Concentration dependence of thermal isomerization process of methyl orange in ethanol

Concentration Dependence of Thermal Isomerization Process of Methyl Orange in Ethanol

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KEYWORDS

Azo dye, thermal isomerization, pump-probe, salt

Abstract

  The thermal isomerization (TI) rates of methyl orange (MO) and 4-dimethylaminoazobenzene (DMAAB) in ethanol (EtOH) are measured. Usually TI rates of azobenzene dyes are known to be concentration independent. However, the TI rate of MO showed a concentration dependence whereas that of DMAAB did not. The TI rate of DMAAB in EtOH became larger by the addition of alkali halide. This phenomenon is caused mainly by the interaction between DMAAB and cation. MO is a derivative of DMAAB in which one end of the azobenzene is substituted by a $SO_3^-Na^+$ group. The interaction with the dissociated Na^+ ion is considered to be an origin of the concentration dependence of the TI rate of MO.

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1. Introduction

The azobenzene dyes are molecular photoswitches [1, 2]. They undergo trans to cis isomerization by the irradiation with an UV-visible light (photoisomerization). The cis to trans isomerization proceeds spontaneously in the dark (thermal isomerization). There are two pathways by which thermal isomerization (TI) proceeds. One proceeds via the inversion of one of the azo nitrogen atoms (by means of the sp-hybridized transition state). The other proceeds via the rotation about the N=N bond. The former process is independent on the solvent polarity, but the latter process is enhanced in polar solvents [3]. Many studies have focused on the effect of the temperature [3, 4], the substituents [5-9], the pressure [4, 9], the solvent polarity [3, 10], the solvent viscosity [10, 11] and pH [6, 12] on the TI rate of azobenzene dyes.

In most cases, the TI processes follow the first order kinetics. p-Hydroxyazobenzene [8, 13,14] and methyl red [15] are exceptions. Their TI rates increase as the dye concentration increases. This tendency has been explained by the formation of dimers [13-15].

There are many reports about the aggregation of azo dyes in aqueous solutions [6, 16-19]. We considered that the concentration dependence of TI rates of azo dyes may not be an unusual phenomenon, though usually the TI processes is expected to follow the first order kinetics. In this paper, we examined the TI process of methyl orange (MO). The aggregation behavior of MO in aqueous solution is well studied. The apparent spectral change of MO in water has been reported (dye concentration; 4.16×10^{-5} and 1.66×10^{-2} (mol/l)) [19]. The absorption peak of the dimer showed a 5 ~ 10 nm blue shift and a little decrease of the extinction coefficient [17]. The absorption band of MO dimer (at ~ 455 nm) is quite different from that of stacking MO aggregates (at ~ 375 nm [20]) or that of salting-outed MO aggregates (at ~360 nm [21]). The structure of MO dimer seems to be different from that of salting-outed MO aggregates.

The concentration dependence of the TI rate of MO has not been reported yet. However, if the aggregation phenomenon has a possibility of enhancing the TI process, MO may also show a concentration dependence of TI rates. When we began to study the TI rate of MO in water, we faced the following problem: The TI rate highly depends on the solvent pH value [14]. In acidic solution, the N=N group changes to the -NH-N- group and the TI process via the rotation

pathway proceeds faster. Thus, we should examine the TI rates in buffered aqueous solutions in order to avoid the influence of CO_2. However, the TI rates of MO in buffered aqueous solutions also depend on the buffer concentration [12]. It is not an easy task to distinguish the interaction between dye molecules from that between a dye molecule and buffer molecules.

In this paper, to avoid this complexity, we measured the concentration dependence of TI rates of dimethylaminoazobenzene dyes, i.e. MO and 4-dimethylaminoazobenzene (DMAAB) in ethanol (EtOH), and discussed the possibility of the contribution of dimer formation to the TI process.

2. Computational Details

The density functional theory (DFT) calculations for optimizing the structures of DMAAB and MO were carried out using WinGamess Ver. 11 [22]. Theoretical UV/vis absorption spectra were obtained by time-dependent density functional theory (TDDFT) calculation. We employed the hybrid B3LYP xc-functional and the 6-31+G(d) basis set and the continuum C-PCM solvation model. The result was visualized using Winmoster [23].

3. Experimental section

The absorption spectra of MO in EtOH solutions were measured by a spectrometer (JASCO Ubest-30).

