),[c] 510 (8.15)[c]	8.2×10^4 at 510 nm
Et_3N	$(0.1-1.0)\times10^{-3}$	390 (1.92)	
	≥ 0.1	390 (1.90)	1.9×10^4 at 390 nm
1,1,3,3-TMG[d]	1.0×10^{-4}	397 (1.70)	
	1.0×10^{-3}	376 (1.23), 577 (2.01)	
	≥ 0.1	366 (0.79), 578 (6.78)	6.8×10^4 at 578 nm
$LiClO_4$	1.0	426 (1.24), 501 (1.18)	
$NaClO_4$	1.0	399 (0.49), 499 (0.16)	
$Mg(ClO_4)_2$	1.0×10^{-2}	448 (0.69)[e]	
	0.10	458 (2.42)[e]	
	1.0	457 (2.26),[e] 563 (0.54)	
$Ba(ClO_4)_2$	1.0	425 (1.50), 503 (1.85)	
Et_4NClO_4	1.0	390 (0.30)	

a) Absorbance with path-length, l = 1.0 cm. b) Corrected values from turbidity. c) Converted from the absorbance with l = 0.1 cm. d) 1,1,3,3-Tetramethylguanidine. e) A combined peak (cf. the text). f) See the test.

With a stronger acid, CF_3SO_3H, of 0.1—1.0 mol dm^{-3}, the absorbance of the peak at 510 nm reached a constant value of 8.15; the molar absorbance was evaluated to be ε = ca. 8.2×10^4 at λ_{max} = 510 nm. The complicated phenomena for Phenol Red in acetonitrile upon the addition of acids can be explained as follows: The initial yellow color of the acetonitrile solution must be caused by the quinonoid form of the sulfonephthalein, which may be formed by the presence of residual H_2O (as a base) in the acetonitrile and/or by the polarity of the solvent, itself. The quinonoid form can be taken back to the colorless γ-sultone form by a small amount of a weaker acid. A further addition of a stronger acid caused a cleavage of the γ-sultone ring of the sulfonephthalein in acetonitrile. Safrik and Stransky[15] have described that, in nonaqueous aprotic solvents, the color changes of Thymol Blue are complicated by the formation of colorless sulfones (as it also occur with other sulfonephthaleins). The above-mentioned acid–base behavior of Phenol Red in acetonitrile can be summarized by Scheme 1. The present scheme is basically consistent with the proposal by Kolthoff et al.[10]

Incidentally, the addition of 5.0 vol% H_2O to acetonitrile caused distinct absorption bands at around 400 and 500 nm for 1.0×10^{-4} mol dm^{-3} Phenol Red. The peak absorbance of 500 nm reached its maximum value at a 10 vol% H_2O content, but the peak disappeared at 20 vol% H_2O. The peak absorbance at 400—427 nm increased with increasing content of H_2O in acetonitrile.

Figure 1 shows the UV-visible absorption spectra of 1.0×10^{-4} mol dm^{-3} Phenol Red in the presence of various concentrations of $LiClO_4$ in dried acetonitrile. The pale-yellow color of the solution turned to a strong orange-red color with increasing concentration of $LiClO_4$; the peak around 410 nm showed bathochromic effects, while the wavelength of the peak at 500 nm remained rather constant. The variation in the peak heights with $LiClO_4$ suggested that the two absorption bands of yellow and red colors were caused by two different species in the solution. Sodium perchlorate gave much smaller effects on the absorption spectra of Phenol Red (cf. Fig. 2). Even at as low as 1.0×10^{-2} mol dm^{-3} $Mg(ClO_4)_2$, the peak at 390 nm of 1.0×10^{-4} mol dm^{-3} Phenol Red developed a band at 448 nm (Fig. 3). The peak around 450 nm increased with the further addition of $Mg(ClO_4)_2$. In the presence of ≥ 0.2 mol dm^{-3} $Mg(ClO_4)_2$, however, a new peak appeared at 560 nm. The effects of $Ba(ClO_4)_2$ on the absorption spectra of Phenol Red were "normal", and were larger than those of $LiClO_4$.

