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# Importance of Solvent Polarity in the Equilibrium Reaction of Leuco Dye and Developer

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The absorbance of the leuco dye and developer solution system showed a maximum by the change of solvent polarity, and a clear correlation between the ratio of coloring species at the maximum and the dielectric constant of polar solvents has been revealed. These results suggest that the polar solvent plays an important role to change the condition of the surroundings, which is an important factor in controlling the equilibrium reaction of a leuco dye and a developer.

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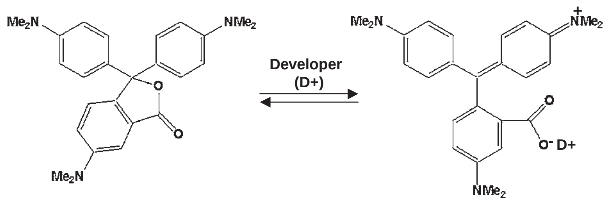
The arrival of a paperless society has been predicted because of the wide spread use of personal computers. However, in actuality, consumption of paper is increasing every year, and more than 60% of paper is used as printing paper in Japan. Although recycling technology for used paper has become well established, the de-inking process generates large amount of carbon dioxide and other wastes. Paper becomes trash because there is something printed or written on its surface, which is useless to the user. If the image were erasable, such trash paper would become a valuable resource. The key is the image-forming material.

To realize this concept, we have developed the erasable ink technology and have applied it to an erasable toner, e-blue$_{\rm TM}$.[1] This erasable toner comprises a leuco dye, a developer, and an eraser. Leuco dyes have been widely employed in thermosensitive recording systems, such as sales receipts, facsimiles, and rewritable papers. The erasable toner is colored when a developer combines with a leuco dye and is discolored when the combination is dissociated by the eraser. A representative equilibrium reaction of 3,3-bis(*p*-*N*,*N*-dimethylaminophenyl)-6-*N*,*N*-dimethylaminophthalide (Crystal Violet Lactone: CVL), one of the most important leuco dyes, with a color developer is proposed as shown in eq 1.[2] The electron-donating CVL reacts with an electron-accepting color developer, yielding a cationic coloring species.



(1)

Compared with standard toner, the color density of the commercialized erasable toner e-blue$_{\rm TM}$ has been insufficient until now. We assume that the same equilibrium as shown in eq 1 is achieved in production (kneading) process of the erasable toner and is dominated by discoloring state. That means, the equilibrium reaction of the leuco dye and the developer is the key to improving the color density of erasable toner. However, there have been few studies on the equilibrium reaction of leuco dyes and developers. We have, therefore, begun fundamental research on the equilibrium reaction and report herein the effect of polar solvent on it.

As shown in Eq 1, the charge was localized in the coloring state of the leuco dye, and the ratio of the coloring and discoloring states would change according to the polarity of the surroundings. Therefore, we investigated the effect of solvent polarity on the absorbance, using 3-(4-diethylamino-2-hexyloxyphenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide (Blue203)[3] and ethyl gallate (3,4,5-trihydroxybenzoic ethyl ester, EG) as a leuco dye and a developer, respectively. To 1:1 mixtures of Blue203 (50 mg, 0.093 mmol) and EG (19 mg, 0.096 mmol) was added a mixed solvent (5 mL) consisting of toluene and other polar solvents in various ratios. Figure 1 shows an example of the results obtained using acetone as a polar solvent. Tetrahydrofuran, acetonitrile, and propylene carbonate were also used as polar solvents, and the similar results as shown in Figure 1 were obtained in every case. When the acetone content was less than 7 vol %, EG did not dissolve completely and a blue suspension was obtained. In this case, EG was removed by filtration and the obtained solution was used for UV–vis absorption spectrum analysis.

As shown in Figure 1, the absorbance at $\lambda_{\max}$ of the leuco dye and developer system showed a maximum by the change of the solvent polarity. In the range of less than 7 vol %, the absorbance increased almost in proportion to the acetone content. As described above, EG did not dissolve completely in this range, and the solubility of EG also increased with increasing acetone content. On the other hand, in the range of more than 7 vol %, the absorbance decreased with increasing the acetone content.

As the initial concentration of leuco dye ($C_0$) differs among polar solvents, owing to solubility, we have defined an index ($C_{\max}/C_0$) for the ratio of coloring species, where $C_{\max}$ is the concentration of the coloring species at the maximum obtained by the Bouguer–Beer law.[4] As shown in Figure 2, a clear correlation was found between $C_{\max}/C_0$ and the dielectric constant of polar solvents. This result suggests the close interaction between the coloring species and the polar solvent. A similar result was reported by Hinckley et al. between the dielectric constants of

