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Elucidation of Salt Effects on the Indicator Acidity in Acetonitrile

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The salt effects on the proton-transfer from CF_3COOH to an acid-base indicator, 'Methyl Yellow' [*p*-(dimethylamino)-azobenzene], were examined in acetonitrile by means of spectrophotometry. The addition of $LiClO_4$ to the indicator (Ind) and CF_3COOF mixture (both 2.0×10^{-4} mol dm^{-3}) caused an increase and a successive decrease in the absorbance ($\lambda_{max}=514$ nm) of $IndH^+$. The promoted increase of the $IndH^+$ concentration with increasing concentration of $LiClO_4$ was explained on a quantitative basis concerning the formation of a triple cation, $CF_3COO^-(Li^+)_2$, as well as an ion pair, $CF_3COO^-Li^+$: $Ind–CF_3COOH+2\,Li^+ \rightleftarrows IndH^+ + CF_3COO^-(Li^+)_2$. The successive decrease in the absorbance at 514 nm with a large excess of $LiClO_4$ was attributed to an ion-exchange reaction: $IndH^+ + Li^+ \rightleftarrows IndLi^+ + H^+$. The addition of $NaClO_4$ to $Ind–CF_3COOH$ caused only an increase in the $IndH^+$ concentration, and no deprotonation from $IndH^+$. Alkaline-earth metal ions ($M^{2+}=Mg^{2+}$, Ca^{2+}, Sr^{2+}, and Ba^{2+}) promoted protonation by the formation of complex species, $CF_3COO^-M^{2+}$. Although distinct deprotonation from $IndH^+$ was observed with $Mg(ClO_4)_2$, no deprotonation occurred with $Ba(ClO_4)_2$. The effects of the chloride ion (Et_4NCl) on deprotonation from $IndH^+$ ($In+CF_3SO_3H$) were explained by the formation of homoconjugated species (HCl_2^-), and not by the mere formation of HCl. The apparent changes in pH or the Hammett acidity function with the presence of various salts were elucidated by the 'complex' formation in acetonitrile.

In solution, transition metal ions form complexes with many ligands. However, it has not been widely accepted that alkali metal ions interact with anions through some additional interaction other than the Coulombic attraction, because ions are strongly solvated in usual cases. Previously,[1] salt effects ($LiClO_4$ and Et_4NCl) upon the deprotonation of tropolone ($C_7H_5O_2H$) by triethylamine in acetonitrile were explained by 'coordination' or complex formation reactions, and not merely by ion-pair exchange reactions or by an exchange between the contact ion pair (CIP) and the solvent-separated ion pair (SSIP):

$$C_7H_5O_2H–NEt_3+2\,Li^+ \rightleftarrows C_7H_5O_2^-(Li^+)_2+Et_3NH^+,$$
$$C_7H_5O_2H–NEt_3+2\,Cl^- \rightleftarrows C_7H_5O_2^- + Et_3NH^+(Cl^-)_2$$

Here, $C_7H_5O_2^-(Li^+)_2$ and $C_7H_5O_2^-$ are the 'reverse-coordinated' and the 'free' tropolonate ions, respectively.

It has been found that in acetonitrile, alkali metal ions ($M^+=Li^+$, Na^+) can combine with carboxylate ions to form 2 : 1 species ($RCOO^-(M^+)_2$) as well as 1 : 1 species ($RCOO^-M^+$).[2,3] The formation constants of complex species, $R_3NH^+(X^-)_n$ (n=1 or 2; $X^-=Cl^-$, Br^-, I^-), have also been obtained polarographically when a large excess of halide ions ($Et_4N^+X^-$) is added to partially-substituted ammonium ions ($R_3NH^+ClO_4^-$) in acetonitrile.[4]

In the present work we would like to explain the salt effects of alkali ($M^+=Li^+$, Na^+) and alkaline-earth metal ($M^{2+}=Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}) ions or halide ions (Cl^-, Br^-, I^-) on an acid-base reaction between trifluoroacetic acid and an acid-base indicator, 'Methyl Yellow', *p*-(dimethylamino)-azobenzene in acetonitrile. The dissociation constants of the conjugate acid, $IndH^+$, of *p*-(dimethylamino)-azobenzene in aqueous and acetonitrile solutions have been reported to be $pK_a=3.3$[5] and 10.05,[5] respectively. The apparent changes in pH or the Hammett acidity function[6] with the addition of alkali and alkaline-earth metal ions or halide ions at a constant ionic strength will be evaluated.

It has been noted that,[7] using alkaline colored indicator, the protonation equilibrium of an amine by acetic acid is strongly shifted toward the protonated species upon the addition of a salt, Na^+X^- or $R_4N^+X^-$ ($X^-=Cl^-$, I^-, ClO_4^-), in acetic acid–inert solvent mixtures.