Here, we would like to mention that the color changes occurred immediately upon the mixing of Phenol Red and the metal ion solutions, and no spectrum changes are observed for at least several hours. A nonmetallic salt, Et_4NClO_4, of 0.1—1.0 mol dm^{-3} caused almost no change in the absorption spectrum of Phenol Red. Judging from the color changes, the γ-sultone ring of Phenol Red in acetonitrile seems to be cleaved by the addition of the metal perchlorates.

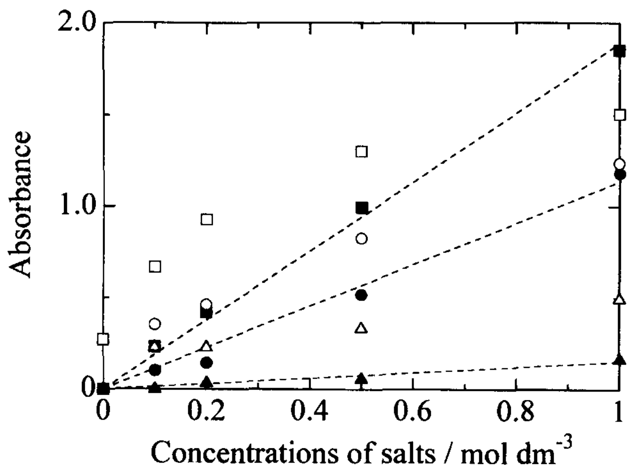


Fig. 2. The absorbances at ca. 420 and 500 nm of 1.0×10^{-4} mol dm^{-3} Phenol Red in the presence of $MClO_4$ or $M(ClO_4)_2$ in acetonitrile: (○) $LiClO_4$; (△) $NaClO_4$; (□) $Ba(ClO_4)_2$. The open symbols show absorbances at ca. 420 nm and the solid symbols at around 500 nm.

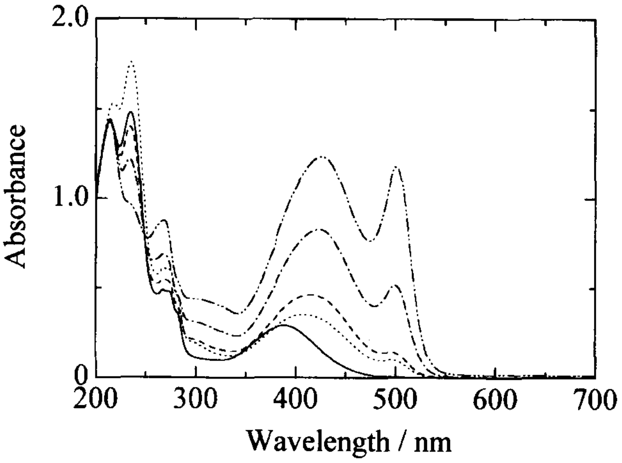


Fig. 1. Changes in UV-visible absorption spectra of 1.0×10^{-4} mol dm^{-3} Phenol Red with increasing concentration of $LiClO_4$ in acetonitrile: (—) 0; (····) 0.1; (- - -) 0.2; (– · –) 0.5; (– ·· –) 1.0 mol dm^{-3} of $LiClO_4$.

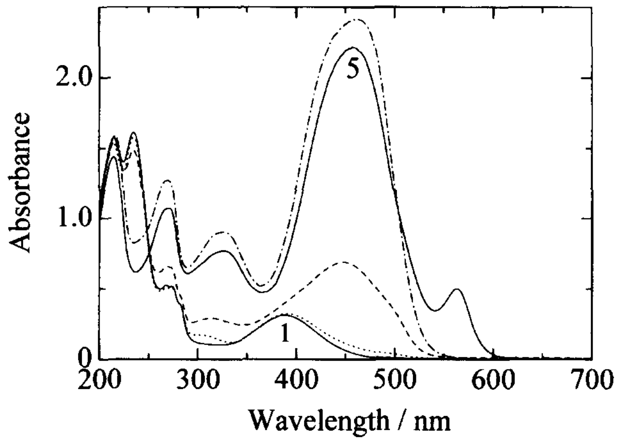


Fig. 3. Changes in UV-visible absorption spectra of 1.0×10^{-4} mol dm^{-3} Phenol Red with increasing concentration of $Mg(ClO_4)_2$ in acetonitrile: (1—) 0; (····) 1.0×10^{-3}; (- - -) 1.0×10^{-2}; (– · –) 0.1; (5—) 1.0 mol dm^{-3} of $Mg(ClO_4)_2$.