We performed the pump-probe experiment to measure the TI rates. In the whole measurement, the sample temperatures were kept at 21 ± 1 Cº. MO and DMAAB in EtOH were excited by a pump beam of an LED (Thorlabs, COP1-A OLYMPUS, the center wavelength of 405 nm, the intensity of ~100 mW). The duration of the irradiation is 5 s. The TI rates were obtained by measuring the transmitted beam intensity of the probe beam of a Laser Diode (Century, BLM20-445D-05, 445 nm, intensity 0.5μW) with a photo-detector (PD). The outputs of the PD were stored by a personal computer using a digital multi-meter or by a digital oscilloscope. The stored

signals were analyzed by a personal computer and the TI rates were obtained from the time dependences of the absorbance.

MO, DMAAB, NaCl, KCL, NaBr, KBr and all alcohols except EtOH (from Junsei Kagaku) are from Kanto Kagaku. We left the prepared solutions in dark room for one night and then measured their TI rates.

The TI rates of MO and DMAAB in EtOH were sensitive to impurities like water and detergent. We used one four-face-transparent $3 \times 10 \times 45$ mm^3 glass cell (3 and 10 mm probe-beam propagation lengths) to measure the TI rates of MO solution of 1.4×10^{-6} (mol/l) $\sim 2.2 \times 10^{-4}$ (mol/l) and one four-face-transparent $10 \times 20 \times 45$ mm^3 cell (10 and 20 mm propagation lengths) to measure those of 3.4×10^{-6} (mol/l) $\sim 1.4 \times 10^{-6}$ (mol/l). When measuring the TI rate of the same sample, we rinsed the cell twice by the sample solution. When measuring the TI rate of $\sim 10^5$ (mol/l) dye solution, we used $3 \times 10 \times 45$ mm^3 and $10 \times 20 \times 45$ mm^3 cells, setting the probe beam propagation lengths of the two cells to be 10 mm. Then we compared the TI rates to check the influence of impurity in cells.

4. Results and Discussion

We measured the TI rates of MO and DMAAB (Figure 1) in EtOH (Concentration range: 1.7×10^{-6} (mol/l) - 2.2×10^{-4} (mol/l)). Figure 2 shows a temporal absorbance change of the MO in EtOH with the dye concentration 6.82×10^{-6} (mol/l), obtained by the pump-probe experiment. The excitation of the sample solution induced the increase of the transmitted intensity of the probe beam. After the pump beam excitation, the intensity decreased due to the thermal isomerization of MO molecules. The sudden increase of the absorbance at t = 5 s is due to the leakage of the pump beam. The temporal change of the magnitude of the absorbance $\Delta A(t)$ at 445 nm was well fitted by a single exponential: $\Delta A(t) = A_0 \exp(-k_{TI}t) + A_1$. The dotted curve is a single exponential fitting with a TI rate (k_{TI}) of 0.156 s^{-1}. For repeated experiments with the same MO solution the standard deviation of k_{TI} was less than $\pm$ 6%, and for experiments with independently prepared solutions, $\pm$ 8%. For DMAAB solution the standard deviation for repeated experiments with a solution was found to be less than $\pm$ 16%, and for experiments with

independently prepared solutions, $\pm 14\%$. The TI rate of DMAAB in EtOH solution was larger than that in propanol. Also, the TI rate of MO in EtOH solution was larger than that in propanol. These dyes are inferred to isomerize via the rotation pathway. The TI rates of DMAAB in EtOH did not show a clear dye concentration dependence (Figures 3, red squares). However, the TI rate of MO showed a dye concentration dependence. The SO_3^- group seems to concern with this tendency.

Initially, we considered that there are two possible origins of the concentration dependence of TI rates of MO in EtOH.

One possible origin is the ion pair association of the $SO_3^-Na^+$ group. In aqueous solution, MO molecules are dissociated completely [18]. Though the Na^+ ions are also solvated in EtOH [24] and the association constants of sodium salts in lower alcohols are not so large (e.g. the ion pair association constants are 44 for NaCl in EtOH and 100 for NaI in propanol [25]), MO in EtOH may show an ion association equilibrium as below.

$$MO\,ion\,pair \; \underset{\longrightarrow}{\overset{\longleftarrow}{}} \; MO\,ion^- + Na^+ \qquad\qquad K_{eq}[Na^+] = \frac{[MO\,ion\,pair\,]}{[MO\,ion^-]}$$

If a MO ion which has a SO_3^- group isomerize slower than a MO ion pair which has a $SO_3^-Na^+$ group, the decrease of the ratio of the ion pair may cause the decrease of TI rates in dilute solution. In the case of either $K_{eq}[Na^+] \gg 1$ or $K_{eq}[Na^+] \ll 1$, MO ion pair or MO ion- is dominant, and we would see no dye concentration dependence of the TI rate. However, at dye concentration around $K_{eq}[Na^+] \approx 1$, we would see a clear dye concentration dependence of the TI rate.