Tetraalkylammonium perchlorates can be used to adjust the ionic strength in aprotic solvents, as alkali metal perchlorates ($MClO_4$) of lower concentrations in aqueous solutions. In the present work, the ionic strengths of all the solutions were kept to be 0.1 with Et_4NClO_4 or n-Bu_4NClO_4 if less than 0.1. For those solutions which were more than 0.1 mol dm^{-3} (for 1 : 1 salts), the ionic strengths were not adjusted. However, the addition of up to 1.0 mol dm^{-3} Et_4NClO_4 or n-Bu_4NClO_4 to an acid-base mixture was found to cause only minor effects (compared with the specific effects by 'active' ions) on the absorption spectra. Therefore, no effects based on a change in the ionic strength were accounted. Temperature changes (20—30 °C) also gave only minor effects for the present system.

Experimental

Commercially obtained acetonitrile (Nacalai Tesque, specially prepared reagents for spectrophotometry) was used as received. *p*-(Dimethylamino)-azobenzene (TCI, GR grade: 90—100% contents) was used without further purification. Trifluoroacetic acid (Wako, GR grade), trifluoromethanesulfonic acid (TCI, >98% or Wako, >98%), and methanesulfonic acid (Wako, >98%) were used as received. Perchloric acid (Wako, GR grade 60%) was diluted with acetonitrile after being titrated with a standard NaOH aqueous solution. Commercially obtained anhydrous $LiClO_4$ (Wako, GR grade>98%) was used as received. Anhydrous $NaClO_4$ was prepared from $NaClO_4 \cdot H_2O$ (Wako, EP grade) by recrystallization from water at 70—80 °C, and drying under a vacuum at 180 °C over P_2O_5. Magnesium perchlorate (Wako, For Elemental Analysis, <17.0% water contents) and barium perchlorate were used after drying under a vacuum at 200 and 180 °C, respectively. Calcium and strontium perchlorates were prepared from $CaCO_3$ and $SrCO_3$, respectively, with an equivalent amount of $HClO_4$ in water. Both salts was dried under a vacuum at 200 °C. The preparation and purification method of Et_4NBr, Et_4NClO_4, n-Bu_4NBr, and n-Bu_4NClO_4 were mentioned before.[4] Commercially obtained Et_4NCl (Wako, GR grade) and n-Bu_4NCl (TCI, GR grade) were dried under a vacuum at 60 °C; however, Et_4NI and n-Bu_4NI (both Wako, Reagent grade) were used as received.

UV-visible spectra were measured using a Hitachi double-beam spectrophotometer (Model U-2000) in 0.1 cm quartz cuvettes at room temperature.

Results and Discussion

Deprotonation from $IndH^+$ with Lithium and Magnesium Ions. An acid-base indicator (Ind), 'Methyl Yellow' [p-(dimethylamino)-azobenzene] gave an absorption peak at 410 nm (molar absorption coefficient, $\varepsilon = 3.0\times10^4$ $cm^{-1}\,mol^{-1}\,dm^3$) in acetonitrile. The addition of sufficient amounts of "strong acids", CH_3SO_3H (0.05 $mol\,dm^{-3}$), CF_3SO_3H (5×10^{-4} $mol\,dm^{-3}$), and $HClO_4$ (2×10^{-4} $mol\,dm^{-3}$) turned a 2×10^{-4} $mol\,dm^{-3}$ indicator solution to a red color ($\lambda_{max}=514$ nm, $\varepsilon=5.8\times10^4$ $cm^{-1}\,mol^{-1}\,dm^3$). The wavelengths and the molar absorption coefficients of Ind and $IndH^+$ were close to the values, respectively, reported by Kolthoff et al.[8]

Figure 1 shows the changes in the UV-visible absorption spectra of 2×10^{-4} $mol\,dm^{-3}$ p-(dimethylamino)-azobenzene upon the addition of various concentrations of CF_3COOH in acetonitrile. The yellow color of the solution suddenly turned to red upon the addition of 1×10^{-2} $mol\,dm^{-3}$ CF_3COOH, whereas the solution color remained yellow at $<1\times10^{-3}$ $mol\,dm^{-3}$ CF_3COOH. In the presence of a large excess of the acid, the protonation of the indicator seems to be assisted by the homoconjugation reaction of trifluoroacetic acid (HA): $Ind+2\,HA \rightleftarrows IndH^+\cdots HA_2^-$. The equilibrium constants of dissociation (pK_a) and the homoconjugation ($HA+A^- \rightleftarrows HA_2^-$: $\log K_{homo}$) for the acid in acetonitrile have been reported to be 12.65 and 3.88, respectively.[9] At any rate, in the presence of 2×10^{-4} $mol\,dm^{-3}$ CF_3COOH, the indicator of 2×10^{-4} $mol\,dm^{-3}$ can not be protonated.

