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Sorption Studies of Reactive Red Dyes

Abstract

The sorption kinetics of reactive dyes, analogues of C.I. Reactive Red 120, on cellulose fibres has been studied. The kinetic studies were carried out in a neutral medium, $pH=7.0\pm 0.1$, at temperatures of $40\pm 1^\circ C$ and $60\pm 1^\circ C$, with various concentrations of sodium chloride ranging from 0 to 40 g/dm^3 . It has been found that the sorption processes of the examined reactive dyes on cellulose fibres proceed in accordance with the reaction model proposed by Vickerstaff. This relationship can be described by the equation $t/c_w = a \cdot t + b$. The effect of the structure of dye on its sorption properties was determined. It has been found that the dye sorption is affected by diamine - the coupling link of the two-chromophore system - as well as by the type of the active component used.

Key words: reactive dyes, sorption of reactive dyes, kinetic of sorption, kinetic model.

Introduction

Reactive dyes, especially the derivatives of 1,2,5-triazine and 4-(β -ethylsulphate) sulphonylanilines, are commonly used for dyeing cellulose fibres. Both types of reactive system are present in dyes that are applied by exhaustion methods [1-4]. The dyeing of cellulose fibres with reactive dyes by exhaustion from the dyebath consists of two basic stages: the sorption of dyes with simultaneous diffusion in fibre pores, and the chemical reaction between the hydroxyl groups of cellulose and dye molecules on fibres [5]. The bonding of dyes with cellulose fibres proceeds under alkaline conditions, and the pH value and temperature of this process depend on the structure of the dye reactive system. Under dyeing conditions, the dyes in an alkaline bath are subject to hydrolysis. A significant role in the application of reactive dyes is played by the affinity of dyes to cellulose fibre. The affinity of dyes is associated with their chemical structure, dyeing temperature, the quantity of electrolyte in the dyebath and the type of dyed cellulose fibre [12].

The aim of the present work was to study the sorption properties of reactive red dyes of the Procion HE type [6], and in particular to examine the relationship between the structure of dye molecule and its sorption properties.

Materials and Methods

Reactive reds derived from 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid were used for the investigation. The chemical structure of these dyes is shown in Figure 1, where:

A - amines (active components),
A-1 - anthranilic acid,
A-2 - 4-(β -ethylsulphate)sulphonylaniline,
A-3 - orthanilic acid;
Dw - diamines,

Dw-1 - phenylene-1,4-diamine,
Dw-2 - phenylene-1,3-diamine,
Dw-3 - phenylene-1,2-diamine,
Dw-4 - diaminostilbene-2,2'-disulphonic acid,
Dw-5 - 4,4'-diaminobenzanilide,
Dw-6 - ethylene-1,2-diamine.

Spectrophotometric measurements were carried out to determine λ_{max} of aqueous dye solutions. The content of sodium chloride was found by potentiometric titration. The chemical structures and salt contents

of the dyes under investigation are given in Table 1.

A bleached cotton woven fabric of the type Noris 1/150 STB was used for dyeing after being washed in a solution containing a non-ionic surface-active agent (Precolor Jet) to remove starch sizes.

The kinetic examinations of dye sorption were carried out using a Mathis BFA12 laboratory dyeing machine from Warner Mathis AG at bath temperatures of $40\pm 1^\circ C$ and $60\pm 1^\circ C$. The dyebath contained 1%

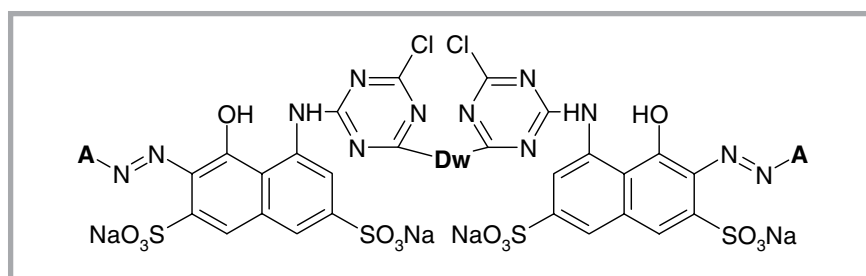


Figure 1. Chemical structure of reactive dyes.