The effects of metal ions differ from each other, depending upon their ionic potentials or coordination abilities. Thymol Blue was examined in a similar way; a strong base, [*n*-Bu_4N]OH, was needed for the indicator to attain complete dissociation in acetonitrile (cf. Table 1) because of its larger pK_a value of 9.20 (in H_2O). The metal salt effects on Thymol Blue were, in general, greater than on Phenol Red.

The salt effects on Bromothymol Blue or Bromocresol Green were somewhat different from those on Thymol Blue or Phenol Red. In a Bromothymol Blue solution, $LiClO_4$ gave a strong yellow color; however, the red colored species, which was given by Thymol Blue or Phenol Red, was not observed. It must be very difficult for Bromothymol Blue to produce the red-colored species in the presence of the salts, probably because the first pK_a value of the indicator would be very small, $pK_a \approx 0$, if estimated from the pK_a values of Thymol Blue (1.65 and 9.20). Bromocresol Green of the estimated first $pK_a < -2.5$ also gave no red colored species in the presence of the metal ions. Surprisingly, the addition of higher concentrations of $Mg(ClO_4)_2$ to Bromothymol Blue caused a blue color solution ($\lambda_{max} = 621$ nm), while only a small peak at 563 nm (purple-red) for Phenol Red was observed, as shown in Fig. 3, and no blue or purple-like band for Thymol Blue. The addition of 1.0 mol dm^{-3} $Ca(ClO_4)_2$, $Sr(ClO_4)_2$, or $Ba(ClO_4)_2$ to $(0.4—5.0)\times10^{-4}$ mol dm^{-3} Bromothymol Blue gave no blue species. A strong blue band ($\lambda_{max} = 619$ nm) was also given by Bromocresol Green in the presence of a large amount of $Mg(ClO_4)_2$. The effects of water, acids, bases, and salts on Bromothymol Blue and Bromocresol Green are listed in Table 2.

Referring to the effects of Brønsted acids and bases on the sulfonephthaleins, we can explain the color changes of Phenol Red upon the addition of alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates, as shown in Scheme 2. The formation of a zwitterion ($R^+–SO_3^-$) from Phenol Red must be the cause of the red color of the solution. The cleavage of the γ-sultone ring takes place through an interaction between M^+ or M^{2+} and a sulfonate ion (function) from the sulfonephthalein. A strong interaction between nLi^+ (n = 1 and 2) and the $PhSO_3^-$ ion in acetonitrile has already been reported.[16] The red-colored species can be converted into yellow-colored species when a proton is taken out from the zwitterion. In the case of Bromothymol Blue or Bromocresol Green, no red colored species remains in the solution at all, because the deprotonation proceeds completely by itself. The neighboring bromine atoms on the aryl groups in Bromothymol Blue or Bromocresol Green should promote the deprotonation from $HO–R^+–SO_3^-$ or $H^+O{=}R–SO_3^-$.

The apparent salt effects increased as Phenol Red < ThymolBlue < BromothymolBlue < Bromocresol Green. As described above, the acidities of the sulfonephthaleins increase as Thymol Blue < Phenol Red < BromothymolBlue < Bromocresol Green. The stability of the carbocations (or zwitterions) as well as the Brønsted acidity of indicator compounds seem to be involved in the apparent salt effects. The substituents on phenyl groups in Thymol Blue should cause the superior stability of the carbocation from Thymol Blue to that from (non-substituted) Phenol Red.

