

Principle Investigation on Electrophoresis of Metal Complex Dyes*

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Abstract

Electrophoresis is one of the basic ways for electronic paper display. The pigment electrophoretic dispersion has been the widely used system. It is, however, worth of attention if molecular dye, instead of pigment, can be used in the display of electronic paper. By carefully selecting the structure of dye, fabricating the cell of display device and studying electrochemical reaction and accumulation of dyes in electrophoretic solution, we found that some dyes, especially metal complex dye could move in the device cell under relatively low bias voltage. The direction of movement was switched when the bias voltage changed its polarity and the display was thought of practical significance. This paper compares the pigment and dye electrophoretic systems and reveals the mechanism of dye electrophoresis in organic solvents.

Key Words: Metal Complex Dye Electrophoresis

Electrochemistry Reaction Driving Voltage

*The study is financially supported by Key Project Funding of Beijing Municipal Education Committee (KZ200610015008); **To whom correspondence should be addressed.

Introduction

The colloidal systems of organic /inorganic pigments dispersed in suitable suspension fluids are always selected as the display materials of electronic paper [1]. Although this display system has been used widely, the stability of the pigment dispersion is a big problem. Efforts in stabilizing the particles have been reported and micro-encapsulation has been proved very effective [2][3]. However, the display lifetime and performance are still affected by the aggregation of pigment particles. Currently, the most popular system used in electrophoresis image display (EPID) is the encapsulated suspension of surface-coated TiO_2 or organic pigments, which suffers of slow response, while being difficult to achieve color display. In addition, the microcapsules are easy to rupture as they are coated into single-layer membrane during fabrication. This decreases the density and contrast of display. Search for a stable and fast response display mechanism and system is, therefore, of significances.

Different from pigment, dye molecules tend to be either in a single molecule or molecular aggregation state when dissolved in solvent. The light fastness of most dyes is not enough, and the majority of the dark cored dyes are of direct dye's structure. They are difficult to be charged and suffer from fading in color when exposed to sunlight and limited outdoor lifetime. Metal complex dyes [4] are of better cover, higher light fastness, relatively darker color, and most importantly, they may generate charge density regional separation in electric field as could be anticipated from

their molecular structures and achieve dye electrophoresis in organic solvents. These characteristics may enable the dye-based electrophoresis-display higher density and contrast. This study is focused on the dissolving state of dyes in organic solvents and the electrophoresis dissolving dyes under the action of charge control agents (CCA). The electrophoresis principle of dye in organic solvent was studied in this paper, too.

1. Experimental

1.1 Redox reaction of dye in organic solvents in the process of electrophoresis

1.1.1 UV-vis absorption of the dye's solution in electrophoresis process

UV-Vis Spectral Abs curves of dye solution were recorded using UV-2101-PC from SHIMADZU. Red04 and anhydrous ethanol were used as the dye and solvent, respectively, and dye concentration was $2.2 \times 10^{-3} \text{ mol/l}$. Data were taken after the solution had been tested for electrophoresis under different voltage.

1.1.2 Electrochemical reaction of the dye solution during the electrophoresis process

Cyclic voltammeter curves of $2.2 \times 10^{-3} \text{ mol / L}$ Red04 and acidic black 1 (AB1) in anhydrous ethanol solution (concentration: $2.2 \times 10^{-3} \text{ mol/l}$) were recorded by LK2005 Electrochemical Workstation from Tianjin Lank like Chemical & Electron Co., Ltd.). Infrared spectra of dye solution were measured using FTIR – 8400 from SHIMADZU before and after electrophoresis experiment.

1.2 Measurement of dye aggregation in solution

Concentrations of alcohol solution of Red 04 (from We Zhou MeiErNou Chemical Engineering Co.,Ltd) and AB1 (Toggling Road Chemicals CO., Ltd) were 0.01 mol / l , 0.005 mol / l , 0.0025 mol / l , 0.00125 mol / l , 0.001 mol / l . Aniline was used as charge control agent and added to the acidic black 1 solution. Particle sizes of aggregated dyes in various concentrations were measured using a dynamic light scattering apparatus from Wyatt Technology Co. (Protein Solutions™, Dynapro Titan). 3 samples were prepared at each concentration and 3 data were taken for each sample, and then averaged particle size of aggregated dye molecules was calculated.

2. Results and Discussion

2.1 Electrochemical reaction of dye solution under the electrophoretic conditions

Fig.1 shows the cyclic volt-ampere curve (-2V to 2V) of Red 04 in ethanol ($2.2 \times 10^{-3} \text{ mol/l}$).