Table 1. Chemical structures of reactive dyes, salt content and λ_{max} in water (*C.I. Reactive Red 120 - model dye).

Dye symbol	Dye structure		Salt content, %	λ_{max} , nm
	Diazo component	Diamine		
B-1	A-1	Dw-1	38.9	517.6
B-2	A-1	Dw-2	56.8	517.6
B-3	A-1	Dw-3	36.9	515.5
B-4	A-1	Dw-4	44.3	515.5
B-5	A-1	Dw-5	38.0	519.8
B-6	A-1	Dw-6	51.4	517.6
B-7	A-2	Dw-1	35.2	515.5
B-8	A-2	Dw-2	48.7	507.1
B-9	A-2	Dw-3	32.4	517.6
B-10	A-2	Dw-4	40.6	519.8
B-11	A-2	Dw-5	45.3	519.8
B-12	A-2	Dw-6	55.1	515.5
B-13*	A-3	Dw-1	37.5	513.3
B-14	A-3	Dw-2	56.1	513.0
B-15	A-3	Dw-3	72.3	513.0
B-16	A-3	Dw-4	62.1	512.0
B-17	A-3	Dw-5	36.7	513.0

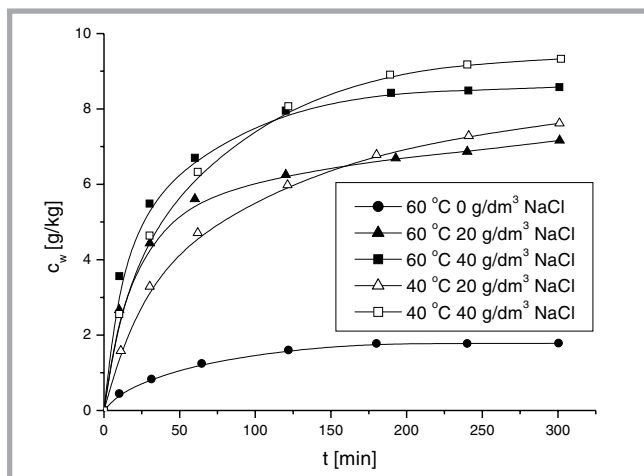


Figure 2. Curves of sorption for dye B-1 ($T=const.$).

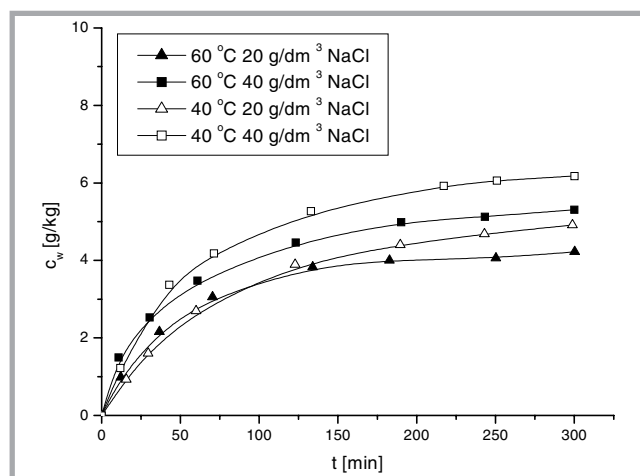


Figure 3. Curves of sorption for dye B-7 ($T=const.$).

