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Diffusion-limited sorption of dyes on modified acrylics and acrylic copolymers

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Acrylonitrile was polymerized using a redox system. The polyacrylonitrile was modified by heating with aqueous 50% H_2SO_4 or with aqueous 50% NaOH. Acrylonitrile was also copolymerized with acrylic acid or acrylamide or methylenebisacrylamide using a redox system. The sorption abilities of the modified acrylics and copolymers were determined from aqueous solutions of two dyes, namely methylene blue and alizarin yellow R. The porous structure of the polymers was determined by using mercury porosimetry. The experimental results of the dye uptake were theoretically treated by using a diffusion-limited adsorption method. The equation was applied for short reaction times and the parameters were graphically determined from log–log plots: the specific rate constant k' from the intercept A and the parameter n ($0 < n < 1$) from the slope. The diffusion coefficient D was calculated from Fick's equation. The results were discussed taking into consideration the pore structure of the polymers as well as the 'pore model' and the 'free volume model' of the diffusion process. The electron donor–acceptor interactions between the functional groups of the polymers and the functional groups of the dyes strongly influence the sorption process.

(Keywords: modified acrylics; acrylic copolymers; sorption)

INTRODUCTION

Acrylic polymers or copolymers are used as fibres, sorbents (e.g. crosslinked porous copolymers and acrylonitrile and divinylbenzene) or flocculants (e.g. polyacrylamides or acrylic acid–acrylamide copolymers)[1-3]. It is difficult to resolve the morphology of polyacrylonitrile (PAN) as it belongs to the category of neither conventionally amorphous nor semicrystalline polymers. It has been suggested that PAN consists of (1) one phase combining some of the properties of both crystalline and amorphous phases, (2) two different amorphous phases with various types of secondary intermolecular forces and of one crystalline phase, and (3) three phases, namely amorphous, paracrystalline and crystalline[4,5]. PAN fibres have poor 'dyeability' because of their high degree of ordering and the orientation of molecular nitrile groups leading to a lack of segmental mobility which makes the penetration of dye molecules difficult. These problems are overcome by copolymerization of acrylonitrile with one or two comonomers. The accessibility of the reactive sites presented in the copolymer also depends on its glass transition temperature (T_g), so that the temperature of the dye bath plays an important role in dyeing acrylic fibres[6,7]. On the other hand, the hydroscopicity of acrylic fibres is also improved[7] by the thermal hydrolysis of acrylonitrile copolymers with 75% H_2SO_4 or 65% HNO_3.

Various electrolytes influence the dyeing rate and the sorption isotherms of some cation dyes on PAN fibres. The influence of pH and ionic strength on equilibrium sorption has been mathematically described based on the Donnan approach[8-10]. The influence of dye size and fibre porosity on the dyeing kinetics in the uptake of cationic dyes on acrylic fibres has been described[11] based on the $t^{1/2}$ plot method. The fraction f of the dye taken at various time intervals $[D_f]_t$ relative to the amount of the dye taken at equilibrium $[D_f]_\infty$ was plotted as a function of the square root of the dyeing time t, below or at the boiling point of buffer solutions. The apparent diffusion coefficients D_{app} were calculated taking into consideration the average diffusion path length L, which is determined from photomicrographs of cross-sections of fibres.

Dyeing kinetics are directly related to diffusion. The dyeing rates can be expressed by exponential converging binomial series. Similar equations have been applied in diffusion-limited enzyme reactions, adsorption on proteins, as well as in diffusion-limited sorption in textile materials[12]. This method is described in the Theoretical section.

Recently[13], structurally modified PAN (not as fibres) has been investigated for its ability to adsorb dyes from aqueous solutions and the results are interpreted in terms of electron donor–acceptor (EDA) interactions between the main groups of the polymers and the dyes. The aim of this work is to investigate the dye uptake on modified acrylics and acrylic copolymers (not as fibres) in order to determine the kinetic parameters. Methylene blue (having electron donor groups) and alizarin yellow (having mainly electron acceptor groups) are chosen as dyes. The dyes were used in aqueous solution without buffer. Such investigations could contribute to the design of new polymer materials based on acrylics with increased sorption ability.