However, the presence of an equivalent amount of a strong acid, trifluoromethanesulfonic acid (2×10^{-3} $mol\,dm^{-3}$ CF_3SO_3H), almost caused a complete protonation of p-(dimethylamino)-azobenzene in acetonitrile. At first, we would like to mention that the addition of (up to 1.0 $mol\,dm^{-3}$) Et_4NClO_4 to the $IndH^+$ solution hardly changed the absorbance of the peak. Figure 2 shows the effects of $LiClO_4$ on the absorption spectra of 2×10^{-4} $mol\,dm^{-3}$ $IndH^+$. The red-colored ($\lambda_{max}=514$ nm) solution of $IndH^+$ turned completely yellow upon the addition of >0.5 $mol\,dm^{-3}$ $LiClO_4$. Figure 3 shows the absorbance changes at around 510 and 410 nm with various concentrations of $LiClO_4$. The effects of $NaClO_4$ were different from those of $LiClO_4$. The absorbance of 514 nm (and 410 nm) remained constant with the presence of even 1.0 $mol\,dm^{-3}$ of $NaClO_4$. The results with $NaClO_4$ indicated that the sodium ion cannot displace

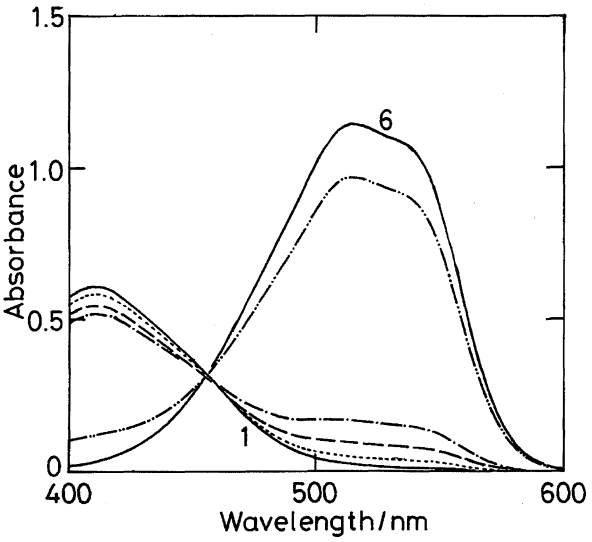

Fig. 1. Changes of UV-visible spectral (l=0.1 cm) of 'Methyl Yellow' (2×10^{-4} $mol\,dm^{-3}$) by the addition of CF_3COOH in acetonitrile. (1—) 0, (····) 2×10^{-4}, (– – –) 5×10^{-4}, (–·–) 1×10^{-3}, (–··–) 1×10^{-2}, (6—) 0.1 $mol\,dm^{-3}$ of CF_3COOH.

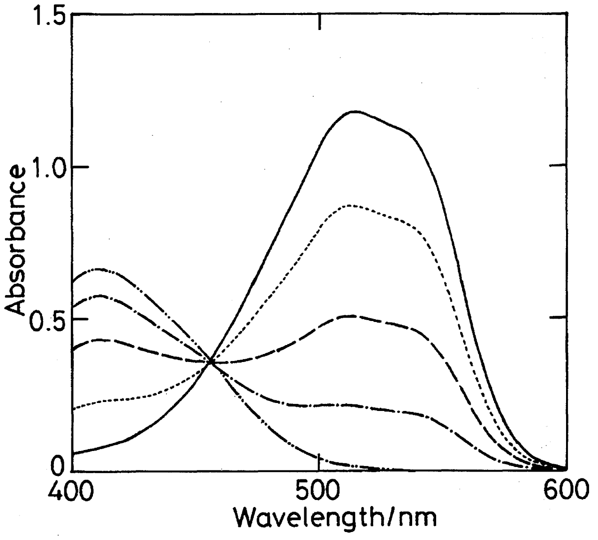

Fig. 2. Changes of UV-visible spectral (l=0.1 cm) of 'Methyl Yellow' (2×10^{-4} $mol\,dm^{-3}$) and CF_3SO_3H (2×10^{-4} $mol\,dm^{-3}$) by the addition of $LiClO_4$ in acetonitrile. (—) 0, (····) 0.1; (– – –) 0.2, (–·–) 0.3, (–··–) 0.5, 0.7, and 1.0 $mol\,dm^{-3}$ of $LiClO_4$.

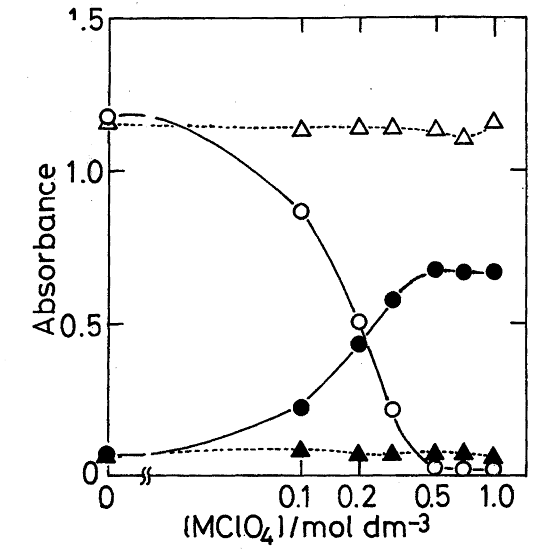

Fig. 3. Observed absorbance changes of 'Methyl Yellow' (2×10^{-4} mol dm^{-3}) and CF_3SO_3H (2×10^{-4} mol dm^{-3}) by the addition of $LiClO_4$ (λ =514 nm: ○, λ =410 nm: ●) and $NaClO_4$ (λ =514 nm: △, λ =410 nm: ▲) in acetonitrile.

