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A. V. Baranov^a; A. P. Moryganov^a

^a Academy of Sciences, Institute of Non-Aqueous Solution Chemistry of the USSR, Ivanovo, Russia

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Regulation of the Plasticizing Ability of Intensifiers: A New Method to Dye Polyester Fibers

A. V. BARANOV and A. P. MORYGANOV

*Institute of Non-Aqueous Solution Chemistry of the USSR Academy of Sciences,
1, Akademicheskaya str., Ivanovo, 153045, Russia*

The interrelation between the state of dyeing intensifiers in the presence of a series of inorganic salts and the effectiveness of their plasticizing action on polyester fiber has been studied by the methods of electron and vibration spectroscopy and thermomechanical analysis. The expediency of application of "intensifier-inorganic salt" mixture to fixation of disperse dyes by polyester fiber under the conditions of continuous and periodic dyeing is illustrated by the examples of benzyl alcohol and biphenyl.

KEY WORDS Polyester fiber, dyeing, plasticifiers.

INTRODUCTION

Chemico-technological treatments of fibrous materials in dyeing-finishing productions and dyeing in particular is based on the transition of fiber-forming polymer from glassy to highly elastic state. In most cases this transition is carried out in the presence of the compounds that possess plasticizing effect on fiber. So, for instance, such compounds as biphenyl¹ and benzyl alcohol² are applied as intensifiers to dyeing of polyester-containing textile materials.

It is noteworthy that the compounds mentioned for this or that reason possess a considerable inclination to self-association, i.e. in solution there is an equilibrium between mono-molecular and associated forms of the state of a compound. Intensifier self-association decreases its plasticizing ability with respect to fiber, since only the mono-molecular form of the intensifier is active.³

It is known⁴ that a solution of inorganic salts in the solvents containing molecular associates is accompanied on the one hand by destruction of a portion of associates, and on the other by bonding of molecules by ions (formation of solvates). Both processes proceed simultaneously and are mutually conditioned.

The present paper is aimed at establishing the interrelation between the state of the dyeing intensifiers in the presence of a series of inorganic salts and the plasticizing ability of intensifiers with respect to polyester fiber, as well as perfection on these bases of the periodic and continuous methods of dyeing of textile materials.

EXPERIMENTAL

Benzyl alcohol, biphenyl and inorganic salts used in this work were reagent-grade chemicals. Acetonitrile was dried thoroughly according to a technique mentioned elsewhere.⁵ As the object of the present investigation, polyester fiber was used as complex thread consisting of 39 filaments 20 microns thick. Textured polyester thread and polyester fabric were also used when performing the dyeing experiments. Before the tests the fiber was purified from lubricant using either in Soxlet apparatus with carbon tetrachloride, or using the aqueous solution of surface-active washing agent with 2 g/l concentration at 313 ± 5 K. UV-absorption spectra of the solutions of benzyl alcohol and biphenyl were registered on spectrophotometer "Specord M40" (Carl Zeiss Jena, Germany) using quartz cuvette with an absorption layer 10 mm thick. IR-absorption spectra were registered on "Specord M/80" spectrophotometer (Carl Zeiss Jena, Germany) using KBr cuvette with an absorption layer 0.058 mm thick.

The plasticizing ability of the solutions investigated with respect to polyester fiber was evaluated from the value of thread shrinkage in solution after 600 sec of treatment at 343 ± 0.5 K.

Polyester fibers were dyed by technical disperse dyes by the continuous and periodic methods. At continuous dyeing, disperse dyes were fixed on fiber in the vapor of an azeotropic mixture of "benzyl alcohol-water" for 180 sec at 373 K. Periodic dyeing of textured polyester thread was performed according to the isothermic high-temperature method "Rapid-Color."

RESULTS AND DISCUSSION

Figure 1 shows UV-absorption spectra of $4 \cdot 10^{-3}$ M solutions of benzyl alcohol in water, as well as in solutions of chlorides of the alkali and alkali-earth metals with

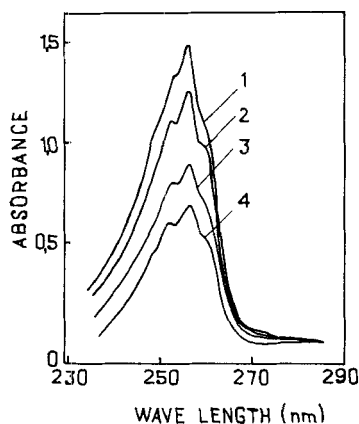


FIGURE 1 Influence of inorganic salts on the spectrum of aqueous solution of benzyl alcohol ($4 \cdot 10^{-3}$ M): 1— NH_4^+ ; 2— Ca^{2+} ; 3—Without salt; 4— Al^{3+} .