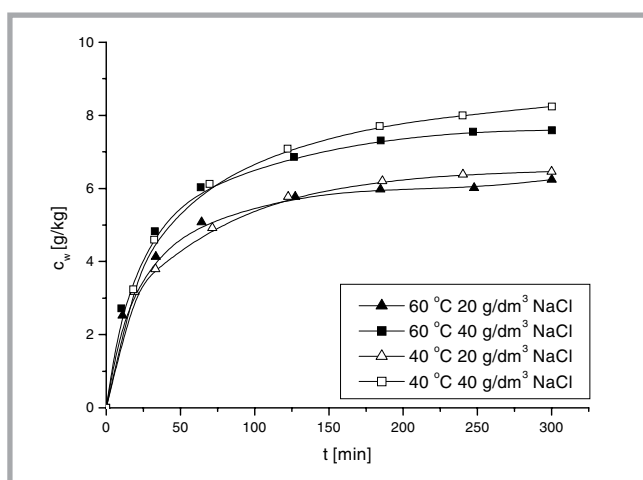


Figure 4. Curves of sorption for dye B-13 ($T=const.$).

of dye (as salt-containing pure dye) in relation to the fibre weight.

The dye sorption process was performed with the liquor ratio of 1:200, pH=7.0 (the pH value of dyebath was corrected with an acetate buffer by the pH-metric method), without and with the addition of sodium chloride in concentrations of 20 and 40 g/dm³ respectively. Cotton fabric samples were placed in the dyebath heated to a specified temperature. The dye concentration in fibre after intervals of $t = 5, 30, 60, 120, 240$ and 300 min was determined by an indirect method, measuring the loss of dye concentration in the dyebath on the basis of spectrophotometric curves of model dyes. The measurements were carried out with the use of a Specol 11 spectrophotometer from Carl Zeiss Jena at a wavelength close to λ_{max} of each dye.

In the studies of sorption processes of Procion HE-type reactive dyes, dyebath temperature, pH, electrolyte concentration and liquor ration were selected so as to diver-

sify their sorption properties and determine their dependence on the structure of dye molecule. Under neutral conditions at a temperature of 60°C the examined dyes behave as direct dyes, while at 80°C and above the reactive dyes react partly with fibre hydroxyl groups. The increase in sodium chloride concentration and the decrease in liquor ratio shift the equilibrium concentration in favour of fibres [6].

Kinetic Model of the Sorption Process

Designations:

- c_w - dye concentration in fibre [g·kg⁻¹],
- c_w^{5h} - dye concentration in fibre after 5 h [g·kg⁻¹],
- c_{theor} - equilibrium concentration of dye in fibre [g·kg⁻¹],
- t - time of dyeing [min],
- $t_{0.5}$ - half-time of dyeing [min],
- k - rate constant of the sorption process [kg·g⁻¹·min⁻¹],
- R - linear correlation coefficient

The dyeing rate V is an increase in the concentration of dye in fibre per time unit

$$V = \frac{dc_w}{dt} \quad (1)$$

The rate of dye exhaustion from the dyebath is expressed in the form of curves of sorption showing the changes in dye concentration in fibre versus time [7-10].

$$c_w = f(t) \quad (2)$$

The curves of sorption can be described with mathematical equations. Different physical and chemical structures of fibres and the differences in the chemical structure of dyes do not allow only one universal equation describing dyeing isotherms of various fibres with different dyes to be used. The kinetic model of the sorption of the reactive dyes under investigation was found on the basis of experimental data. Examples of experimental curves of sorption of selected dyes B-1, B-7 and B-13 are shown in Figures 2-4.

The assumption was made in this work that the process of sorption of the red dyes under examination would proceed according to the reaction model described by equation (3) [7-11]:

$$\frac{dc_w}{dt} = k(c_{\infty} - c_w)^2 \quad (3)$$

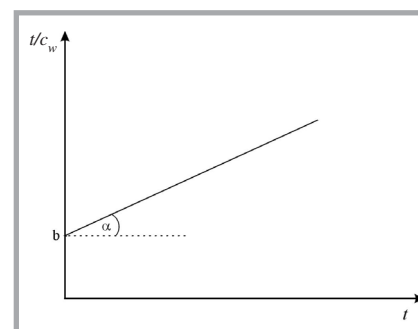


Figure 5. Dependence of $t/c_w = f(t)$ for the model of the sorption process.