the proton from $IndH^+$. The deprotonation from $IndH^+$ with the addition of a large excess of Li^+ may be described by

$$IndH^+ + Li^+ \rightleftarrows IndLi^+ + H^+. \qquad (1)$$

Figure 4 shows the effects of Mg^{2+} and Ba^{2+} on 2×10^{-4} mol dm^{-3} $IndH^+$. The addition of >0.1 mol dm^{-3} $Mg(ClO_4)_2$ caused a decrease in the absorbance at 514 nm, and an increase of that at 410 nm. On the contrary, the addition of up to 1.0 mol dm^{-3} $Ba(ClO_4)_2$ did not change the absorbance of 514 or 410 nm. Upon the addition of >0.2 mol dm^{-3} $Ca(ClO_4)_2$ or $Sr(ClO_4)_2$, the absorbance at 514 nm began to decrease. The above results confirmed the deprotonation from $IndH^+$ with alkaline-earth metal ions, M^{2+}, except for Ba^{2+},

$$IndH^+ + M^{2+} \rightleftarrows IndM^{2+} + H^+ \qquad (2)$$

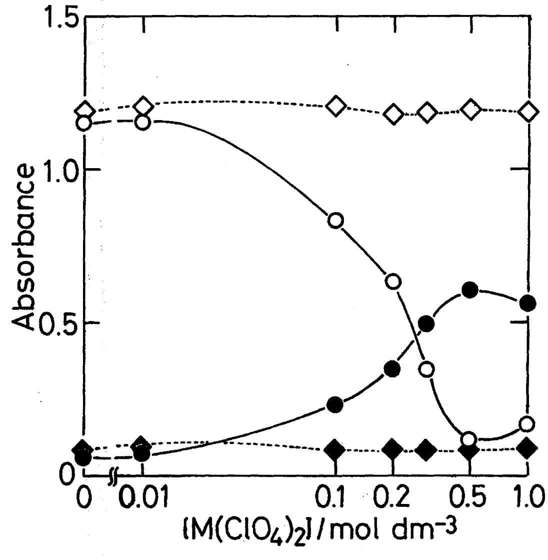

Fig. 4. Observed absorbance changes of 'Methyl Yellow' (2×10^{-4} mol dm^{-3}) and CF_3SO_3H (2×10^{-4} mol dm^{-3}) by the addition of $Mg(ClO_4)_2$ (λ =514 nm: ○, λ =410 nm: ●) and $Ba(ClO_4)_2$ (λ =514 nm: ◇, λ =410 nm: ◆) in acetonitrile.

The effects of $LiClO_4$ on Ind–$HClO_4$ mixtures were somewhat different from those on Ind–CF_3SO_3H mixtures. The presence of even 1.0 mol dm^{-3} $LiClO_4$ to a 2×10^{-4} mol dm^{-3} Ind–$HClO_4$ caused a mere 20% reduction in the absorbance at 514 nm, and the solution color remained red. The difficulty in deprotonation with Li^+ from Ind–$HClO_4$ can be attribute to the stronger interaction between Ind and H^+ from $HClO_4$ than CF_3SO_3H. We think that the effects of the additional water (<1 mmol dm^{-3}) which come from 60% $HClO_4$ can be neglected, compared to the residual water (<10 mmol dm^{-3}) in the purified acetonitrile. The acidities of $HClO_4$ and CF_3SO_3H should be different, due to the fact that the indicator was completely protonated to be $IndH^+$ by an equivalent amount of $HClO_4$, but not completely (just almost) by CF_3SO_3H, (as mentioned before). Recently,[10] we found a decisive proof for the dimerization of CF_3SO_3H molecules in a less-basic solvent, benzonitrile.

The Promotion of Proton-Transfer by the Addition of Alkali and Alkaline-Earth Metal Ions. In the previous section the deprotonation from $IndH^+$ in the presence of a large excess of $LiClO_4$ or $Mg(ClO_4)_2$ was discussed. The present section deals with the promotion of proton-transfer from CF_3COOH by the addition of salts. The yellow color of a 2×10^{-4} mol dm^{-3} Ind+2×10^{-4} mol dm^{-3} CF_3COOH (cf. Fig. 1) solution was changed to red by the addition of $LiClO_4$. The peak at around 510 nm increased along with increasing concentration of $LiClO_4$. Surprisingly, a further addition of >0.3 mol dm^{-3} $LiClO_4$ made the solution turn yellow again. The first increase in the absorbance at around 510 nm should not have been caused by the increase in the ionic strength, since it was kept at 0.1 with Et_4NClO_4. The higher ionic strength, i.e., the presence of (up to 1.0 mol dm^{-3}) Et_4NClO_4 or n-Bu_4NClO_4 to an Ind+CF_3COOH (both 2×10^{-4} mol dm^{-3}) solution caused an increase in the absorption spectra of >500 nm only slightly. By the way, it was found that the addition of 1.0 mol dm^{-3} n-Bu_4NClO_4 to the indicator (2×10^{-4} mol dm^{-3}) caused λ_{max} to shift from 410 to 415 nm without changing the peak absorbance.