EXPERIMENTAL

Production method

Acrylonitrile after appropriate washing, drying and distillation under vacuum for removal of inhibitor and purification, was polymerized using a redox system at 20°C under N_2. This system consisted of a 5% aqueous solution of $K_2S_2O_8$ (oxidizing agent), 0.01 g of $FeSO_4.7H_2O$ in 100 ml of H_2O and 2 ml of concentrated H_2SO_4 (reducing agent based on $FeSO_4$), and a 5% aqueous solution of $Na_2S_2O_5$ (second reducing agent). The polymer was precipitated with methanol, followed by filtration, washing with distilled water and drying at 50°C.

The PAN was modified with an aqueous solution of 50% H_2SO_4 for 2 h at 90°C or with an aqueous solution of 50% NaOH for 45 min at 90°C. The modified polymer was obtained by filtration, washed with distilled water and dried at 50°C.

The copolymerization of acrylonitrile with acrylic acid or acrylamide or methylenebisacrylamide follows, generally, the procedure described for the homopolymerization of acrylonitrile using a redox system. Details of the polymerization method as well as the characterization of products are referred to elsewhere[13].

Characterization of the polymer products

The sorption abilities of modified acrylics or copolymers were determined from aqueous solutions of two dyes, namely methylene blue and alizarin yellow R, with initial concentrations of 0.0320 g l^{-1}. For this determination a certain amount of the polymer was mixed with a known amount of an aqueous solution of the dye at 25°C without stirring during the adsorption process. The colour of the solution was determined after various time intervals by using a colorimetrical calibration scale and the colorimeter Lovibond Tintometer model E.

The porous structure of the polymers was determined using the mercury porosimetry (Porosimeter 2000/ Milestone 200). The capillary radius was 1.5 mm, the dilatometer volume 15 cm^3, the maximum pressure 200 MPa and the calculation model was based on the cylindrical approach of pores.

THEORETICAL

Diffusion rates in simple geometric shapes can be obtained for a variety of initial and boundary conditions from Fick's differential equation in the form of trigonometric or other series. However, even in simple geometric shapes, the calculation of diffusion rates from these infinite series is laborious due to the individual members of the series which often converge to zero slowly. It is more difficult to describe the diffusion rates in more complex, irregular or porous structures. It has been found that, for diffusion-limited sorption in textile materials and other diffusion-limited systems, the diffusion rates can be accurately expressed by exponential converging binomial series[12]. The following equation can be written:

$$a = A_e[1 - \exp(-kA_0t)]^n \quad (1)$$

where a is the sorption in time t, A_e is the equilibrium sorption (at $t \to \infty$), A_0 is the concentration of a sorbent, k is the specific rate constant and n is the heterogeneous structural diffusion resistance constant ($0 < n < 1$).

Rearrangement of equation (1) yields:

$$-kA_0t = \ln[1 - (a/A_e)^{1/n}] \quad (2)$$

For a low value of parameter t, the ratio a/A_e is low, so that expanding the right-hand side of equation (2) into a Taylor series and neglecting higher order terms, the following equation is obtained:

$$kA_0t = \sim(a/A_e)^{1/n} \quad (3)$$

Setting in equation (3), $t = 1$ min and $A = a(t = 1)$:

$$k' = kA_0 = \sim(A/A_e)^{1/n} \quad (4)$$

where k' is the rate constant, A is the intercept at $t = 1$, ($A = a$ at $t = 1$), n is the slope and A and n are determined by plotting log a *versus* log t.

For short reaction times, Fick's equation for a cylinder can be approximated:

$$D = (\pi r^2/16t)(a/A_e)^2 \quad (5)$$

where D is the diffusion coefficient and r is the radius of the cylinder.