Our DFT calculation suggested that the bond length of the N=N group of neutral cis-methyl orange (cis-MO) molecule which has a SO_3Na group is slightly longer than that of cis-MO ion. This result shows a possibility that a cis-MO ion pair whose structure is similar to that of neutral cis-MO molecule may isomerize via the rotation about the N=N group easier than a cis-MO ion, due to the decrease in the double bond character.

The absorption peak of trans-MO ion and that of neutral trans-MO molecule calculated by the TDDFT appeared at almost the same position (442.4 nm = 2.80eV, 445.6 nm = 2.78 eV,

respectively). We note that TDDFT errors are expected to be in 0.2 - 0.3 eV range, in the case of B3LYP [26]. The experimental peak appeared at ~ 418 nm (2.97 eV). We consider that the change of the ratio of the ion pair would not cause a large change of UV/vis spectrum. Actually, in the UV/vis spectra of trans-MO in EtOH, we observed no noticeable change of the absorption spectrum which depends on the dye concentration (Figure 4). Thus, the ion-pair association is a possible origin of the concentration dependence of the TI rate and is not against the observed UV/vis spectra of MO.

The other possible origin is aggregation. The MO molecules aggregate in aqueous solution. We consider that if MO molecules also aggregate in EtOH and the TI rate of a monomer is smaller than that of an aggregate, the TI rates will decrease in dilute solution. There is no noticeable change of the absorption spectrum of trans-MO in EtOH which depends on the dye concentration (Figure 4), whereas the dimerization of trans-MO molecules in water causes a 5 ~ 10 nm blue shift and the decrease of the absorption intensity [17]. Therefore, aggregation may be not the origin of the concentration dependence of the TI rate. However, there remains a possibility that the aggregation of MO in EtOH does not show a noticeable blue shift. We considered that another experiment is needed to confirm whether the aggregation of MO occurs in EtOH.

The TI rate of MO showed a dye concentration dependence. However, DMAAB does not. If this tendency is caused by the absence of the aggregation behavior of DMAAB, the electrostatic interaction of the SO_3^- group should be concerned with dye aggregation. If there is such interaction, the addition of Na^+ ions would change the SO_3^- group to SO_3Na group, hinder the electrostatic intermolecular interaction and the TI rate of MO solution would decrease. On the other hands, if the ion pair association equilibrium is the origin of the concentration dependence of the TI rate, the addition of Na^+ ions decreases the ratio of the free ion and the TI rate of MO solution will increase. In both cases, the TI rate of DMAAB solution is expected to be unchanged.

Based on these inferences, we added a small amount of NaCl aqueous solution to the MO-EtOH solution and DMAAB-EtOH solution, and measured the TI rates of both solutions (NaCl aqueous solution/dye-EtOH solution, 1:99 v:v). To distinguish the influence of water from that of salt ions, we also added the same amount of water to another dye solutions, and measured

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their TI rates. The addition of 1 volume% pure water made the TI rates of MO solution and DMAAB solution slightly larger (Table 1).

The TI rate of MO solution was increased largely by adding NaCl aqueous solution. We initially expected that the TI rate of DMAAB solution would not be changed. However, the addition of NaCl aqueous solution made the TI rate of DMAAB solution much larger.

The result of the experiment with DMAAB solution shows that the TI process is enhanced by the interaction between dimethylaminoazobenzene moiety and Na^+ / Cl^- ion. Then, which of the two ions enhance the TI process? To answer this question, we added NaCl, KCl, NaBr and KBr aqueous solutions to DMAAB-EtOH solutions and measured TI rates (Table 2). We did not use NaI due to its deliquescence property. We also did not use NaF because NaF aqueous solution is alkalescent and the TI rates depend on pH value of the solution. We added 1 volume% of electrolyte solutions (concentration: 1.39×10^{-1} (mol/l)) to the DMAAB-EtOH solutions (concentration: 1.39×10^{-5} (mol/l)). The molar ratio of dye/electrolyte was set to be 1/100 in these solutions. The concentrations of electrolytes in dye solution are below their solubility in EtOH (i.e. 3.60×10^{-3} (mol/l) for KCl, 7.43×10^{-3} (mol/l) for NaCl, 1.96×10^{-1} (mol/l) for NaBr [27] and 8.97×10^{-3} (mol/l) for KBr [28] at 298K).