Figure 5 shows the changes of absorbance at around 510 and 410 nm with various concentrations of $LiClO_4$. The absorbance at around 510 nm reached a maximum value (0.54) at 0.1 mol dm^{-3} $LiClO_4$, and the absorbance at 410 nm showed a minimum at the same concentration of $LiClO_4$. For a 1×10^{-4} mol dm^{-3} Ind + CF_3COOH mixture, a maximum absorbance of 0.19 was obtained at 0.05 mol dm^{-3} of $LiClO_4$, whereas, for a 4×10^{-4} mol dm^{-3} mixture, the absorbance reached its maximum (1.34) at 0.2 mol dm^{-3} $LiClO_4$, and then began to decrease by a further high concentration of Li^+.

On the other hand, $NaClO_4$ to a 2×10^{-4} mol dm^{-3} Ind+CF_3COOH mixture caused only an increase in the absorbance at around 510 nm, and not a decrease, at least until 0.5 mol dm^{-3} $NaClO_4$. The increase in the absorbance at 514

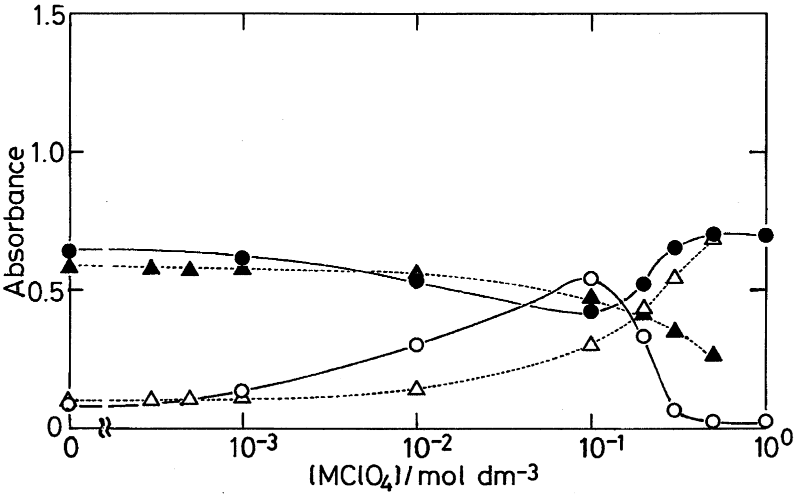

Fig. 5. Observed absorbance changes of 'Methyl Yellow' (2×10^{-4} mol dm^{-3}) and CF_3COOH (2×10^{-4} mol dm^{-3}) by the addition of $LiClO_4$ (λ =514 nm: ○, λ =410 nm: ●) and $NaClO_4$ (λ =514 nm: △, λ =410 nm: ▲) in acetonitrile.

nm due to an addition of alkali metal ions can be explained by the following equation:

$$Ind\text{–}CF_3COOH + 2M^+ \rightleftarrows IndH^+ + CF_3COO^-(M^+)_2, \qquad (3)$$

where Ind–CF_3COOH shows the mixture of an equivalent amount of the indicator and CF_3COOH. The successive decrease in the absorbance should have been caused by Eq. 1. If the lithium ion did not have the ability of proton displacement, the absorbance of 514 nm would have increased monotonically (up to the theoretical value of 1.16) upon the addition of $LiClO_4$.

We have confirmed strong interactions between carboxylate ions and Li^+ or Na^+ in protophobic aprotic solvents by means of polarography[2)] and spectrophotometry:[3)] $RCOO^- + 2M^+ \rightleftarrows RCOO^-(M^+)_2$. The (overall) formation constants of the ion pair (M^+X^-) and the triple ions (M_2X^+ and MX_2^-) of CF_3COOLi in acetonitrile have been reported to be 1.9×10^4 and 5.0×10^6 based on conductometry.[11)] For Eq. 3, although the ion-pair formation between CF_3COO^- and Li^+ may also contribute to the protonation of Ind, the combination of the "triple cation" ($CF_3COO^-(Li^+)_2$) and the ion pair ($CF_3COO^-Li^+$) should construct the whole picture of the reaction scheme. On the other hand, the displacement of H^+ by a large excess of Li^+ may be justified, because a monoamine as well as polyamines have been found to interact with Li^+ in acetonitrile.[12)]

Thus, the addition of salts completely changed the indicator acidity. The changes in the indicator acidity were caused by the chemical reactions in solution. The contribution of changes in the ionic strength was found to be very small in the present system. The effects of $MClO_4$ were estimated on the apparent values of the pH or the Hammett acidity function (H_o)[6)] by *p*-(dimethylamino)-azobenzene for CF_3COOH. The Hammett acidity function (H_o) with the neutral indicator is expressed by

$$H_o = pK(IndH^+) - \log([IndH^+]/[Ind]), \qquad (4)$$

where the $pK(IndH^+)$ value of *p*-(dimethylamino)-azobenzene is 10.05.[5)] In the presence of 2.0×10^{-4} mol dm^{-3} CF_3COOH, the apparent pH or Hammett acidity function was changed from 11.2 to 10.2 by the addition of 0.1 mol dm^{-3} $LiClO_4$. The value decreased down to 9.9 with 0.5 mol dm^{-3} $NaClO_4$ (cf. Table 1).

