Electrochemical Evaluation of Hydrogen Bond Donor Ability of Sulfonylurea Molecules by Cyclic Voltammetry

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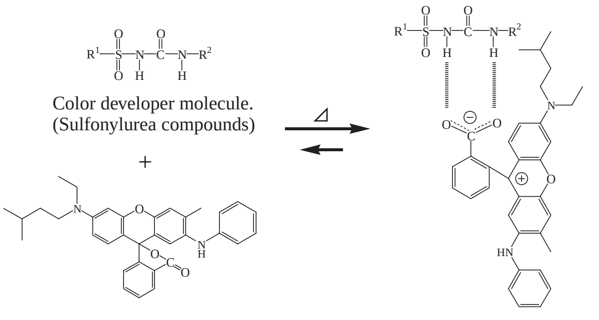
Hydrogen bond donor ability, which is an essential factor for strong black color developing and its durability on the thermal paper, of the sulfonylurea (color developer) can be evaluated well in terms of the reduction potential for the leuco dye and the sulfonylurea system in DMF by cyclic voltammetry.

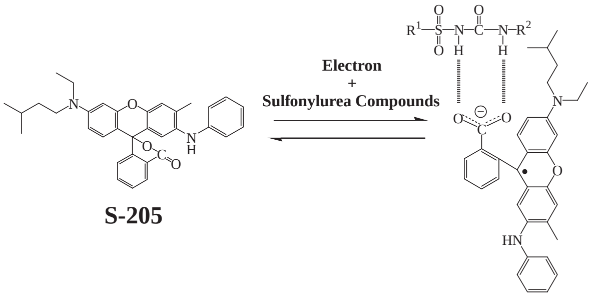
In order to acquire strong black color developing and its high durability of the developed color on the thermal paper comprised of the leuco dye and color developer molecule, hydrogen bond donor ability of the color developer molecule is essential because hydrogen bond donor ability of the color developer enables to stabilize a π-delocalized zwitterion generated from the leuco dye by heat-induced lactone ring opening by forming hydrogen bond as shown in Scheme 1.

A proper and efficient color developer for thermal papers that is actually on the market is a sulfonylurea compound. Hydrogen-bond formation between a pair of H atoms in two N–H residues in sulfonylurea and the carboxylate anion from the leuco dye contributes a lot for stabilization of the π-delocalized zwitterion. In our previous paper,[1] we have reported that hydrogen bond donor ability of color developer molecules is correlated very well with high black color developing and that the parameter $\alpha_2{}^{\mathrm{H}}$ proposed by Abraham et al.[2] is a proper index to evaluate hydrogen bond donor ability of the color developer. By using this hydrogen bond donor ability $\alpha_2{}^{\mathrm{H}}$ parameter, rational and efficient molecular design of a functional color developer is possible. At present, standard method to evaluate hydrogen bond donor ability with $\alpha_2{}^{\mathrm{H}}$ scale is to measure UV–vis spectra for the color developer and leuco dye solutions by monitoring the absorption intensities of the chromophore for black color developing. In this paper, new method to evaluate hydrogen bond donor ability by using cyclic voltammetry is shown. Electrochemical study with cyclic voltammetry is useful and convenient to monitor hydrogen-bond interaction and to investigate electronic effects of various functional groups for hydrogen-bond interaction.[3–5] Electrochemical reduction potential of 2′-anilino-6′-(*N*-ethyl-*N*-isopentylamino)-3′-methylspiro [isobenzofuran-1-(3*H*),9′-(9*H*)xanthen]-3-one (**S-205**), a popular fluoran dye precursor used in the thermal paper on the market, has been measured with cyclic voltammeter by sweeping the potential into reductive direction. Then, shifts in half-wave potential, $|\Delta E_{1/2,\mathrm{red}}|$, by adding 0.5 equivalent molar of various sulfonylurea molecules were investigated.



Scheme 1. Color developing mechanism by the formation of hydrogen-bond complex between the open-form fluoran dye precursor (**S-205**) and a color developer such as sulfonylurea.