Comparing equation (5) with equation (4) (for $t = 1$ min) the following equations result:

$$D = (kA_0)^{2n}(\pi r^2/16) \quad (6)$$

$$D = (k')^{2n}(\pi r^2/16) \quad (7)$$

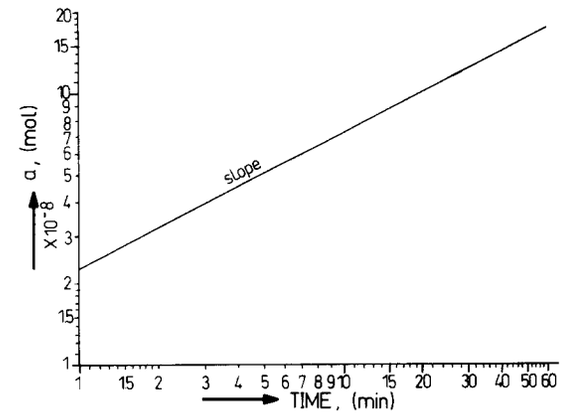

Figure 1 Plot of sorbed dye (a) *versus* time (t) for the graphical determination of n (from the slope) and A (from the intercept at $t = 1$)

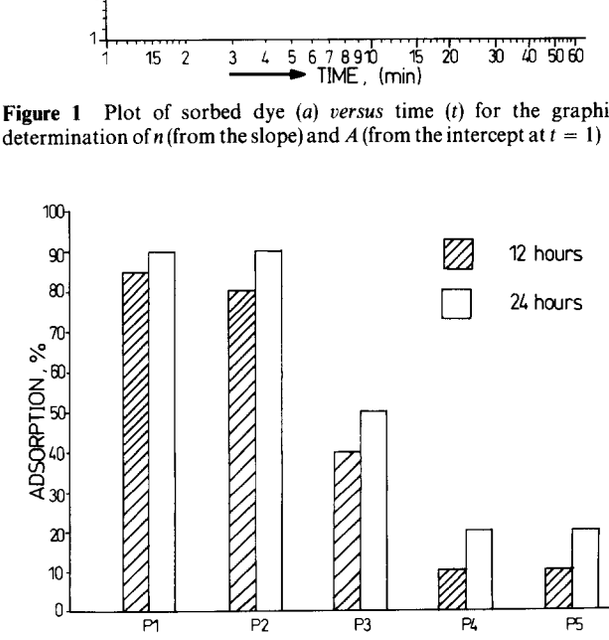

Figure 2 Sorption of methylene blue from aqueous solution on modified acrylics and acrylic copolymers in 12 and 24 h. (The sorption is calculated as $(X/X_0) \times 100$, where X is the sorbed amount of dye and X_0 is the initial amount of dye in the solution before sorption. For P1–P5, see *Table 1*)

This model was applied for short reaction times and the parameters were determined graphically (*Figure 1*) from the log–log plots of sorbed dye and time t: the parameter A (mol) was obtained from the intercept at $t = 1$ and the parameter n from the slope. The rate constant k' was determined from equation (4). The diffusion coefficient D was calculated from equation (7) assuming a radius of $r = 0.0010$ cm (denoted by D_0)[12] or according to the pore radius average (denoted by D_a).

RESULTS AND DISCUSSION

Table 1 refers to the production conditions of modified acrylics and acrylic copolymers. The dye uptake of polymers for the aqueous solutions of methylene blue and alizarin yellow in 12 and 24 h is represented in *Figures 2* and *3*, respectively. The dye uptake is increased with increasing time for the corresponding polymers. The methylene blue uptake is increased according to the order of polymers: P1 > P2 ≫ P3 > P4, P5. The alizarin yellow uptake is increased according to the order of polymers: P1 > P5 > P4 > P2 ≫ P3.