Figure 6 shows the effects of Mg^{2+} and Ba^{2+} on 2×10^{-4} mol dm^{-3} Ind–CF_3COOH mixtures in acetonitrile. Upon the addition of 2×10^{-4} mol dm^{-3} $Mg(ClO_4)_2$ to the mixture, the solution color turned red (absorbance of 0.52 at 513 nm). The peak around 510 nm increased up to 0.95 at 2×10^{-2} mol dm^{-3} Mg^{2+}, and decreased with $\geqslant 5\times10^{-2}$ mol dm^{-3} Mg^{2+}. The absorbance at 410 nm showed a behavior opposite to that at 510 nm. The effects of $Ba(ClO_4)_2$ were much different from those of $Mg(ClO_4)_2$. The absorbance at around 510 nm increased monotonically with increasing concentration of $Ba(ClO_4)_2$ (up to 1.0 mol dm^{-3}); the ab-

Table 1. Apparent Values of Hammett Acidity Function,[a)] H_o, of CF_3COOH (2×10^{-4} mol dm^{-3}) with Changing Concentration of Alkali or Alkaline-Earth Perchlorates in Acetonitrile

	H_o					
Concn of salts[b)]	Li^+	Na^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1×10^{-4}	11.1	—	10.4	10.6	11.0	10.9
2×10^{-4}	—	11.1	10.2	10.4	—	10.8
5×10^{-4}	—	11.1	10.0	10.2	—	10.8
1×10^{-3}	11.0	11.1	9.8	10.1	10.6	10.5
1×10^{-2}	10.6	10.9	9.5	9.6	10.3	10.0
0.1	10.2	10.5	9.8	9.3	9.7	9.4
0.2	10.5	10.3	10.1	9.3	9.3	9.2
0.3	11.3	10.2	10.3	9.3	9.1	9.1
0.5	—	9.9	10.6	9.5[c)]	9.1	9.0

a) $H_o = pK(IndH^+) - \log([IndH^+]/[In])$, Ind=*p*-(dimethylamino)-azobenzene (2×10^{-4} mol dm^{-3}), $pK(IndH^+)$=10.05 (cf. Ref. 5), H_o=ca. 11.2 without salts. b) Ionic strength was kept to be 0.1 with Et_4NClO_4, when less than 0.1. c) Concentration of $Ca(ClO_4)_2$ was 0.37 mol dm^{-3}.

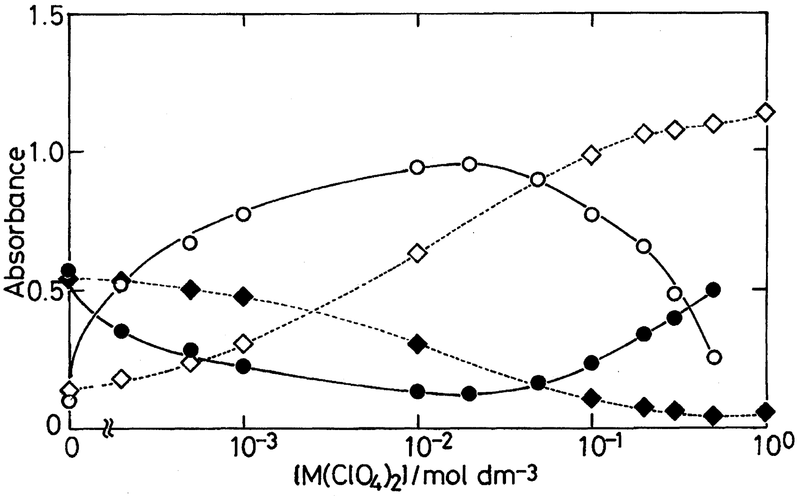

Fig. 6. Observed absorbance changes of 'Methyl Yellow' (2×10^{-4} mol dm^{-3}) and CF_3COOH (2×10^{-4} mol dm^{-3}) by the addition of $Mg(ClO_4)_2$ (λ =514 nm: ○, λ =410 nm: ●) and $Ba(ClO_4)_2$ (λ =514 nm: ◇, λ =410 nm: ◆) in acetonitrile.

sorbance at 410 nm only decreased. By the addition of $Ca(ClO_4)_2$ and $Sr(ClO_4)_2$ to 2×10^{-4} mol dm^{-3} Ind–CF_3COOH mixtures, the peak at 514 nm reached its maximum value of 1.06 and 0.95 at 0.2 mol dm^{-3} Ca^{2+} and 0.3 mol dm^{-3} Sr^{2+}, respectively. The effects of alkaline-earth metal ions on the Ind–CF_3COOH can be explained as follows:

$$\text{Ind–CF}_3\text{COOH} + \text{M}^{2+} \rightleftarrows \text{IndH}^+ + \text{CF}_3\text{COO}^-\text{M}^{2+} \qquad (5)$$