In cyclic voltammetry experiment scanning cathodic wave which causes the reduction of the substrate, **S-205** solution without sulfonylurea becomes gradually black, and we can observe reduction wave peak at $E_{1/2,\mathrm{red}}$ (**S-205**) indicating lactone ring opening of **S-205** and producing anion radical of **S-205**. By adding sulfonylurea into this **S-205** solution, this reductive wave peak shifts to more negative side (Figure 1).[6]



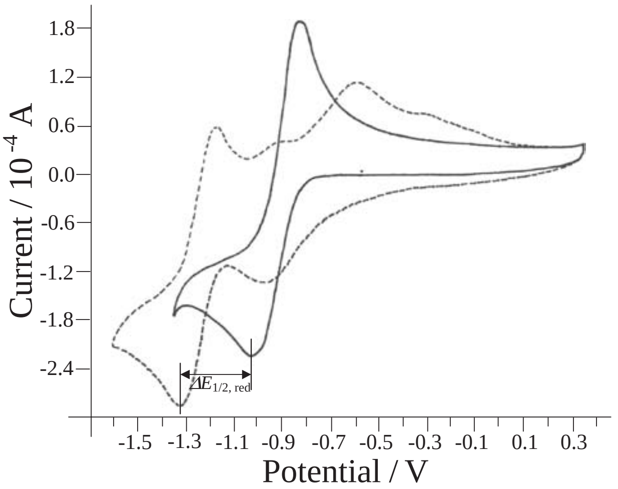
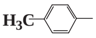
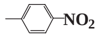
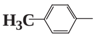
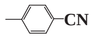
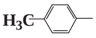
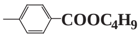
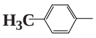
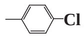
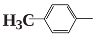
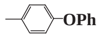
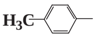
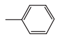
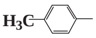
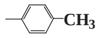
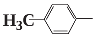
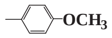
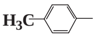


Figure 1. Cyclic voltammograms of 10 mM Leuco Dye (**S-205**), in 0.1 M $\mathrm{NBu_4PF_6}$/DMF by itself (—) and in the presence of 5 mM Sulfonylureas (···). Scan rate = 50 mV/s.

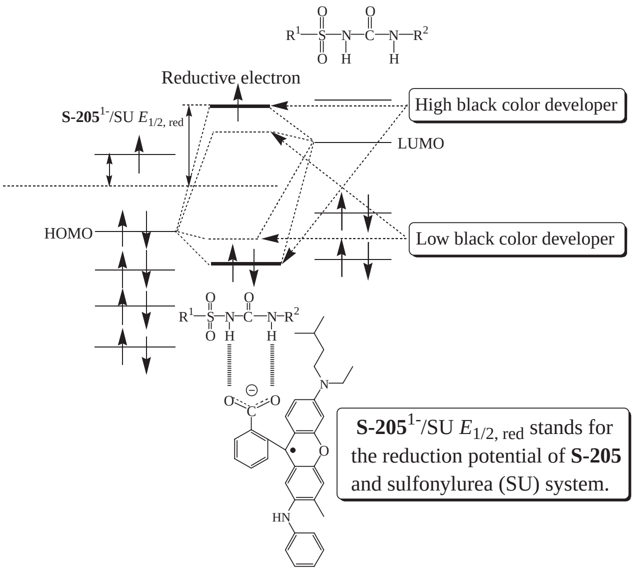
Table 1. The determined reduction potential shift ($|\Delta E_{1/2,\mathrm{red}}|$) by cyclic voltammetry measurement and the hydrogen bond donor parameter $\alpha_2{}^{\mathrm{H}}$ values[1] for the sulfonylurea

Compounds	R^1	R^2	$\alpha_2{}^{\mathrm{H}}$	$\lvert\Delta E_{1/2,\mathrm{red}}\rvert$ /mV
1			1.089	415
2			1.052	380
3			1.000	365
4			0.963	345
5			0.941	340
6			0.917	285
7			0.899	290
8			0.896	280
9		$-(CH_2)_2CH_3$	0.742	170
10	H_3C-	$-(CH_2)_2CH_3$	0.669	150

