NOTES Bull. Chem. Soc. Jpn., 57, 2005—2006 (1984)

The Adsorption Behavior of Monoionic Dyes at the Aqueous Solution/Air Interface

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(Received January 5, 1984)

Synopsis. The surface tension of the aqueous solutions of six dyes have been measured as a function of dye concentration at 298.15 K under atmospheric pressure. The adsorbed films of four azo dyes have been found to transform from the gaseous phase to the expanded phase. The relation between the molecular structure of dye and the state of the adsorbed film has been discussed by making use of the surface pressure *vs.* mean area curve.

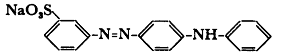
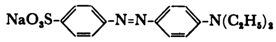
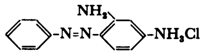
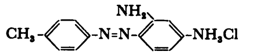
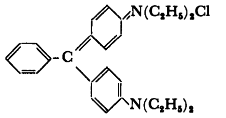
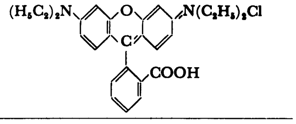
It is necessary to have a detailed knowledge of the adsorption behavior of dyes at interfaces in order to understand the dyeing process on fibers. Properties of the adsorbed films of dyes, however, have been scarcely clarified. The purpose of this paper is to obtain information about the adsorption behavior of dyes at their aqueous solution/air interface and about the effect of the molecular structure of dyes on it. The surface tension of the aqueous solutions of dyes, which have different molecular structures, was measured and analyzed by making use of thermodynamic equations.

Experimental

The dyes used in the present study are summarized in Table 1. The commercially available dyes, except for Ethyl Orange and 2,4-diamino-4′-methylazobenzene chloride (DAM), were used by the recrystallization from distilled water and then ethanol several times. Ethyl Orange was prepared by coupling diazotized sulfanilic acid with *N,N*-diethylaniline and then recrystallized from distilled water and ethanol. DAM was synthesized by the coupling of *m*-phenylenediamine and diazotized *p*-toluidine according to the usual way and recrystallized from the aqueous solution of 1% hydrochloric acid. Water was twice distilled from alkaline permanganate solution.

The surface tension was measured by the drop volume method with a precision better than 0.05 mN m^{-1}.[1] The drop was stood for about 15 min to reach the adsorption equilibrium.

TABLE 1. C. I. NUMBER AND STRUCTURAL FORMULA OF DYE

	Dye	C. I. Number	Structural formula
(1)	C. I. Acid Yellow 36	C. I. 13065	
(2)	Ethyl Orange		
(3)	C. I. Basic Orange 2	C. I. 11270	
(4)	DAM[a)]		
(5)	C. I. Basic Green 1	C. I. 42040	
(6)	C. I. Basic Violet 10	C. I. 45170	

a) 2,4-Diamino-4′-methylazobenzene monohydrochloride.

Results and Discussion

The surface tension γ *vs.* molality of dye m_1 curves are shown in Fig. 1. It is seen that γ decreases with increasing m_1. However, it should be noted that the γ *vs.* m_1 curves of Ethyl Orange, C. I. Basic Orange 2, DAM, and C. I. Acid Yellow 36 consist of two portions, *i.e.*, the linear one with a small slope and the curved one with a relatively large slope. Such a break point on the curve has been observed in the cases of various surfactants.[1,2] It has been proved thermodynamically that the adsorbed film of the surfactant transforms from a gaseous to an expanded phase at the concentration of the break point.[1,2] It may be said, therefore, that the phase transition takes place in the adsorbed films of these azo dyes.

On the other hand, the γ values of the aqueous solutions of C. I. Basic Green 1 and C. I. Basic Violet 10 decrease monotonously with increase in m_1. Moreover, the γ *vs.* m_1 curve of C. I. Basic Violet 10 seems to approach a constant value. Taking into account that a large number of dyes associate to form aggregates in their aqueous solution,[3–6] the shape of the γ *vs.* m_1 curves can be attributed to the formation of aggregates. It is concluded, therefore, that the adsorbed films of C. I. Basic Green 1 and C. I. Basic Violet 10 are not attended by the phase transition within the present concentration range.

To clarify the state of adsorbed films, it is advantageous to evaluate the surface density of dye molecules. According to the thermodynamics,[1] the surface excess number of moles per unit area of a dye $\Gamma_1^{\rm H}$ can be

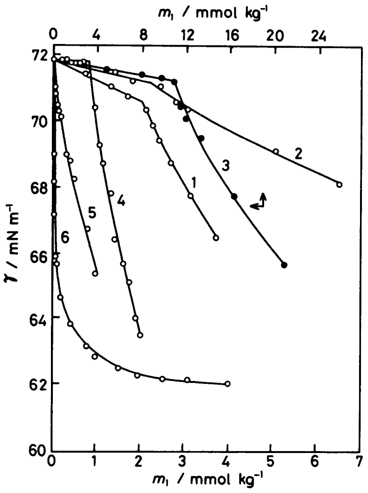


Fig. 1. Surface tension *vs.* molality curves of six dyes at 298.15 K.
1: C. I. Acid Yellow 36, 2: Ethyl Orange, 3: C. I. Basic Orange 2, 4: DAM, 5: C. I. Basic Green 1, 6: C. I. Basic Violet 10.