Figure 4 shows the effects of $LiClO_4$ on a 1.0×10^{-4} mol dm^{-3} Phenol Red solution in the presence of 1.0×10^{-3}

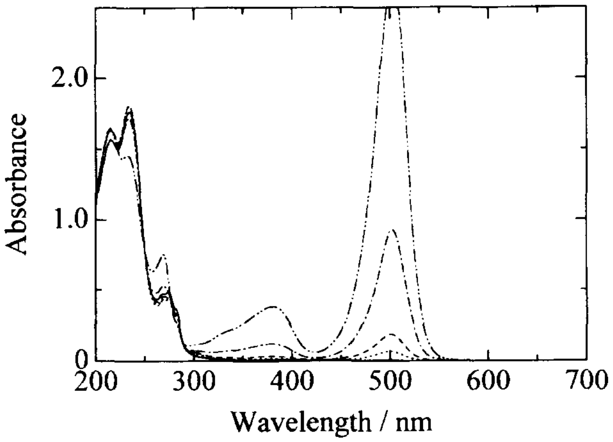
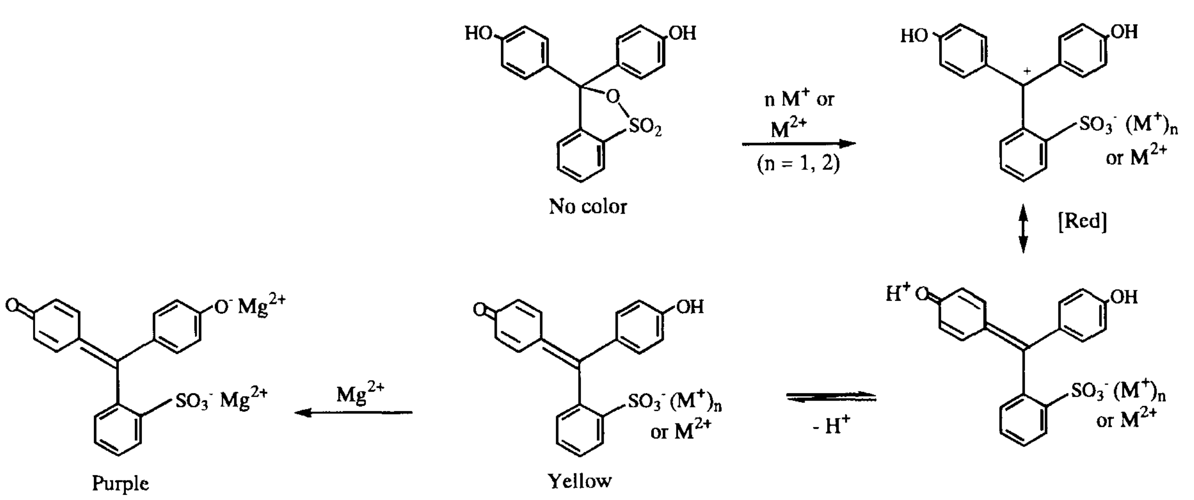


Fig. 4. Effects of $LiClO_4$ on the absorption spectra of 1.0×10^{-4} mol dm^{-3} Phenol Red in the presence of 1.0×10^{-3} mol dm^{-3} CH_3SO_3H in acetonitrile: (—) 0; (····) 0.1; (- - -) 0.2; (– · –) 0.5; (– ·· –) 1.0 mol dm^{-3} $LiClO_4$.



Scheme 2. A proposed reaction scheme of Phenol Red in the presence of M^+ or M^{2+}.

Table 2. UV-visible Absorption Data of 1.0×10^{-4} mol dm^{-3} Bromothymol Blue and Bromocresol Green in the Presence of Various Acids, Bases, and Salts in Acetonitrile