The TI rates became larger by adding electrolyte (Table 2). However, the UV/vis spectra of DMAAB did not show a noticeable spectral change despite the excess addition of electrolyte (Figure 5). The effect of Na^+ ion on the TI rate was smaller than that of K^+ ion. An ion with a small ionic radius such as Na^+ ion is solvated effectively in EtOH. Therefore, the interaction of solvated Na^+ ion with an anion is smaller than that of solvated K^+ ion. For example, the ion pair association constant of NaCl is smaller than that of KCl in EtOH (At 298 K, the ion pair association constants of NaCl and KCl are 44 and 95, respectively [25].). We infer that there is an electrostatic interaction between cation and DMAAB molecule, which enhance the TI process, and the interaction of DMAAB molecule with K^+ ion is larger than that with Na^+ ion.

Then, how about the effect of anions? In EtOH, the small Cl^- ion is solvated more effectively than Br^- ion. For example, the ion pair association constant of Me_4NCl is smaller than that of Me_4NBr in EtOH (At 298 K, the ion pair association constants of Me_4NCl and Me_4NBr are 122 and 146, respectively [29].) The ion pair association constant of Bu_4NCl is also smaller than that

of Bu$_4$NBr (At 298 K, the ion pair association constants of Bu$_4$NCl and Bu$_4$NBr in EtOH are 39 and 75, respectively [29].). The electrostatic interaction of solvated Cl$^-$ ion with a cation is smaller than that of solvated Br$^-$ ion in EtOH. Although the data somewhat scatter, our repeated measurements showed that the effect of Br$^-$ ion on the TI rate was similar to that of Cl$^-$ ion (Table 2). We note that the effect of Na$^+$ ion on the TI rate was apparently smaller than that of K$^+$ ion for every experiment. We infer that (1) there is no interaction between DMAAB and anions, or (2) there is some interaction between them, which does not have an apparent effect on the TI rates. The TI rate seems to be determined mainly by the interaction between DMAAB and cation.

Finally, we consider the origin of the concentration dependence of the TI rate of MO EtOH solution again. We initially considered that there were two possible origins of this phenomenon, i.e. the aggregation and the ion pair association of the SO$_3^-$Na$^+$ group.

First, we consider the possibility of aggregation. The TI rate of MO showed dye concentration dependence, while DMAAB does not. If the concentration dependence of the TI rate of MO is caused by the aggregation, the origin of the aggregation would be the electrostatic interaction between dimethylaminoazobenzene moiety of a MO molecule and the SO$_3^-$ group of another MO molecule. However, a large effect of the anion on the TI rates of DMAAB was not observed in the experiments with electrolytes. If there is some interaction between dimethylaminoazobenzene moiety of a MO molecule and the anionic group of another MO molecule, the interaction would not enhance the TI process of MO. Moreover, in the UV/vis spectra of trans-MO in EtOH (Figure 4), there is no noticeable shift or a change of the absorption intensity which depends on the dye concentration whereas the dimerization of trans-MO molecules in water causes a 5 ~ 10 nm blue shift and the decrease of the absorption intensity [17]. We infer that the aggregation behavior is not responsible for the concentration dependence of MO solutions.

The other possible origin was the ion pair association of the SO$_3^-$Na$^+$ group. Our DFT calculation suggests that a trans-MO ion pair isomerizes via the rotation about the N=N group faster than a trans-MO ion does, due to the decrease in the double bond character. However, it is difficult to confirm the validity of this inference experimentally. The results of experiment with electrolytes showed the third possible origin; the enhancement of TI process by cation. MO is a

sodium salt. At higher dye concentrations, the concentration of the Na^+ ions increase and the interaction between dimethylaminoazobenzene moiety and Na^+ ion would also increase. We consider that the increase of this interaction is one origin of the concentration dependence of the TI rate of MO solution (A possible scheme is shown in Fig. 6.).

The TI rates of MO in buffered aqueous solutions increase at higher buffer concentrations (supporting Info. of Ref. [12]). This phenomenon can be explained by a similar interaction between MO and cations. We also consider that although TI rates of azo dyes usually do not depend on the dye concentrations, the dyes with ionic groups may show concentration dependence at a certain concentration range. For example, the TI rates of methyl red in octanol increases as the dye concentration increases above the dye concentration of $\sim 6 \times 10^{-6}$ mol/l [15]. This tendency was previously explained assuming the formation of dimers. Methyl red is a derivative of DMAAB in which the o-position of the aromatic ring of the azobenzene is substituted by a COO^-H^+ group. We consider that this phenomenon may be another example of the enhancement of TI process by the interaction between dye and a cation dissociated from ionic group. H^+ ion is known to enhance the TI process.