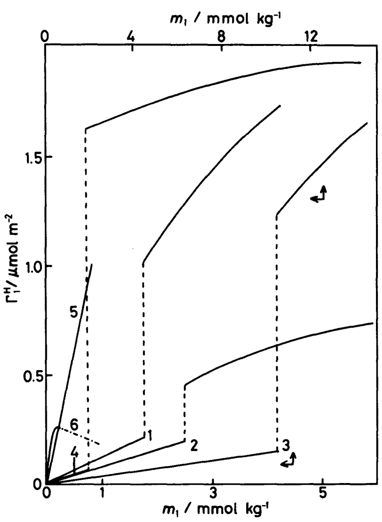


Fig. 2. Surface density *vs.* molality curves of six dyes at 298.15 K.
1: C. I. Acid Yellow 36, 2: Ethyl Orange, 3: C. I. Basic Orange 2, 4: DAM, 5: C. I. Basic Green 1, 6: C. I. Basic Violet 10.

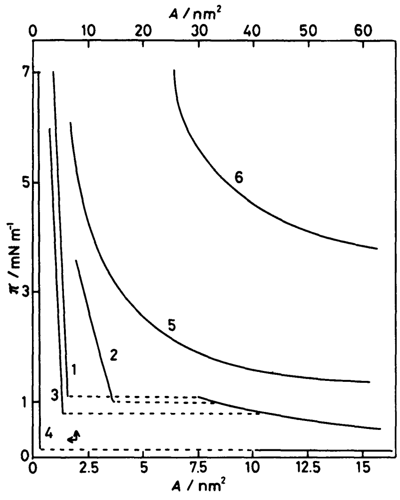


Fig. 3. Surface pressure *vs.* mean area curves of six dyes at 298.15 K.
1: C. I. Acid Yellow 36, 2: Ethyl Orange, 3: C. I. Basic Orange 2, 4: DAM, 5: C. I. Basic Green 1, 6: C. I. Basic Violet 10.

calculated by the following equation:

$$\Gamma_1^H = -m_1(\partial\gamma/\partial m_1)_{T,p}/2RT, \qquad (1)$$

where R is the gas constant. Shown in Fig. 2 are the surface density *vs.* molality curves at 298.15 K under atmospheric pressure. It is seen that the values of Γ_1^H increase with increasing m_1 except for C. I. Basic Violet 10. The fact that the Γ_1^H *vs.* m_1 curve of C. I. Basic Violet 10 has a maximum is explicable by the nonideality of its aqueous solution,[7] which results from the formation of the aggregates. As is expected, the discontinuous change in Γ_1^H is observed for the dye which has the break point on γ *vs.* m_1 curve in Fig. 1. This fact confirms that the phase transition takes place in the adsorbed films and, taking into account that the surface tension is equivalent to the Gibbs free energy, it is the first order. The surface pressure π *vs.* the area per adsorbed molecule A curve is useful to elucidate the state of adsorbed film. Here, $\pi=\gamma^0-\gamma$ and $A=1/N_A\Gamma_1^H$, where γ^0 is the surface tension of pure water and N_A Avogadro's number. The results are shown in Fig. 3. It is seen that the π *vs.* A curves of the azo dyes are a typical one attended by the phase transition. Taking into account that the values of the transition pressure and area are comparable to those of the surfactants,[1,2] the phase transition can be said to take place from a gaseous state to an expanded state. On the other hand, the π *vs.* A curves of C. I. Basic Green 1 and C. I. Basic Violet 10 at 298.15 K are found to be a two-dimensional isotherm at a temperature higher than the critical temperature of the phase transition between gaseous and expanded states.

It should be noted that the azo dyes differ significantly from one another in the A value of the expanded film. However, the order of the A value is found to be the same as that of the transition pressure value except for Ethyl Orange. Taking into account that the molecules of these dyes are linear and similar in cross sections, this order represents that of the strength of the intermolecular interaction in the adsorbed film. A large value of A for Ethyl Orange may be attributable to the bulky diethylamino substituent. On the other hand, since the molecules of C. I. Basic Green 1 and C. I. Basic Violet 10 have nonlinear structures, their intermolecular interactions at the surface are too weak to cause the phase transition from the gaseous film to the expanded film.

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