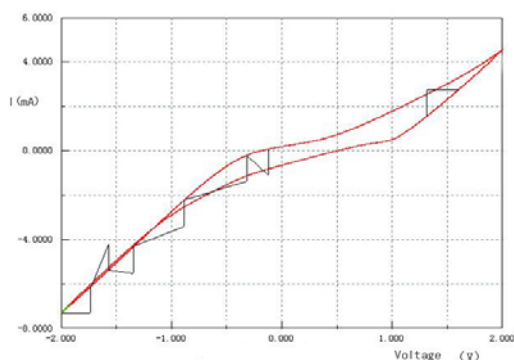


Fig.1 Cyclic volt-ampere curves of Red 04 in ethanol.

Generally speaking, no sharp changes in current can be observed in the cyclic volt-ampere curve unless the voltage reaches the point where electrochemical reaction happens between the electrode and the reactant. Apparent changes in current were observed over the entire range of voltage scanning (from -2V to +2V) and current peak appeared at about 1 V. For no symmetrical peak appeared during the reverse scanning. It is considered the redox reaction in this experiment was not reversible. It is considered that the redox voltage of Red 04 metal complex dye is about 1 V, and during the electrophoresis process of Red 04 in ethanol, the dye was changed into other products.

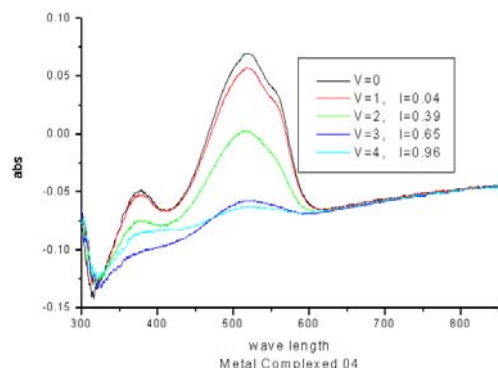


Fig.2 UV-Vis Spectra of Red 04 under different driving voltages

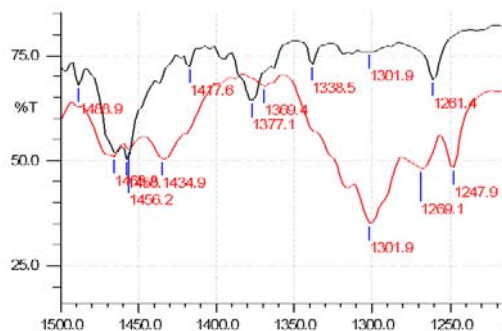


Fig.3 IR curves of Red 04 before (lower) and after (upper) electrophoresis

UV-Vis spectra of Red 04 ethanol solutions were taken under 5 different driving voltages, i.e., 0, 1, 2, 3 and 4 volts and shown in

Fig.2. The results indicated that the absorption peak at about 370nm, which was attributed to the absorption of azo compounds, decreased gradually with increasing driving voltage. These decreases were thought to have been caused by the decomposition of azo structure and provided the direct evidence that electrochemical reaction took place during the electrophoresis process. In order to identify the products in this reaction, IR spectra of the dye samples before and after electrophoresis were taken. It was found from the Fig.3 that new peaks at 1377.1, 1338.5, 1261.4 and 1465 cm⁻¹ were generated, while peaks at 1424.9, 1301.9, 1269.1 and 1247.9 cm⁻¹ disappeared after electrophoresis. As revealed by the data listed in table 1[5], it could be concluded that the main electrochemical products in this reaction were oxidized azobenzene, not hydrogenised azobenzene which was supposed the main product, i.e., reduced azo benzene when azo dye was involved in electrochemical reaction [6].