Brønsted acids and bases or salts	Concn mol dm^{-3}	λ_{max} nm (Abs.)[a]	ε cm^{-1} mol^{-1} dm^3
	[Bromothymol Blue]=1.0×10^{-4} mol dm^{-3}		
None		399 (0.25)	
CH_3SO_3H	0.1×10^{-4}—0.1	No absorption for > 300 nm	
	1.0	409 (0.10), 561 (0.33)	
	2.0	410 (0.38), 563 (1.30)	
	5.0	411 (1.39),[b] 563 (4.53)[b]	—[f] at 563 nm
Et_3N	1.0×10^{-4}	400 (1.95)	1.95×10^4 at 400 nm
1,1,3,3-TMG[c]	1.0×10^{-4}	398 (1.42), 632 (2.66)	
	1.0×10^{-2}	395 (0.95),[b] 631 (6.18)[b]	6.2×10^4 at 631 nm
	0.10	395 (0.89),[b] 631 (5.91)[b]	
$LiClO_4$	0.10	406 (0.91)	
	1.0	426 (1.57)	
$Mg(ClO_4)_2$	0.50	404 (1.41),[b] 621 (2.75)[b]	
	1.0	402 (1.37),[b] 621 (4.26)[b]	
$Ba(ClO_4)_2$	0.50	436 (1.81)	
	1.0	444 (2.00)	
Et_4NClO_4	0.10	400 (0.32)	
	1.0	403 (0.56)	
	[Bromocresol Green]=1.0×10^{-4} mol dm^{-3}		
None		407 (0.28)	
CH_3SO_3H	1.0×10^{-4}—0.1[d]	No absorption for > 300 nm	
CF_3SO_3H	1.0×10^{-4}—1.0×10^{-2}	No absorption for > 300 nm	
	0.10	421 (0.04), 566 (0.12)	
	0.50	423 (0.45), 568 (1.33)	
	1.0	425 (1.25),[e] 568 (2.15)	—[f] at 568 nm
Et_3N	0.5×10^{-4}	407 (1.32),[b]	
	1.0×10^{-4}	407 (2.11),[b]	2.1×10^4 at 407 nm
	2.0×10^{-4}	400 (1.45),[b] 623 (2.75)[b]	
	1.0×10^{-3}	393 (0.97),[b] 623 (4.82)[b]	
	1.0×10^{-2}	392 (0.90),[b] 623 (5.09)[b]	—[f] at 623 nm
$LiClO_4$	0.10	413 (1.47)	
	1.0	419 (1.82)	
$NaClO_4$	0.10	409 (0.92)	
	1.0	416 (1.91)	
$Mg(ClO_4)_2$	0.10	412 (1.88)	
	1.0	400 (1.14),[b] 619 (5.92)[b]	
$Ba(ClO_4)_2$	0.10	414 (1.58)	
	1.0	428 (1.80)	
Et_4NClO_4	0.10	410 (0.54)	
	1.0	411 (0.94)	
[*n*-Bu_4N]ClO_4	0.10	408 (0.53)	

a) Absorbance with path-length, l = 1.0 cm. b) Converted from the absorbance with l = 0.1 cm. c) 1,1,3,3-Tetramethylguanidine. d) Cloudiness for ≥ 0.2 mol dm^{-3} CH_3SO_3H. e) Approximate values by its shoulder. f) Not evaluated because the absorbance may not be the ultimate value yet.

mol dm^{-3} CH_3SO_3H. At the first stage, the "initial" yellow color of Phenol Red had been diminished completely by the addition of CH_3SO_3H, as mentioned above. However, two absorption bands at 380 and 500 nm developed with increasing concentration of $LiClO_4$. A single species seemed to give both the peaks at 380 and 500 nm, since the absorbance of the former peak was in accordance with the latter. Indeed, almost only the red species was produced by the addition of $LiClO_4$ with the assistance of a small amount of CH_3SO_3H. In the absence of the acid, both the yellow and red colored species had been produced by the addition of $LiClO_4$ (vide supra, cf. Scheme 2). However, in the present system, protonation to the yellow-colored species (λ_{max} = 390 nm) of Phenol Red would have been achieved almost completly by the Brønsted acid. Similar, but stronger, metal effects were given by Mg(ClO_4)$_2$ and Ba(ClO_4)$_2$. It is remarkable that the addition of $LiClO_4$ to a Bromothymol Blue and CH_3SO_3H system also caused only the red-color species (554 nm (and 413 nm)) and no yellow species. The red-colored species should have been produced by protonation to the yellow species (λ_{max} = 426 nm) in the presence of $LiClO_4$. Thus, lithium and the alkaline earth metal perchlorates could apparently assist the Brønsted acid effects in these cases.