5. Conclusion

The measurements of the TI rates of DMAAB and MO in EtOH solutions showed that the TI rate of MO is concentration dependent, while the TI rate of DMAAB is independent on the dye concentration. The TI rates of DMAAB in EtOH solutions were increased by the addition of electrolyte solutions (NaCl, KCl, NaBr and KBr aqueous solutions). The excess addition of electrolyte made no noticeable spectral change of the UV/vis spectra of DMAAB.

The effect of Na^+ ion on the TI process of DMAAB was smaller than that of K^+ ion, whereas the influence of Cl^- ion on the TI rate was almost the same as that of Br^- ion. We consider that there is an electrostatic interaction between cation and DMAAB molecule, which enhances the TI process. We also consider that the interaction between anions and DMAAB is not large enough to have an effect on the TI process, and the TI rate is enhanced mainly by the interaction of DMAAB with cation.

There are two possible origins of the concentration dependence of TI rates for MO solutions in EtOH. One is the ion pair association of the $SO_3^-Na^+$ group. Our DFT calculation suggested that there is a possibility that a cis-MO ion pair isomerizes via rotation about the N=N group easier than a cis-MO ion. However, it is difficult to confirm the validity of this inference experimentally. The other is the enhancement of the TI process by cation. MO is a sodium salt. At higher dye concentrations, the interaction between dimethylaminoazobenzene moiety and Na^+ ion would increase. We consider that the increase of this interaction would be one origin of the concentration dependence of MO in EtOH solution.

We suppose that other dyes with ionic groups such as SO_3Na and COOH, may show similar concentration dependence at a certain concentration range.

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Notes

The authors declare no competing financial interest.

REFERENCES

[1] J. Garcia-Amoro´s, A. Sa´nchez-Ferrer, W.A. Massad, S. Nonell, D. Velasco, Kinetic study of the fast thermal cis-to-trans isomerisation of para-, ortho- and polyhydroxyazobenzenes, *Phys. Chem. Chem. Phys.* 12 (2010), 13238-13242.

[2] H.M. Dhammika Bandara, S.C. Burdette, Photoisomerization in different classes of azobenzene, Chem. Soc. Rev. 41 (2012) 1809-1825.

[3] N.K. Joshi, M. Fuyuki, A. Wada, Polarity Controlled Reaction Path and Kinetics of Thermal Cis-to-Trans Isomerization of 4-Aminoazobenzene, J. Phys. Chem. B 118 (2014) 1891-1899.

[4] T. Asano, T. Yano, T. Okada, Mechanistic Study of Thermal Z-E Isomerization of Azobenzenes by High-Pressure Kinetics, J. Am. Chem. Soc. 104 (1982) 4900-4904.

[5] P.D. Wildes, J.G. Pacifici, G. Irick, Jr., D.G. Whitten, Solvent and Substituent Effects on the Thermal Isomerization of Substituted Azobenzenes. A Flash Spectroscopic Study, J. Am. Chem. Soc. 93 (1971) 2004-2008.

[6] N.J. Dunn, W.H. Humphries IV, A.R. Offenbacher, T.L. King, J. A. Gray, pH-dependent cis → trans Isomerization Rates for Azobenzene Dyes in Aqueous Solution, J. Phys. Chem. A 113 (2009) 13144-13151.

[7] N.A. Wazzan, P.R. Richardson, A.C. Jones, Cis-Trans isomerization of azobenzenes studied by laser-coupled NMR spectroscopy and DFT calculations, Photochem. Photobiol. Sci. 9 (2010) 968-974.

[8] D. Schulte-Frohlinde, ÜBER DIE THERMISCHE UND KATALYTISCHE cis→trans-UMLAGERUNG SUBSTITUIERTER AZOBENZOLE, Liebigs. Ann. Chem. 612 (1958) 138-152.

[9] T. Asano, T. Okada, S. Shinkai, K. Shigematsu, Y. Kusano, O. Manabe, Temperature and Pressure Dependences of Thermal Cis-to-Trans Isomerization of Azobenzenes Which Evidence an Inversion Mechanism, J. Am. Chem. Soc. 103 (1981) 5161-5165.