Table 2 shows the results according to the described theoretical treatment for the adsorption of methylene blue and alizarin yellow on the polymers. It can be noticed that the dye uptake is generally increased by decreasing value of n and increasing values of A, k' and D_0. In particular, for increasing values of the parameter

Table 1 Modified acrylics and acrylic copolymers

No.	Symbol	Modification	Copolymerization
1	P1	PAN modified with 50% H_2SO_4	
2	P2	PAN modified with 50% NaOH	
3	P3		Acrylonitrile and acrylic acid
4	P4		Acrylonitrile and acrylamide
5	P5		Acrylonitrile and methylene-bisacrylamide

Shape of products: P1, very fine powder; P3, powder ($\Phi = \sim 63\ \mu m$); P2, P4, P5, grains ($\Phi = \sim 1.0$ mm)

Table 2 Kinetic constants of modified acrylics and acrylic copolymers

No.	Symbol	Dye	n	A (mol) ($\times 10^{-8}$)	k' (min^{-1}) ($\times 10^{-2}$)	D_0 ($cm^2\ s^{-1}$) ($\times 10^{-10}$)
1	P1	MB	0.41	5.50	0.8780	1.40500
2	P2	MB	0.34	3.40	0.1150	1.21000
3	P3	MB	0.64	0.23	0.0260	0.00026
4	P4	MB	0.58	0.14	0.0050	0.00017
5	P5	MB	0.58	0.14	0.0048	0.00016
6	P1	AY	0.38	10.65	1.3600	3.330000
7	P2	AY	0.55	1.70	1.3900	0.196000
8	P3	AY	0.70	0.03	0.0045	0.000005
9	P4	AY	0.40	2.50	0.0430	0.140000
10	P5	AY	0.30	3.50	0.0100	0.669000

MB, methylene blue; AY, alizarin yellow; P1, P2, P3, P4, P5, see *Table 1*; n, A, k', D_0, see equations in the Theoretical section

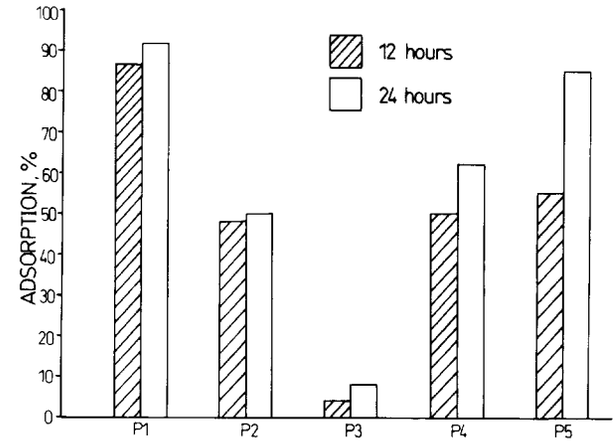

Figure 3 Sorption of alizarin yellow from aqueous solution on modified acrylics and acrylic copolymers in 12 and 24 h

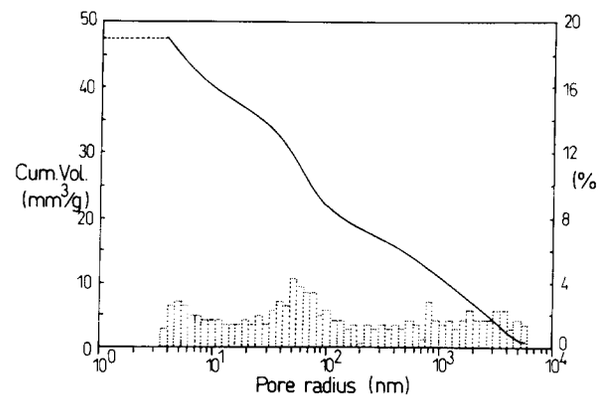

Figure 4 Pore size distribution of polymer P2 (see *Table 1*)

Table 3 Porosimetry characteristics and diffusion coefficient D_a of modified acrylics and acrylic copolymers