It was found that ions with smaller ionic sizes can easily increase the concentration of $IndH^+$: $Mg^{2+} \gg Ca^{2+}$, $Sr^{2+} > Ba^{2+}$. At the same time, the Mg^{2+} ion showed the highest ability of proton-displacement from $IndH^+$ (Eq. 2), the Ba^{2+} ion having the lowest or no ability (cf. also Table 1). We have found by means of spectrophotometry that the benzoate and nitro-substituted benzoate ions interact with alkaline-earth metal ions to form non-charged species, $M^{2+}(RCOO^-)_2$ (sparingly soluble, except for Mg^{2+}) at $[M^{2+}]:[RCOO^-]=1:2$ and single-charged species, $M^{2+}RCOO^-$ (soluble) at $[M^{2+}]:[RCOO^-]=1:1$ in acetonitrile.[13)]

Effects of Halide Ions. The effects of halide ions on the $IndH^+$ ion were examined. Figure 7 shows the changes in the UV-visible spectra of ca. 2×10^{-4} mol dm^{-3} $IndH^+$ (Ind+CF_3SO_3H) with increasing concentration of Et_4NCl, where the ionic strength was kept to be 0.1 with Et_4NClO_4. Upon the addition of 2×10^{-4} mol dm^{-3} Et_4NCl, the absorbance of $IndH^+$ decreased to 0.70, and the peak at 514 nm completely disappeared at 0.1 mol dm^{-3} Et_4NCl. The alternation of the indifferent cation (from Et_4NCl to *n*-Bu_4NCl) caused no essential alteration to the behavior of the spectra. It can, therefore, be safely stated that tetraalkylammonium ions have no effects on $IndH^+$, besides the minor effect with the ionic strength. By the way, we could not find any difference between Ind–$HClO_4$ and Ind–CF_3SO_3H in the changes of the absorption spectra upon the addition of Cl^- (up to 0.1 mol dm^{-3}). Table 2 shows the apparent values of the Hammett acidity function[6)] for 2×10^{-4} mol dm^{-3} CF_3SO_3H in the presence of Et_4NCl, Et_4NBr, and Et_4NI in acetonitrile.

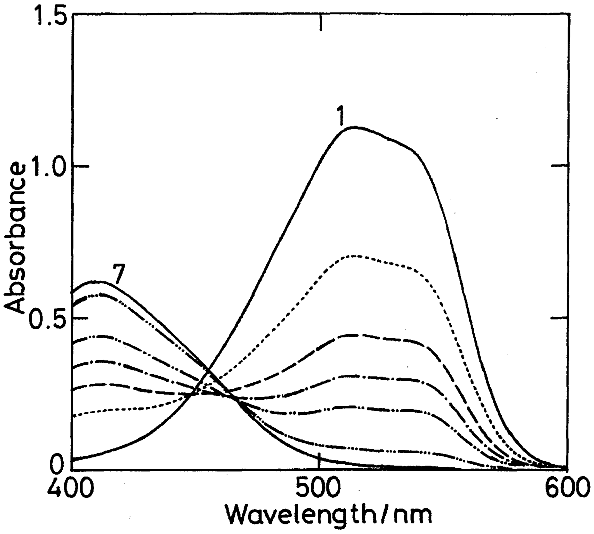

Fig. 7. Changes of UV-visible spectral (l=0.1 cm) of 'Methyl Yellow' (2×10^{-4} mol dm^{-3}) and CF_3SO_3H (2×10^{-4} mol dm^{-3}) by the addition of Et_4NCl in acetonitrile. (1—) 0, (····) 2×10^{-4}, (– – –) 5×10^{-4}, (–·–) 1×10^{-3}, (–··–) 2×10^{-3}, (–···–) 1×10^{-2}, (7—) 0.1 mol dm^{-3} of Et_4NCl. Ionic strength was kept to be 0.1 with Et_4NClO_4.

The basicity of Cl^- in acetonitrile is not weak, since the pK_a value of HCl has been reported to be 8.9 in MeCN.[9)] In addition, the formation constant of the homoconjugation species ($HCl+Cl^- \rightleftarrows HCl_2^-$) has been reported to be $\log K_{homo}=2.2$ in acetonitrile.[9)] We think that the deprotonation from $IndH^+$ must be driven mainly by the formation of HCl_2^- because the complete deprotonation occurs only at a large excess of Cl^-.

$$\text{IndH}^+ + 2\text{Cl}^- \rightleftarrows \text{Ind}\cdots\text{HCl}_2^- . \qquad (6)$$

However, the formation of HCl may not be completely excluded as a candidate of the driving forces of the deprotonation from $IndH^+$, admitting that the basicity of Cl^- (pK_a=8.9)[9)] is weaker than that of Ind (pK_a=10.05)[5)] in ace-