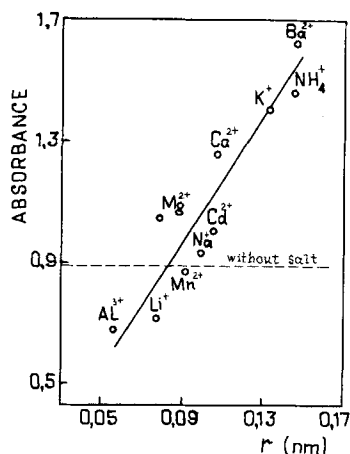


FIGURE 2 Correlation between the magnitude of salt cation radius and optic density ($\lambda = 257$ nm) of $4 \cdot 10^{-3}$ M solution of benzyl alcohol.

0.5 M concentration. The figure shows that the optic density of benzyl alcohol solutions changes considerably in the presence of salts. The change in benzyl alcohol absorption intensity without the shift in the absorption bands is evidently determined by changing association degree of benzyl alcohol in solution. The correlation analysis carried out has shown that there is a linear dependence between the intensity of 257 nm band corresponding to π - π^* transition in benzene ring and cationic radius (Figure 2). When analyzing the dependence between the salt cation radius and the optic density of benzyl alcohol solution, two observations attract attention: first, one group of cations (in particular, NH_4^+ , K^+ , Ba^{2+}), decreases the association degree of benzyl alcohol, and the other (Al^{3+} , Li^+) increases it; secondly, the composition of these groups corresponds almost entirely to the gradation of cations judging by their influence on water structure,⁶ viz., the first group exerts the structure-breaking, and the second, the structure-ordering action.

The magnitude of shrinkage of complex polyester thread in benzyl alcohol and in saturated solutions of salts in benzyl alcohol at 70°C was defined to evaluate the influence of the association degree of benzyl alcohol on its plasticizing ability with respect to polyester fiber. The analysis of the results obtained has shown a good correlation between the magnitude of the thread shrinkage and the values of the optic density of benzyl alcohol solutions that contain the chlorides of alkali and alkali-earth metals (Figure 3).

Studies on the influence of halide-ion on the state of benzyl alcohol were performed using the method of vibration (IR-) spectroscopy, since I^- and Br^- anions absorb in the same region of UV-spectrum as benzyl alcohol. The processes of association in liquids are investigated by the vibration spectroscopy method proceeding from the comparison between the frequencies and integral intensities of the bands of the stretching vibrations of the functional groups of non-associated molecules and the respective characteristics of these bands in complexes. A monomolecular form of benzyl alcohol was obtained in diluted solutions of aprotic solvent-acetonitrile, since when used as the medium, this solvent allows with sufficient approximation for the transfer of results obtained on aqueous solutions,

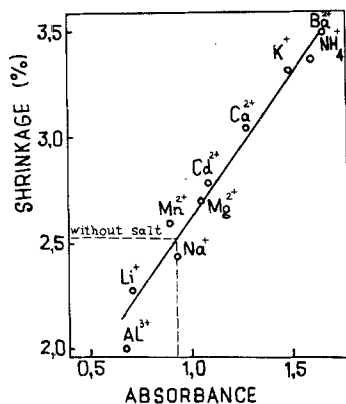


FIGURE 3 Interrelation between the optic density of benzyl alcohol and its plasticizing ability with respect to polyester fiber.

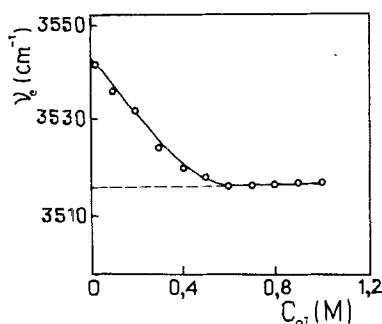


FIGURE 4 Influence of benzyl alcohol concentration in acetonitrile on the frequency of stretching vibrations of bonded OH-groups.

because hydrogen bonding water-acetonitrile is, judging by its energy, similar to hydrogen bonding between water molecules.⁴

Figure 4 shows the influence of benzyl alcohol concentration in acetonitrile on the position of the band of the stretching vibrations of the alcohol hydroxyl groups that are connected by hydrogen bond (ν_C) either to each other ($\nu_{C-C} = 3516 \text{ cm}^{-1}$) or to acetonitrile molecules ($\nu_{C-A} = 3544 \text{ cm}^{-1}$).

The figure shows that with increasing benzyl alcohol concentration there is a gradual displacement of the band of the stretching vibrations of hydroxyl groups towards lower frequencies; this is an indication of the increase of the ratio of more stable associates "benzyl alcohol-benzyl alcohol" in the system "benzyl alcohol-acetonitrile."