[10] F. Serra, E.M. Terentjev, Effects of Solvent Viscosity and Polarity on the Isomerization of Azobenzene, Macromolecules 41 (2008) 981-986.

[11] K. Gille, H. Knoll, K. Quitzsch, Rate Constants of the Thermal Cis-Trans Isomerization of Azobenzene Dyes in Solvents, Acetone/Water Mixtures, and in Microheterogeneous Surfactant Solutions, Int. J. Chem. Kinet. 31 (1999) 337-350.

[12] A.M. Sanchez, M. Barra, R.H. de Rossi, On the Mechanism of the Acid/Base-Catalyzed Thermal Cis-Trans Isomerization of Methyl Orange, J. Org. Chem. 64 (1999) 1604-1609.

[13] G. Gabor, Y.E. Frei, E. Fisher, Tautomerism and Geometric Isomerism in Arylazophenols and Naphtols IV. Spectra and Reversible Photoreactions of m- and p-Hydroxyazobenzene, J. Phys. Chem. 72 (1968) 3266-3272.

[14] M. Kojima, S. Nebashi, K. Ogawa, K. Kurita, Effect of solvent on cis-to-trans isomerization of 4-hydroxyazobenzene aggregated through intermolecular hydrogen bonds, J. Phys. Org. Chem. 18 (2005) 994-1000.

[15] T. Joukai, K. Kita, R. Yano, Pump–Probe Spectroscopy of Thermal Cis-Trans Isomerization Process of Methyl Red in 1-Octanol, JPS Conference Proceedings 1 (2014) 012052.

[16] E. Crasmareanu, N. Plesu, S.G. Muntean, M. Tara-Lunga-Mihari, V. Simulescu, G. Ilia, An EIS and UV-Vis Spectroscopy Assay for Aggregation of Monoazo Acid Dye, Rev. Chem. (Bucharest) 63 (2012) 768-771.

[17] G. Alberghina, R. Bianchini, M, Fichera, S. Fisichella, Dimerization of Cibacron Blue F3GA and other dyes: influence of salts and temperature, Dyes Pigm. 46 (2000) 129-137.

[18] M. Mitsuishi, Y. Yamaguchi, The Activities of Methyl Orange and Homologs in Aqueous Solutions, Bull. Chem. Soc. Jpn. 52 (1979) 3496-3498.

[19] F. Quadrifoglio, V. Crescenzi, The Interaction of Methyl Orange and Other Azo-Dyes with Polyelectrolytes and with Colloidal Electrolytes in Dilute Aqueous Solution, J. Colloid Interface Sci. 35 (1971) 447-459.

[20] M. Mitsuishi, H. Kikuchi, K. Yonezawa, S. Nakano, M. Hamai, K. Hamada, T. Ishiwatari, EFFECT OF CHARGE SEPARATION ON AGGREGATION OF METHYL ORANGE HOMOLOGUES BOUND TO IONENES, SEN-I GAKKAISHI 47 (1991) 537-543 (in Japanese).

[21] J.G. Dawber, D.T. Fisher, P.R. Warhurst, The Metachromism of Methyl Orange with Electrolytes and Possible Salting-out, J. Chem. Soc. Faraday Trans. I 82 (1986) 119-123.

[22] M.W. Schmidt, K.K. Baldridge, J.A. Boats, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, General Atomic and Molecular Electronic Structure System, J. Compt. Chem. 14 (1993) 1347.

[23] Norio Senda, Development of molecular modeling and visualization package software "Winmostar", IDEMITSU TECHNICAL REPORT, 49 (2006) 106-111 (in Japanese).

[24] I. Sakamoto, Studies on Ion-Solvent Interactions IV. Measurements of Electrolytic Conductivity and Ion Association Equilibria of Electrolytes, Shimane University Bulletin 21 (1987) 101-136 (in japanese).

[25] R.L. Kay, An Application of the Fuoss-Onsager Conductance Theory to the Alkali Halides in Several Solvents, J. Am. Chem. Soc. 82 (1960) 2099-2105.

[26] D. Jacquemin, B. Mennucci, C. Adamo, Excited-state calculations with TD-DFT: from benchmarks to simulations in complex environments, Phys. Chem. Chem. Phys. 13 (2011) 16987-16998.

[27] S.P. Pinho, E.A. Macedo, Solubility of NaCl, NaBr, and KCl in Water, Methanol, Ethanol, and Their Mixed Solvents, J. Chem. Eng. Data 50 (2005) 29-32.