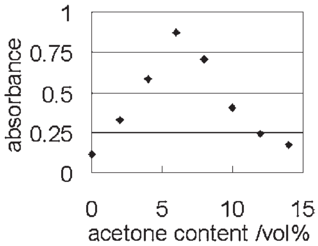


**Figure 1.** The remarkable change of the absorbance with the solvent polarity.

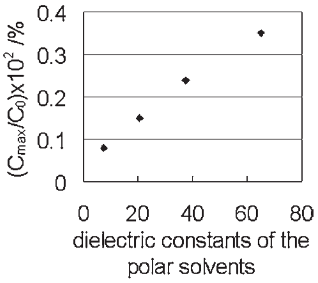


**Figure 2.** A clear correlation between $C_{\max}/C_0$ and the dielectric constant of the polar solvents.

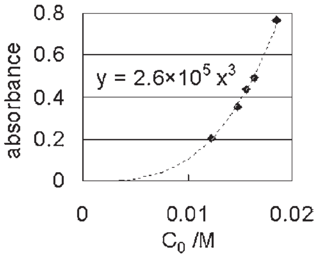


**Figure 3.** The relationship between $C_0$ and the absorbance.

protic solvents and the natural log of the equilibrium constant in the system of rhodamine B.[5] We also revealed an interesting relationship between $C_0$ and the absorbance. According to the Bouguer–Beer law, when a dye and a developer are used 1:1 molar ratio, the absorbance will increase in proportion to $C_0$.[2] However, as shown in Figure 3, the absorbance increased almost in proportion to $C_0$.[3] This result indicates that there are some additional interactions in the coloring species besides the 1:1 interaction of the leuco dye and the developer, and one of the candidates is the interaction between the developer and the polar solvent.

Although accurate understanding of these phenomena is difficult, we propose one hypothesis described below. In the initial state, the leuco dye and the developer are supposed to be separated into two phases, a liquid phase (leuco dye solution) and a solid phase (micro crystals of developer) and equilibrium cannot be achieved. When a polar solvent is added here, it solvates the developer, thus taking the developer into the liquid phase of the leuco dye solution to achieve equilibrium. These phenomena are summarized as eqs 3 and 4: In the first step, the developer interacts with the polar solvent and the generated complex combining with the leuco dye to form a coloring species.

$$\mathrm{D} \overset{\mathrm{P}}{\rightleftharpoons} \mathrm{D}\cdot\mathrm{P_m}, \tag{2}$$

$$\mathrm{L} + \mathrm{D}\cdot\mathrm{P_m} \rightleftharpoons \mathrm{L} - \mathrm{D}\cdot\mathrm{P_m}, \tag{3}$$

$$\mathrm{L} - \mathrm{D}\cdot\mathrm{P_m} \overset{\mathrm{P}}{\rightleftharpoons} \mathrm{L} + \mathrm{D}\cdot\mathrm{P_n}, \tag{4}$$

(L: leuco dye, D: developer, P: polar solvent, $n > m$)

When the polar solvent content is small, the equilibrium reaction of the developer and the polar solvent is dominative, because the developer dose not dissolve completely, promoting the formation of the coloring species. At the maximum of Figure 1, the polar solvent is assumed to work most effectively. On the other hand, Figure 1 shows that, when the polar solvent content is large, corresponding to the range of more than 7 vol %, the decolorization is accelerated by the polar solvent. Decolorization is due to the dissociation of the coloring species. That means, the dissociation of the coloring species is due to the excess addition of the polar solvent. In our study, the polar solvents used were all electron-donating solvent. We consider that the electron acceptivity of EG, important for the formation of the coloring species, is lowered by the excess electron donation by the polar solvent, leading the dissociation of the coloring species, as shown in eq 4. Previously, Oguchi et al. investigated the behavior of a leuco dye and developer in solution by using the $^{13}$C NMR technique, and reported that one set of coalescent signals was observed at the averaged resonance frequency of the coloring and discoloring states.[6] This result suggests that the equilibrium reaction between the coloring and discoloring states is very fast and the activation energy is very small. Also, they calculated the Gibbs free energy at room temperature for the system, similar to eq 1, to be 2.97 kJ/mol. These results show that the equilibrium reaction of the leuco dye and developer is easily changeable. Such a sensitive system, a little change of the polarity of surroundings brings the remarkable change of the absorbance. MacLaren and White also examined a similar system and states that there is a competition between a dye and a solvent for interaction with a developer in a thermochromic system.[7] They revealed that raising the temperature of the system allowed the movement of the developer from the colored dye–developer complex to the solvent–developer complex, leading to the decolorization of the mixture. This also shows the sensitivity of the coloring system of the leuco dye and developer.

The results obtained here indicate that the additive possessing the same function as the polar solvent in this work is effective in controlling the color density of the erasable toner. More simply, we might control it by the dielectric constant of the medium. Further studies on the application to the erasable toner are in progress.

## References and Notes

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4 The molar absorptivity of Blue203 was estimated to be 36,000 mol$^{-1}$·L·cm$^{-1}$ based on the hypothesis that the leuco dye were developed completely in acetic acid.

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