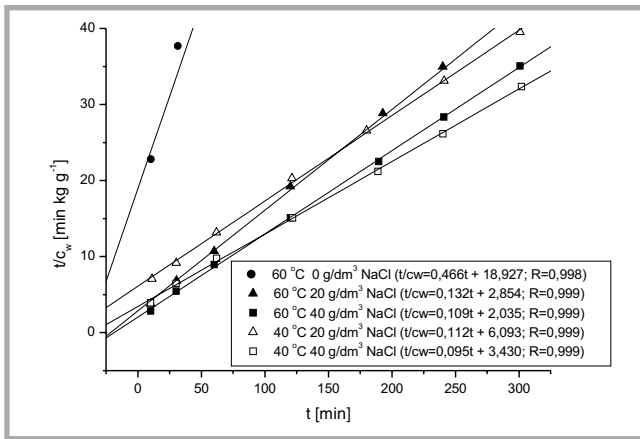


Figure 6. Dependence of $t/c_w = f(t)$ for dye B-1.

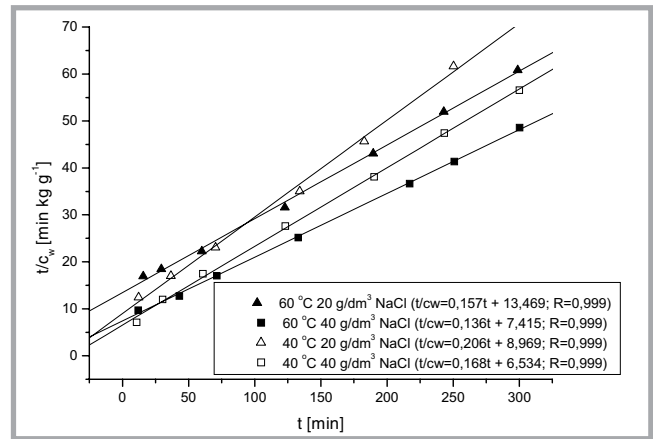


Figure 7. Dependence of $t/c_w = f(t)$ for dye B-7.

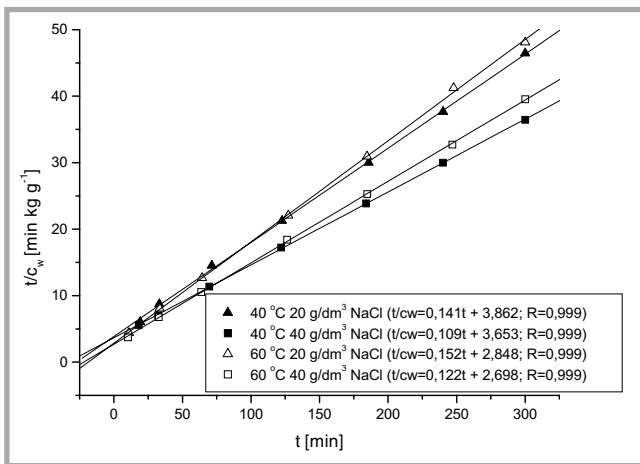


Figure 8. Dependence of $t/c_w = f(t)$ for dye B-13.

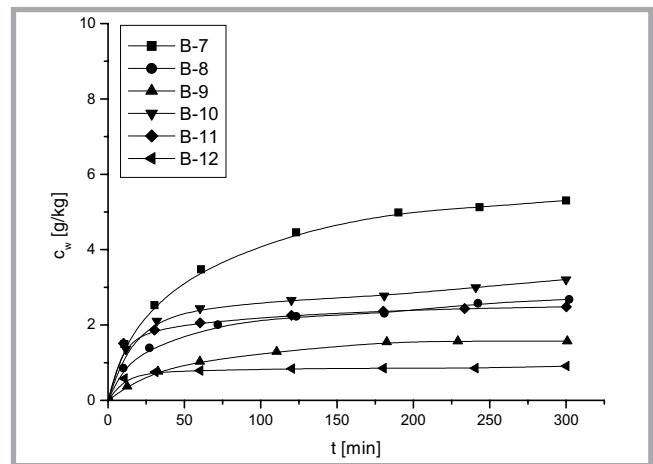


Figure 9. Curves of sorption for dyes derived from 4-(β -ethylsulphate) sulphonylaniline (dyes B-7 - B-12) determined at 60°C in dyebath containing 40 g/dm³ of sodium chloride.