[28] S.P. Pinho, E.A. Macedo, Experimental measurement and modelling of KBr solubility in water, methanol, ethanol, and its binary mixed solvents at different temperatures, J. Chem. Thermodynamics 34 (2002) 337-360.

[29] D.F. Evans, P. Gardam, Transport Processes in Hydrogen-Bonding Solvents. I. The Conductance of Tetraalkylammonium Salts in Ethanol and Propanol at 25 C^o, J. Phys. Chem. 72 (1968) 3281-3286.
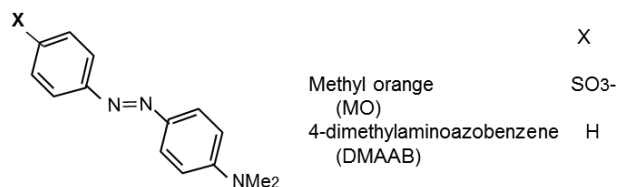
Figures

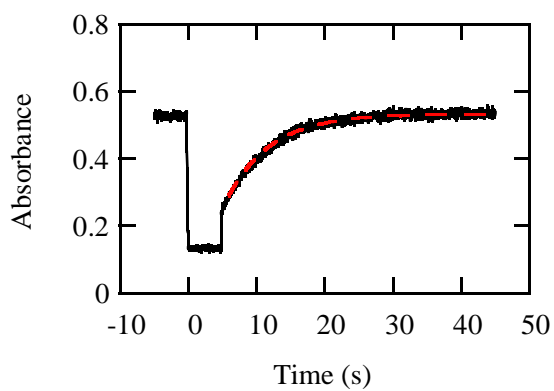**Figure 1.** Structures of dimethylaminoazobenzene dyes

Figure 2. Temporal changes of absorbance of MO in EtOH (6.82×10^{-6} (mol/l)) The pump beam excited the sample for 5.0 s. The dashed curves are single exponential fittings with TI rates of 0.156 s^{-1}.
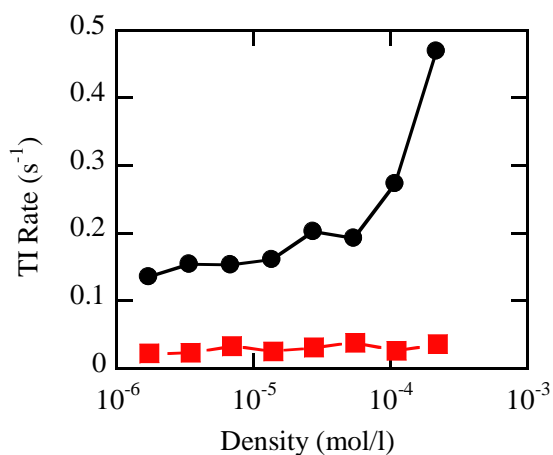
Figure 3. Concentration dependence of thermal isomerization rates of DMAAB (red squares) and MO (black circles) in EtOH.
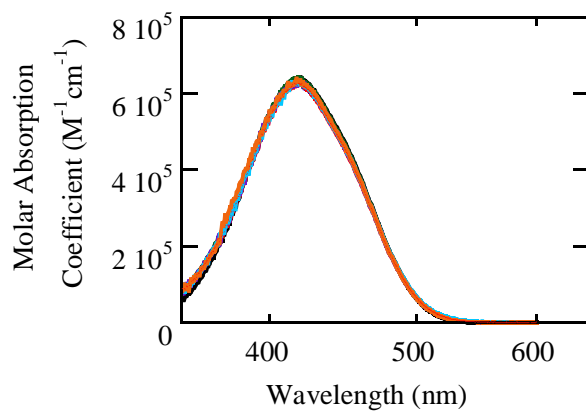