Table 2. Apparent Values of Hammett Acidity Function,[a)] H_o, of CF_3SO_3 (2×10^{-4} mol dm^{-3}) with Changing Concentration of Tetraethylammonium Halides in Acetonitrile

	H_o		
Concn of salts[b)]	Et_4NCl	Et_4NBr	Et_4NI
1×10^{-4}	9.5	9.1	9.1
2×10^{-4}	9.7	9.1	—
5×10^{-4}	10.1	9.2	—
1×10^{-3}	10.4	9.2	9.2
1×10^{-2}	11.2	9.3	9.2
0.1	11.7	9.7	10.0

a) $H_o=pK(IndH^+)-\log([IndH^+]/[In])$, Ind=p-(dimethylamino)-azobenzene (2×10^{-4} mol dm^{-3}), $pK(IndH^+)=10.05$ (cf. Ref. 5), H_o=ca. 9.0 without salts. b) Ionic strength was kept to be 0.1 with Et_4NClO_4.

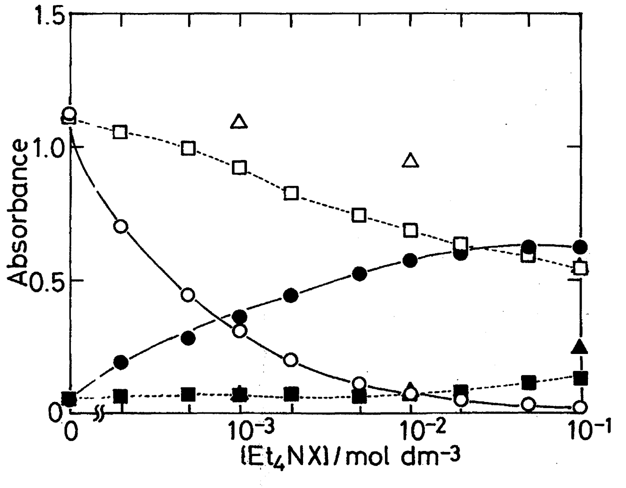

Fig. 8. Observed absorbance changes of 'Methyl Yellow' (2×10^{-4} mol dm^{-3}) and CF_3SO_3H (2×10^{-4} mol dm^{-3}) by the addition of Et_4NCl (λ=514 nm: ○, λ=410 nm: ●), Et_4NBr (λ=514 nm: □, λ=410 nm: ■), and Et_4NI (λ=514 nm: △, λ=410 nm: ▲) in acetonitrile.

tonitrile. The complexity in the isosbestic points (around 460 nm) appearing in the spectra of Fig. 7 would indicate the successive formation of Ind···HCl and Ind···HCl_2^- with an increase in the Cl^- concentration. The effects of Br^- and I^- were much smaller than that of Cl^- (Fig. 8). The pK_a and $\log K_{homo}$ values of HBr in acetonitrile have been reported to be 5.5 and 2.4, respectively.[9)] We have determined that the (overall) formation constants of $PhNMe_2H^+(Br^-)_2$ and $PhNMe_2H^+I^-$ ($PhNMe_2H^+$: N,N-dimethylanilinium ion) are $10^{6.0}$ and $10^{2.7}$, respectively.[4)] However, we have failed to obtain those of $PhNH_3^+(Cl^-)_n$ or $PhNMe_2H^+(Cl^-)_n$ polarographically because the acidities of the anilinium ions are strong enough to react with a large excess of Cl^- (a base), and to produce another cathodic wave in MeCN.[4)] The acidity of the conjugated acid ($IndH^+$) of p-(dimethylamino)-azobenzene (pK_a=10.05) must be similar to those of the anilinium ions (pK_a=10.7 for aniline)[9)] in acetonitrile. Judging from the definitely small increase in the absorbance (0.14) of "free" Ind (410 nm) and the bathochromic shift (λ_{max}=517 nm, absorbance of 0.55) of $IndH^+$ at 0.1 mol dm^{-3} Br^-, complete deprotonation from $IndH^+$ with Br^- may not occur, though the protonated indicator seems to exists as complex forms: $IndH^+Br^-$ and $IndH^+(Br^-)_n$ (n=1 and 2) may also exist. The effects of the iodine ion on the deprotonation from $IndH^+$ were larger than expected from the effects of Br^- and Cl^-.

Steigman and Lorenz[14)] have reported on the deprotonation from $IndH^+$ by n-Bu_4NBr in benzene, suggesting that the bromide ion serves as a hydrogen-bonding base in competition with the indicator base. However, we think that the basicity of Br^- must also be much weaker than that of Ind in benzene. The deprotonation ability of Cl^- seems to be very strong, because the presence of 0.1 mol dm^{-3} n-Bu_4NCl caused a decrease of ca. 65% in the absorbance at 514 nm of a 2×10^{-4} mol dm^{-3}+0.1 mol dm^{-3} CF_3COOH (or 0.05 mol dm^{-3} CH_3SO_3H) solution (cf. only a 15% decrease in the absorbance at 514 nm due to the presence of 0.1 mol dm^{-3} $LiClO_4$).

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