where k , in $\text{kg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$, is a rate constant of reaction. Equation (3) after integration assumes the following form:

$$\frac{1}{c_\infty - c_w} - \frac{1}{c_\infty} = k \cdot t \quad (4)$$

or respectively:

$$\frac{t}{c_w} = \frac{1}{c_\infty} \cdot t + \frac{1}{k \cdot c_\infty^2} \quad (5)$$

Equation (5) describes the linear dependence of the function $t/c_w = f(t)$ (Figure 5), while the values of c_∞ , k and $t_{0.5}$ can be calculated on the basis of this equation.

$$c_\infty = \frac{1}{\text{tg}\alpha} \quad (6)$$

$$k = \frac{1}{b \cdot c_\infty^2} \quad (7)$$

$$t_{0.5} = \frac{1}{k \cdot c_\infty} \quad (8)$$

Based on the analysis performed, it was found that the sorption of the reactive dyes under investigation onto cellulose fibres proceeds in accordance with the model of reaction proposed by Vickerstaff [12]. This is confirmed by the rectilinear diagrams

of sorption of selected reactive dyes. The diagrams are shown in Figures 6-8 and described by model equations.

Results and Discussion

The kinetic parameters of the sorption of reactive dyes onto cellulose fibres are listed in Tables 2, 3 and 4, including the experimentally found half-times of dyeing, equilibrium dye concentration in fibre and the theoretical kinetic parameters of sorption calculated from equations 6-8.

As follows from the sorption curves obtained (Figures 2-4), despite the fact that the sorption process was carried out for 5 h, the equilibrium dye concentration in fibre was not always reached. This mainly concerns the sorption processes carried out at a temperature of 40°C. The lack of equilibrium is probably the main reason for the differences which appeared between the equilibrium concentrations of dyes in fibre found experimentally and the equilibrium concentration calculated from equation (6).

The chemical structure of dye molecules exerts an influence on the dye sorption properties. This concerns the effect of diamine, the coupling link of two reactive systems as well as the active component (amine). In the group of dyes derived from anthranilic acid, the highest equilibrium concentration in fibre, with the same initial concentration of dye in the dyebath, is shown by the B-1 dyes (derivatives of phenylene-1,4-diamine) and B-2 dyes (derivatives of phenylene-1,3-diamine). These dyes have similar sorption properties at temperatures of 40 and 60°C. Dye B-2 is absorbed by cellulose fibre faster without electrolyte at 60°C. The kinetic constant for dye B-1 amounts to 12.6×10^{-3} , while that for dye B-3 is $89.4 \times 10^{-3} [\text{kg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}]$. The very low equilibrium concentrations in fibres were obtained by dyes B-3, B-9 and B-15 (derivatives of phenylene-1,2-diamine) and dyes B-6 and B-12 (derivatives of ethylene-1,2-diamine). The dyes derived from phenylene-1,2-diamine are not linear and coplanar. The dyes derived from aliphatic amines are characterised by a low affinity to cellulose fibres.

Dyes B-7 to B-12 (Figure 9) are characterised by a lower affinity than that of the dyes derived from anthranilic acid. This would confirm the thesis that the increase in the number of sulphonic groups in the dye molecule increases the electro-kinetic potential of the dye solution and decreases the affinity to cellulose fibres [13]. Despite the same number of sulphonic groups, the dyes derived from orthonilic acid show higher indicators of exhaustion from the dyebath than their analogues derived from 4-(β -ethylsulphate)sulphonylaniline. It is the position of the sulphonic group that is of decisive importance in this case. In this group, the highest exhaustion indicators are shown by the derivative of phenylene-1,4-diamine. It has been calculated by semi-empirical methods that the sulphonic group in the dyes derived from orthonilic acid interacts with the chromophore system (the results of these calculations will be reported in the next paper). In the group of dyes B-13 to B-17 (derivatives of orthonilic acid), the highest equilibrium concentrations were obtained for dye B-17 (derivative of 4,4'-diaminebenzanilide) and dye B-13 (derivative of phenylene-1,4-diamine). Dye B-13 is produced by several companies as C.I. Reactive Red 120.