No.	Symbol	Total cumulative volume ($mm^3\ g^{-1}$)	Specific surface area ($m^2\ g^{-1}$)	Pore radius average (PRA) (nm)	Dye	D_a calculated with PRA ($cm^2\ s^{-1}$) ($\times 10^{-14}$)
1	P1[a]			(53)	MB	0.613000
2	P2	48	4.0	53	MB	0.703000
3	P3	1.095	4.4	422	MB	0.004700
4	P4	280	18.3	38	MB	0.000250
5	P5	14	3.0	9	MB	0.000001
1	P1[a]			(53)	AY	0.495000
2	P2	48	4.0	53	AY	0.000267
3	P3	1.095	4.4	422	AY	0.000093
4	P4	280	18.3	38	AY	0.021670
5	P5	14	3.0	9	AY	0.005410

[a]Very fine powder. Impossible to be measured by mercury porosimetry. Accepted value in parentheses for the PRA as for the other modified polymer (P2)

A, the polymers follow the same order shown above for both dyes.

Figures 4–7 are graphs of the pore size distribution of the polymers. The pore size distribution of P2 (*Figure 4*) is very broad compared to the copolymers P3 (*Figure 5*), P4 (*Figure 6*) and P5 (*Figure 7*) having narrow pore size distribution. Such narrow pore size distribution is also observed for PAN which was not treated with acid or base.

Table 3 presents the porosimetry characteristics as well as the diffusion coefficient D_a for methylene blue and alizarin yellow calculated with the pore radius average. It must be mentioned that the measurement of the pore structure of the polymers was quite difficult due to their powder form and their higher compressibility compared to pressed specimens.

The diffusion coefficient D is strongly dependent on the radius of the cylinder r of the approximated Fick's equation, equation (5), and the corresponding equation, equation (7). Different considerations concerning the type and the values of r have been referred to in the literature.

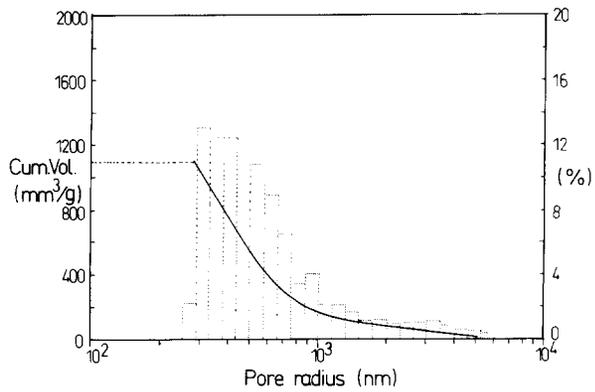

Figure 5 Pore size distribution of polymer P3 (see *Table 1*)

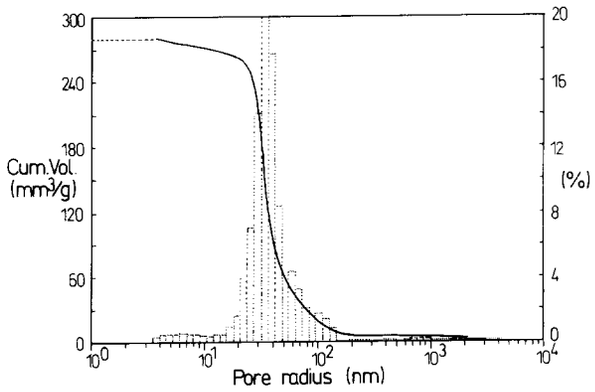

Figure 6 Pore size distribution of polymer P4 (see *Table 1*)

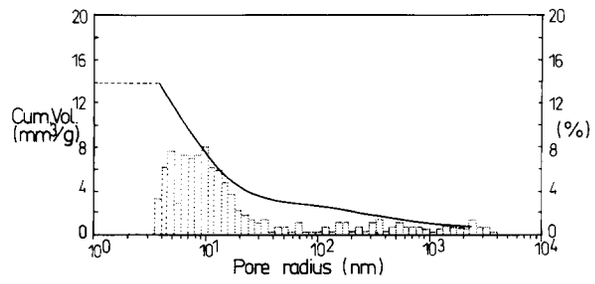

Figure 7 Pore size distribution of polymer P5 (see *Table 1*)