However, the same salt stimulated the effects of a base in another instance. The addition of $LiClO_4$ or Mg(ClO_4)$_2$ to a mixture of 1.0×10^{-4} mol dm^{-3} Phenol Red and 1,1,3,3-TMG promoted the production of the purple-red species (ca. 560 nm). A more distinct instance was obtained by the system of Bromothymol Blue. Figure 5 shows the effects of $LiClO_4$ on 1.0×10^{-4} mol dm^{-3} Bromothymol Blue in the presence of 1.0×10^{-4} mol dm^{-3} Et_3N. A band at 624 nm increased at the expense of the band at 400 nm with increasing concentration of $LiClO_4$. The absorbance at 624 nm reached its maximum value of 2.82 at 0.1 mol dm^{-3} $LiClO_4$, and decreased again upon the further addition of the salt.

The deprotonation from Phenol Red or Bromothymol Blue in the yellow form (cf. Schemes 1 and 2) by the addition of $LiClO_4$ in the presence of 1,1,3,3-TMG or Et_3N (B) can take place through the interaction between Li^+ and the phenolate ion (function) on the molecule as

$$\mathrm{O{=}R(SO_3^-){-}OH} + n\mathrm{Li}^+ (n = 1 \text{ and } 2) \rightleftarrows \mathrm{O{=}R(SO_3^-){-}O^-(Li^+)}_n + \mathrm{H}^+. \qquad (2)$$

The deprotonation from a few nitrophenols in the presence of appropriate bases, by the addition of alkali metal and alkaline earth metal perchlorates, has been observed in acetonitrile.[3b]

Confirmation of the Zwitterion Formation by ^{1}H NMR. It is well known that ^{1}H NMR signals of ring protons on triphenylmethyl cation (Ph_3C^+) are shifted much toward downfield, compared with the mother compounds, Ph_3CX. The ring current and positive charge contribution to the chemical shift for *ortho*, *meta*, and *para* protons of Ph_3C^+ has been discussed.[17] Both a computer simulation[18] and ab initio molecular orbital calculations[19] have indicted the order of the chemical shift values (δ) as being *ortho* < *meta* < *para*-protons in Ph_3C^+. The same order would be kept in the ring protons of the sulfonephthalein cations (or zwitterions).

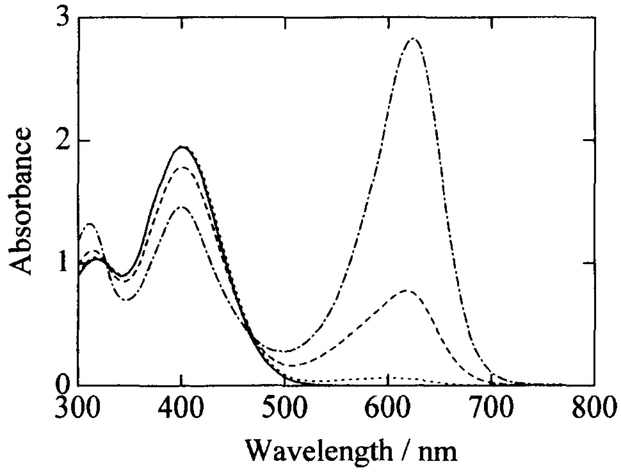


Fig. 5. Effects of $LiClO_4$ on the absorption spectra of 1.0×10^{-4} mol dm^{-3} Bromothymol Blue in the presence of 1.0×10^{-4} mol dm^{-3} Et_3N in acetonitrile: (——) 0; (····) 1×10^{-3}; (- - -) 1×10^{-2}; (– · –) 0.1 mol dm^{-3} $LiClO_4$.

Figure 6 shows the ^{1}H NMR spectra of Phenol Red in the presence of Mg(ClO_4)$_2$ for various concentrations in acetonitrile. In the absence of Mg(ClO_4)$_2$, all signals were observed at $\geq$6.81 ppm. With 0.1 mol dm^{-3} Mg^{2+}, signals appeared at $\geq$ ca. 6.9 ppm without changing of the spectrum pattern very much. However, with 0.5 mol dm^{-3} Mg^{2+}, all signals became very broad, except for the singlet peak at 7.63 ppm which is supposed to be due to the phenolic proton. At last, with 1.0 mol dm^{-3} Mg(ClO_4)$_2$, the signals approached the value of the carbocation or the zwitterion ($\geq$7.16 ppm) which is produced by 2.8 mmol dm^{-3} Phenol