The extent of potential shift $|\Delta E_{1/2,\mathrm{red}}|$ ($|E_{1/2,\mathrm{red}}$ (**S-205** + sulfonylurea)$| - |E_{1/2,\mathrm{red}}$ (**S-205**)$|$) correlates well with the hydrogen bond donor ability parameter $\alpha_2{}^{\mathrm{H}}$ values. The determined reduction potential shifts ($|\Delta E_{1/2,\mathrm{red}}|$) for the various sulfonylureas are compiled in Table 1 together with the reported hydrogen bond donor parameter $\alpha_2{}^{\mathrm{H}}$. Thus, larger potential shift $|\Delta E_{1/2,\mathrm{red}}|$ values are observed for proper sulfonylurea molecules with high black color developing power (larger $\alpha_2{}^{\mathrm{H}}$ values). The good correlation plot between $|\Delta E_{1/2,\mathrm{red}}|$ and $\alpha_2{}^{\mathrm{H}}$ ($R^2 = 0.976$) could be recognized. Linear regression equation is expressed as in eq 1.

$$|\Delta E_{1/2,\mathrm{red}}| = 662.5 \times \alpha_2{}^{\mathrm{H}} - 305.4 \quad R^2 = 0.976 \qquad (1)$$

Reduction potential shift as expressed by $|\Delta E_{1/2,\mathrm{red}}|$ can be explained by hydrogen-bond interaction between the sulfonylurea and **S-205**. In a reduction step of the sulfonylurea + **S-205** system, hydrogen-bond complex formed between lactone ring opened π-delocalized zwitterion originating from **S-205** and the sulfonylurea may be destabilized because reductive electron will be occupied in the antibonding frontier orbital comprised of the HOMO of the zwitterionic form of **S-205** and the LUMO of sulfonylurea (hydrogen-bond donor) as shown in Scheme 2. If frontier orbital interaction is so effective to lead to much more stabilization of the hydrogen-bond complex (High black color developing), the extent of destabilization in antibonding frontier orbital becomes larger. Simply speaking, if the zwitterionic form of **S-205** binds more strongly with sulfonylurea by hydrogen-bond interaction, it makes it more difficult to reduce thus stabilized hydrogen-bond complex, and the reductive half-wave potential of this hydrogen-bond complex shifts toward more negative potential in the presence of the sulfonylurea. Therefore, proper color developer sulfonylurea, which forms more stable hydrogen-bond complex with **S-205**, may well have large reductive potential shift $|\Delta E_{1/2,\mathrm{red}}|$ as shown in Scheme 2. Molecular orbital study on the hydrogen-bond complex (color developing complex) as shown in Scheme 1 supports the above explanation, and the calculated frontier orbital energy levels and the stabilized energy by forming hydrogen-bond complex were consistent with the results by cyclic voltammetry. The detailed calculation results will be reported soon.



Scheme 2. Frontier orbital energy diagram for **S-205** and sulfonylurea (SU) system. The left side shows frontier orbitals of the **S-205**, and the right side shows those of the sulfonylurea. The central part represents frontier orbital interactions between the HOMO of **S-205** and the LUMO of the sulfonylurea when black color developing complex (**CDC**) is formed by the hydrogen bond. In the case that high black color is developed in **CDC** (sulfonylurea with large $\alpha_2{}^{\mathrm{H}}$ value), reductive electron will be occupied in the LUMO of **CDC** with higher energy level by cathodic wave scan in the cyclic voltammetry experiment.

In conclusion, cyclic voltammetric study is useful and effective to monitor the formation of the color-developing complex stabilized by hydrogen bond and to carry out the molecular design of the functional thermal paper with high color developing and the durability of the developed color.

References and Notes

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6 All electrochemical experiments were performed on a HOKUTO DENKO HA-501 potentiostat. The electrolyte solution was prepared from NBu_4PF_6 using spectroscopic grade *N*,*N*-dimethylformamide (0.1 M). A three electrode configuration was used with a Pt black working electrode, a $Ag/AgNO_3$ reference electrode and a platinum wire as the counter electrode. Scan rate is set to be $50\,\mathrm{mV\,s^{-1}}$. O_2 was removed from the electrolyte solution by bubbling N_2 through the solvent for several minutes prior to making a measurement.

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