When introducing inorganic salt into the benzyl alcohol solution, the change in the ratio of associates "benzyl alcohol-benzyl alcohol" occurs; this influences the intensity of ν_{C-C} band.

Figure 5 shows the influence of anionic radius on the intensity of ν_{C-C} band of 0.5 M solution of benzyl alcohol in acetonitrile and on the plasticizing ability of benzyl alcohol with respect to polyester fiber. As the figure shows, the change in

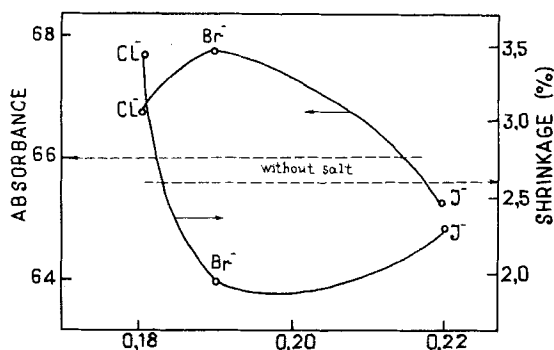


FIGURE 5 Interrelation between the magnitude of anionic radius, optic density of 0.5 M solution of benzyl alcohol in acetonitrile and plasticizing ability of saturated solutions of potassium halides in benzyl alcohol with respect to polyester fiber.

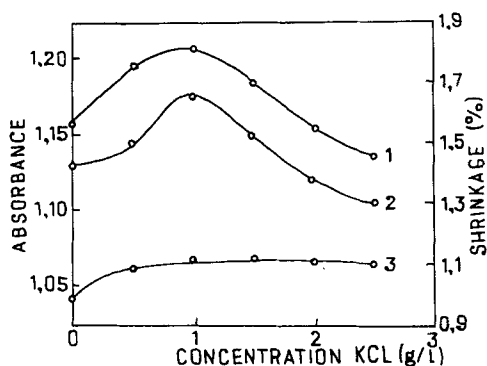


FIGURE 6 Influence of KCl on the optic density ($\lambda = 249$ nm) (1) and on plasticizing ability with respect to polyester fiber of 10^{-4} M aqueous solution of biphenyl (2) and water (3).

the plasticizing ability of benzyl alcohol in the presence of salt is inversely proportional to the change in the content of benzyl alcohol self-associates.

One can thus assume that it is possible to change the association degree of alcohol, and change its plasticizing ability with respect to polyester fiber over a very wide range by way of introduction of this or that inorganic salt into benzyl alcohol solution. The analysis of the results obtained shows that of the inorganic salts studied, BaCl_2 , NH_4Cl , KCl possess the highest activating action on benzyl alcohol. Taking into account the high activating action of these salts on benzyl alcohol, they are proposed to be used as intensifiers of the continuous method of fixation of disperse dyes on polyester fiber; this method is based on application of the vapor of boiling azeotropic mixture "benzyl alcohol-water" as the fixing medium.⁷ Investigation of the influence of inorganic salts on the fixation of disperse dye on polyester fabric has shown that the amount of the dye fixed on fiber under the condition of short-term (3 min) treatment increases by 10–15% after introduction of 15–20 g/l of NH_4Cl or KCl into the padding bath.

Uneven dyeing and, as a consequence, lower quality of textile consumer goods,

is the main difficulty resulting from the periodic dyeing of textured polyester threads in packs. To improve the evenness of dyeing of textured polyester threads in practice, the substances possessing the plasticizing action on fiber and favoring redistribution of dye are used. A preparation of the base of biphenyl (Remol HT) is in particular used as such a leveling agent.

Investigation of KCl influence on the optic density of 10^{-4} M solution of biphenyl in UV-region ($\lambda = 249$ nm) and on the plasticizing ability of this solution with respect to polyester fiber has shown (Figure 6) that, similar to the system "benzyl alcohol-inorganic salt," the change in the plasticizing ability of biphenyl in the presence of inorganic salt correlates with the change in the association degree of biphenyl in solution. Investigation of the influence of the chlorides of alkali metals on the state of Remol HT solution in water ($C = 1$ g/l) has shown that the majority of the salts studied increases the plasticizing ability of Remol HT with respect to polyester fiber, the optimum ratio between Remol HT and inorganic salt being unique for every case. A series of compositions for the periodic dyeing of complex polyester thread according to isothermic high-temperature method "Rapid-Color" is proposed on the basis of the completed investigation. The industrial tests on the dyeing of complex polyester thread have shown that application of mixed intensifier "Remol HT-inorganic salt" decreases the output of rejects by 1.4–1.6 times with a simultaneous one-half decrease in Remol HT expenditures.

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