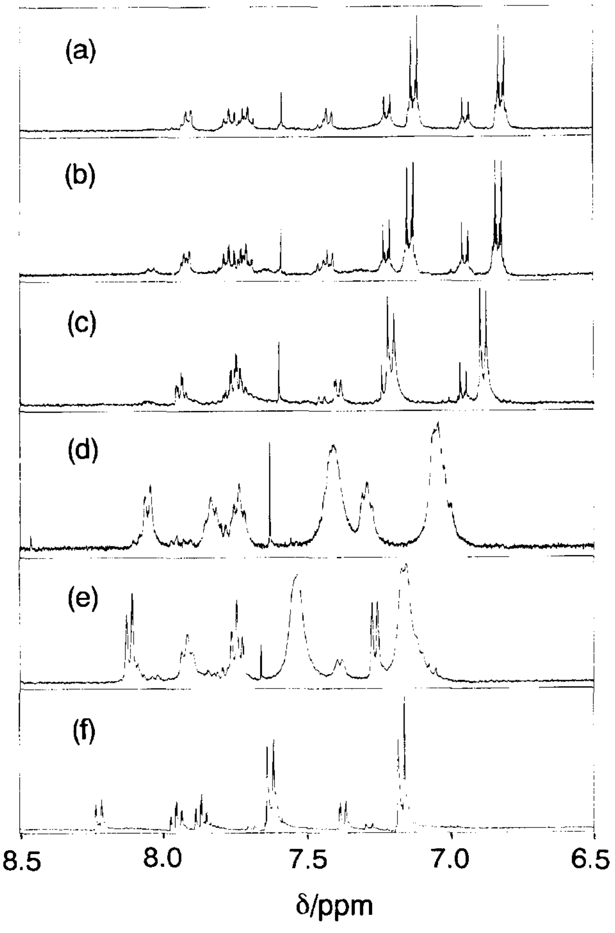


Fig. 6. ^{1}H NMR spectra of saturated ($\leq$0.0028 mol dm^{-3}) Phenol Red with increasing concentration of Mg(ClO_4)$_2$ in CD_3CN: (a) 0; (b) 0.01; (c) 0.1; (d) 0.5; (e) 1.0 mol dm^{-3} Mg(ClO_4)$_2$; (f) 0.1 mol dm^{-3} CF_3SO_3D. TMS is the internal reference for the chemical shift. Accumulated 100 times.

Red and 0.1 $\mathrm{mol\,dm^{-3}}$ CF_3SO_3D. Thus, in the presence of 1.0 $\mathrm{mol\,dm^{-3}}$ $Mg(ClO_4)_2$, the formation of a carbocation center is suggested, although the spectrum pattern is different from that of the "pure" carbocation by CF_3SO_3D. The NMR spectrum with $Mg(ClO_4)_2$ must be composed of a mixture of the yellow and purple species in Scheme 2, according to the UV-visible spectrum of the lower Phenol Red concentration (Fig. 3). The effects of other metal ions were also examined; with 1.0 $\mathrm{mol\,dm^{-3}}$ $LiClO_4$, the signals from Phenol Red were shifted to ≥ 6.96 ppm without line broadening. The effects of 0.5 $\mathrm{mol\,dm^{-3}}$ $Ba(ClO_4)_2$ were almost the same as those of a lower concentration, 0.1 $\mathrm{mol\,dm^{-3}}$, of $Mg(ClO_4)_2$.

Figure 7 shows the effects of metal ions on the ^{1}H NMR spectra of Phenol Red in the presence of a small amount of CF_3SO_3D. The presence of ca. 5.5 $\mathrm{mmol\,dm^{-3}}$ CF_3SO_3D caused almost no change in the NMR spectrum (≥ 6.82 ppm, cf. ≥ 6.81 ppm without the acid), although the solution color turned slightly red color from the pale-yellow color. By the addition of 1.0 $\mathrm{mol\,dm^{-3}}$ $Mg(ClO_4)_2$, the signals were shifted much downfield (≥ 7.18 ppm); the whole spectrum (concerned with the present study) was almost identical to that of the Phenol Red zwitterion. The effects of other metals were smaller than those of Mg^{2+}. Now, we may safely conclude that the γ-sultone ring of Phenol Red is opened by the Mg^{2+} ion to produce the red-colored species (in Scheme 2) in the presence of a small amount of the "strong" acid.