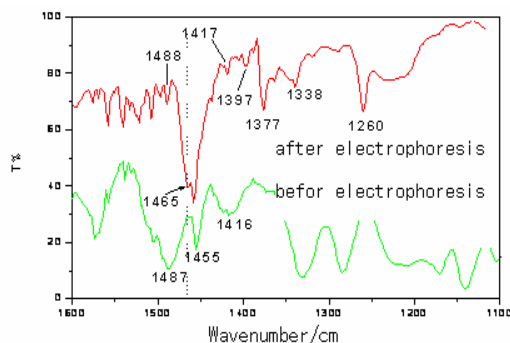


Fig. 4 IR spectra of AB1 before and after electrophoresis

Table 1 IR frequency some groups

Wavenumber ⁻¹ /cm ⁻¹	Groups
1468-1360 (vs) extend vibration	Ar-N=N-
1494.7 (vs) Obey extend vibration	
PV1558.4 (vs) Sym extend vibration	Ar-NO ₂
1332.7(s) Asym extend vibration	
1417.6(vs) anti henyl -C=N extension	Ar-N=N(→O)
1261-1377 extension N→O	

Based on the above study, and combined with the IR spectra of AB1 (Figure4), it was found that the 1465cm⁻¹, 1377cm⁻¹ characteristic peaks appeared obviously. They were due to the absorption of oxidized azobenzene. It was concluded that redox reaction of azo dye was not uncommon during electrophoresis in organic solution. Electrochemical activity of azo dye could not be eliminated, though its stability was greatly improved by metal complex.

2.2 Dye aggregation and electrophoresis mechanism in organic solvents

Table 2 Particle size of aggregated dye molecules

Table 2. Particle size of aggregated dye molecules						
C _{dye} ×10 ⁴ mol/L		100	50	25	13	10
AD	R04-A	99	89	134	100	84
	AB1-A A	76	82	74	47	65

C_{dye}: Concentration of dye solution; A:alcohol; AD: Average Diameter in nm; AA: acohol and aniline

Particle size of aggregated dye molecules did not deviate much among different data and samples at certain concentration, and their averages were given in the table above against dye concentrations. Red04 aggregates in different dye concentrations were fluctuated in size within a narrow range of between 84~100nm, except that at 0.0025 mol/l, which generated 134nm sized aggregates. And AB1 aggregates at different concentrations were distributed between 45~82nm.

Based on the above results, it could be concluded that the aggregated state of dye in organic solution was less influenced by its concentration. Intermolecular force between dye molecules was the major force driving dye molecules to aggregate, while intermolecular force between dye and solvent molecules tend to destroy or dissolving the aggregates. Particle size of aggregated dye molecules should be determined by the dynamic balance between the dissolving and aggregating forces. This was believed the reason why the dye molecules aggregation maintained in a certain range, less influenced by dye concentration.

Based on the chemical structure and bonding length of dye, the size of original Red 04 molecule is estimated to be about 5nm and that of the complex one could hardly exceed 10 nm because the complex ratio of Red04 is 1:2. As revealed by Table 2, the dye molecules in solvent were not singly isolated one, but aggregated clusters. So when dye moves in organic solvent directionally, it is in the aggregation state.

Louis acid-base reaction of charge control agents (CCA) is generally believed as the major process in which pigments particles distributed in the suspension are charged, and the charged pigment particles move directionally when bias voltage is applied [7]. In the case of AB1, Louis acid-base reaction was believed to progress between aniline and dye molecules. As a result of this reaction, the dye aggregates became charged and electrophoresis took place when bias voltage was applied. Red 04 was, however, different, because no CCA was added. Charging of the dye aggregates were believed to have come from the clustered individual dipoles of the molecules under the action of electrical field generated by the bias voltage.

The aggregated day molecules would have two different conditions, i.e., closely packed or loosely packed. In the c loosely packed structure, the aggregates uld b in a meta- stable state, and as a result, the cluster structure and surface charges of the aggregates were not stable. This would affect the electrophoresis speed and was believed to be responsible for the low response speed of the dye in

electrophoresis. The response speed was even lower than pigment based electrophoresis systems. This difference was believed to have come from the different mass carried by the moving unite during the electrophoresis process. Pigment based systems were of much bigger particle size, usually around 500 nm and much stronger light reflection and absorbing capabilities in addition, resulted in faster displaying response.

3. Conclusion

Dye electrophoresis is realized in organic solution. It is found that the charging principle of dye changes according to the molecular structure. And the dye electrophoresis principle is not the same as pigment dispersion. The self charge excursion of metal complex dye, lead to the imbalance of dye congeries under the driving voltage.

The oxidation azobenzene was produce in the electrochemical reaction during Red 04 electrophoresis in alcohol. So did the azo group oxidized in Acid Black1 organic solution.

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Author Biography

Lu-hai LI received his BS in fine chemicals from the University of Tianjin (1985) and her PhD in applied chemistry from Dalian University of technology (2004). Since then he has worked in the Beijing Institute of Graphic Communication. His work has focused on the development of functional print material. & information recording material. He is a professor and a senior engineer.