Figure 4 Absorbance of MO in EtOH. The dye concentrations are 2.18×10^{-4}, 1.09×10^{-4}, 5.45×10^{-5}, 2.72×10^{-5}, 1.36×10^{-5}, 6.82×10^{-6}, and 3.14×10^{-6} (mol/l). All the curves coincide well with each other.
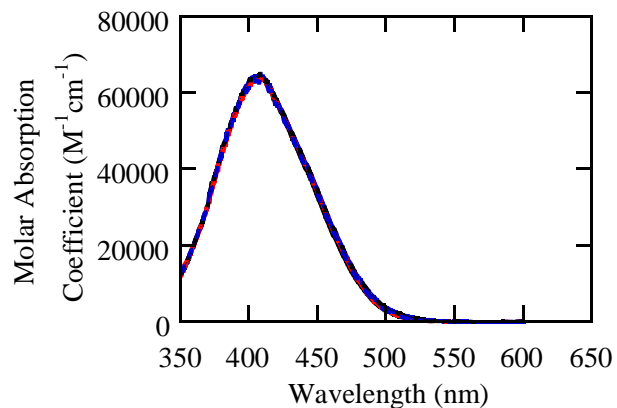
Figure 5. Spectra of trans-DMAAB in EtOH. The absorption curves are DMAAB in ethanol solution (black solid curve), DMAAB in EtOH solution with an addition of water (red solid curve), addition of NaBr (blue solid curve), addition of NaCl (black dashed curve), addition of KBr (red dashed curve), and addition of KCl (blue dashed curve).
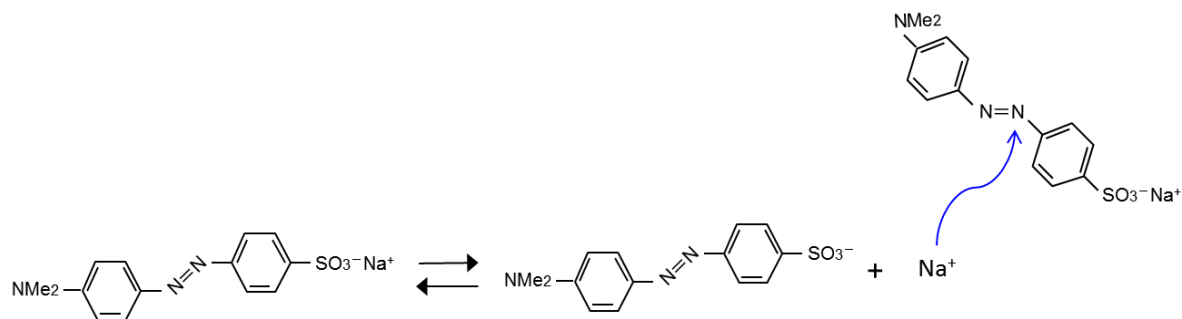

Figure 6. Interaction between a Na^+ ion and MO molecule

Tables

solution	additive (*)	TI rates (s⁻¹)	
		before addition	after addition
MO ethanol solution (*1)	water (1 volume%)	0.23	0.59
	NaCl aqueous solution (*3) (1 volume%)	0.26	1.6
DMAAB ethanol solution (*2)	water (1 volume%)	0.028	0.049
	NaCl aqueous solution (*3) (1 volume%)	0.027	0.67

Table 1. The change of TI rates of dimethylazobenzene dyes in EtOH

Concentration: * 1: 3.05×10^{-5} (mol/l). * 2: 4.44×10^{-5} (mol/l). *3: 0.86 (mol/l)

additive (*)	TI rates (s⁻¹)	
	before addition	after addition
water	0.02	0.04
KCl aqueous solution	0.03	0.23
NaCl aqueous solution	0.03	0.11
KBr aqueous solution	0.02	0.21
NaBr aqueous solution	0.02	0.10

Table 2. The change of TI rates of DMAAB-EtOH solutions by adding electrolyte solutions

* Dye concentration is 1.39×10^{-5} (mol/l).

The addition of electrolyte aqueous solutions makes the ratio of dye/electrolyte 1/100.

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Figure 1. Structures of dimethylaminoazobenzene dyes

Figure 2. Temporal changes of absorbance of MO in EtOH (6.82×10^{-6} (mol/l)) The pump beam excited the sample for 5.0 s. The dashed curves are single exponential fittings with TI rates of 0.156 s^{-1}.

Figure 3. Concentration dependence of thermal isomerization rates of DMAAB (red squares) and MO (black circles) in EtOH.

Figure 4 Absorbance of MO in EtOH. The dye concentrations are 2.18×10^{-4}, 1.09×10^{-4}, 5.45×10^{-5}, 2.72×10^{-5}, 1.36×10^{-5}, 6.82×10^{-6}, and 3.14×10^{-6} (mol/l). All the curves coincide well with each other.

Figure 5. Spectra of trans-DMAAB in EtOH. The absorption curves are DMAAB in EtOH solution (black solid curve), DMAAB in ethanol solution with an addition of water (red solid curve), addition of NaBr (blue solid curve), addition of NaCl (black dashed curve), addition of KBr (red dashed curve), and addition of KCl (blue dashed curve).

Figure 6. Interaction between a Na$^+$ ion and MO molecule

Tables

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