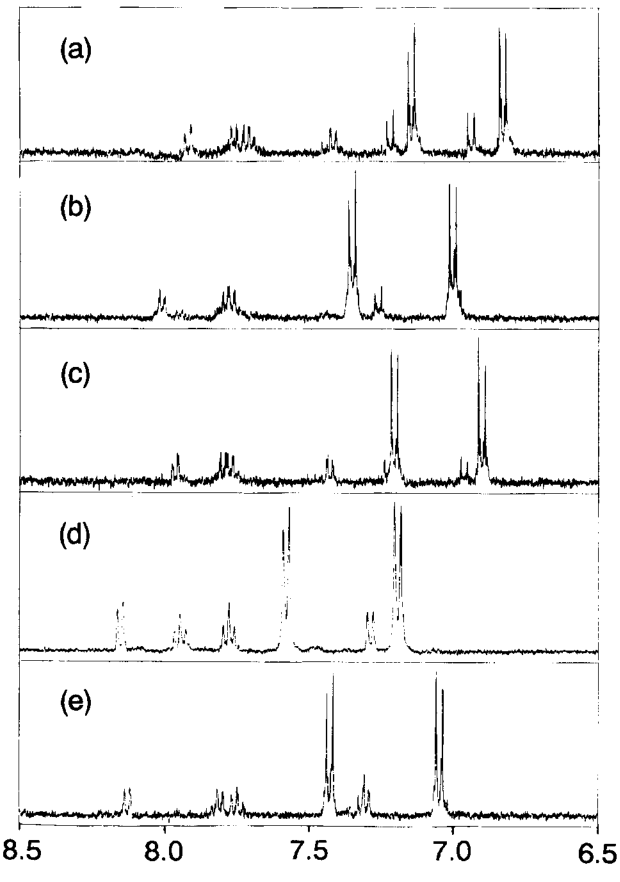


Fig. 7. Effects of metal ions of 1.0 $\mathrm{mol\,dm^{-3}}$ on the ^{1}H NMR spectra of saturated (≤ 2.8 $\mathrm{mmol\,dm^{-3}}$) Phenol Red in the presence of 5.5 $\mathrm{mmol\,dm^{-3}}$ CF_3SO_3D in CD_3CN: (a) no metal ion; (b) $LiClO_4$; (c) $NaClO_4$; (d) $Mg(ClO_4)_2$; (e) $Ba(ClO_4)_2$ of 1.0 $\mathrm{mol\,dm^{-3}}$. Accumulated 8 times.

Comparing Figs. 6 and 7, the line broadening or the different spectrum pattern in Fig. 6 may suggest deprotonation from the phenolic function by the Mg^{2+} ion. It is of interest to note that the presence of Brønsted bases caused the signals of Phenol Red in CD_3CN to shift towards upfield: 6.48 and 6.25 ppm at 0.1 $\mathrm{mol\,dm^{-3}}$ Et_3N and 1,1,3,3-TMG, respectively. With both bases, the γ-sultone ring of Phenol Red is supposed to be opened (cf. Scheme 1 and Table 1). Thus, the deprotonation and ring-opening by Brønsted bases of the sulfonephthalein causes a chemical shift toward upfield. Therefore, it is likely that not only protons, but metal ions, especially the Mg^{2+} ion, can combine with the phenolate or sulfonate ion (function) of the sulfonephthalein (cf. Scheme 2) to contribute to chemical shifts toward downfield. The ^{1}H NMR spectra of other sulfonephthaleins were considered in a similar manner.

Conclusion

By the addition of alkali metal and alkaline earth metal perchlorates in an acetonitrile solution, the γ-sultone rings were opened to give zwitterions, which can exist as a variety of species, depending upon the stability of the carbocations (or the zwitterions) as well as the Brønsted acid–base ability of the parent molecules. The direct interaction between anions (or zwitterions) and alkali metal or alkaline earth metal ions may cause some error when detecting the end-point of an acid–base titration in an acetonitrile solution, if it contains metal salts, or even in an aqueous solution containing highly concentrated electrolytes.

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