For the sorption of direct dyes on cotton from a finite bath (at $T \geqslant 50°C$) the average radius of cotton fibres $r = 0.0010$ cm ($= 10.000$ nm) has been taken for the calculation of the diffusion coefficient D[12] which is calculated to be of the order of 10^{-10} cm^2 s^{-1}. For the diffusion kinetics of various cationic dyes on acrylic fibres (at $T = 60$–$98.5°C$), the average diffusion path length L in the fibres (depending on the shape and the geometry of the fibre) has been taken in order to calculate the parameter D (L was determined to be of the order of 0.0004 cm)[11,14] and not according to the pore radius average (determined by nitrogen adsorption isotherms as $r_a = 3.3$ or 4.0 nm depending on the fibre). The diffusion coefficient is calculated to be of the order of 10^{-10} cm^2 s^{-1} at higher temperatures and 10^{-12} cm^2 s^{-1} in some cases at $\sim 70°C$.

The parameters n, A, k' appear to have values (*Table 2*) having the same order as in literature[12]. On the other hand, the diffusion coefficient D_a calculated on the basis of the pore radius average (*Table 3*) deviates strongly from the results of the literature as mentioned above. Bulk diffusion is observed into macro- and mesopores (mesopores diameter: $50 > d > 2$ nm) due to collisions among the molecules of the sorptive substance. Diffusion, especially of gases, into pores having diameters in the range of the mean free path of the gas molecule (100 nm) is called molecular or surface or Knudsen diffusion. In this case, the collisions between the gas molecules and the pore walls occur more often than among the gas molecules[15]. The D_0 (*Table 2*) calculated assuming the value of $r = 0.0010$ cm is very near to the results in the literature. Therefore, the average diffusion path length must be near this value and it seems that the model of the equations described refers to bulk diffusion.

The question arises as to whether the sorption is more influenced by the pore structure of the polymers or by the functional groups they contain. The half width of the dye cations of methylene blue is 0.38 nm (or a little higher, e.g. 0.63 nm, for other dye cations having a second aromatic ring perpendicular to the fused aromatic rings)[11]. This value is significantly lower than the pore radius average (*Table 3*) so that the dyes can diffuse into the pores. The influence of the pore structure of the polymers on the sorption of methylene blue and alizarin yellow must lead to the same sorption ability of the polymers for both dyes. However, this does not occur because the increasing order of polymers for methylene blue differs from that of alizarin yellow. On the other hand, the sorption abilities of these polymers for both dyes used can be explained based on the EDA interactions between the functional groups of the polymers and the functional groups of the dyes[13].

The mechanism of dye migration from an aqueous solution into a polymer is a complicated process due mainly to inhomogeneities of the substrate (surface layers of water, pores and voids, various kinds of ordered and disordered regions of polymers, swelling, etc.). Two models have been mainly proposed to explain the mechanism of dye migration, namely the 'pore model' and the 'free volume model'. According to the second model, the rate of diffusion is determined by the mobility of segments of the polymer chains. This mobility is increased above the T_g of the polymer. Acrylic polymers, e.g. acrylic fibres, have a $T_g = 91°C$ or more[11]. The dyes have been sorbed on the polymers used at 25°C, which is much lower than the T_g. The 'pore model' assumes

that the polymer, e.g. fibre, in the dyeing conditions contains a network of channels or pores filled with solution (aqueous dye bath). The dissolved dye molecules diffuse into these pores and will be sorbed onto the pore surfaces. It is important that the diameter of these pores is sufficiently large compared to the size of the dye molecules or ions[14]. In acrylic fibre dyeing (mainly at the boiling point or at temperatures a little below), free volume diffusion takes place simultaneously with pore diffusion[11]. For our sorption results, the 'pore model' is more appropriate because the sorption takes place at much lower temperatures than the T_g. Furthermore, the EDA interactions between the functional groups of the polymers and the functional groups of the dyes strongly influence the sorption process.

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