As expected, the final equilibrium states of dye in fibre is affected by the structure of the dye molecule, temperature and electrolyte concentration in dyebath. With the increase in the electrolyte concentration in the dyebath, the electro-kinetic potential of dye in solution decreases [13] and the dye concentration in fibre increases. The increase in temperature causes the dye concentration in cellulose fibres to decrease. As follows from the data given in Tables 2-4, in some cases the half-times of dyeing decrease with the increase in the sorption temperature. The increase in the electrolyte concentration in the dyebath is accompanied by the decrease in the sorption kinetic constants. The kinetic examinations performed present the relationship between the structure of the dye molecules and the sorption properties of the dyes.

Conclusion

It has been found that the sorption processes of the examined reactive dyes in cellulose fibres proceed in accordance with the model of reaction proposed by Vickerstaff, and their course is dependent on the chemical structure of the dye molecule.

Table 2. Kinetic parameters of sorption of reactive dyes B-1 to B-6 derived from anthranilic acid.

Dye symbol	Temperature of sorption, °C	Content of NaCl, g/dm ³	t _{0.5} , min		k' ₂ × 10 ³ , kg · g ⁻¹ · min ⁻¹	c _w ^{5h} , g · kg ⁻¹	c _{theor.} ⁷ , g · kg ⁻¹
			exper.	theor.			
B-1	40	20	42.9	54.4	2.06	7.62	8.92
		40	33.2	35.9	2.65	9.33	10.5
		~0	36.8	38.7	12.6	1.79	2.05
	60	20	21.3	21.5	6.15	7.16	7.55
		40	18.6	18.6	5.88	8.58	9.14
B-2	40	20	37.8	42.9	2.66	7.58	8.75
		40	34.3	36.6	2.76	8.76	9.89
		~0	13.1	8.20	89.4	1.32	1.37
	60	20	21.9	20.9	6.12	7.27	7.82
		40	17.4	16.2	6.86	8.29	8.77
B-3	60	~0	41.1	55.3	13.9	1.07	1.30
		20	37.2	30.7	14.4	20.6	2.26
		40	15.7	17.2	21.5	2.50	2.70
B-4	40	20	44.8	79.6	20.8	4.77	6.04
		40	34.7	57.2	24.6	5.94	7.11
		~0	25.8	28.0	19.3	1.67	1.85
	60	20	37.6	53.1	4.17	3.83	4.52
		40	19.7	28.8	6.23	5.09	5.58
B-5	60	~0	15.5	8.80	65.1	1.68	1.74
		20	23.4	23.4	8.89	4.45	4.81
		40	22.1	25.6	6.90	5.29	5.67
B-6	60	~0	41.2	55.7	13.7	1.07	1.31
		20	33.9	39.4	10.9	2.06	2.33
		40	21.7	22.1	16.7	2.51	2.71

Table 3. Kinetic parameters of sorption of reactive dyes B-7 to B-12 derived from 4-(β -ethylsulphate)sulphonylaniline.

Dye symbol	Temperature of sorption, °C	Content of NaCl, g/dm ³	t _{0.5} , min		k' ₂ × 10 ³ , kg · g ⁻¹ · min ⁻¹	c _w ^{5h} , g · kg ⁻¹	c _{theor.} ⁷ , g · kg ⁻¹
			exper.	theor.			
B-7	40	20	52.2	43.5	4.74	4.91	4.85
		40	37.4	38.9	4.32	6.18	5.95
	60	20	38.6	43.5	4.70	4.22	4.85
		40	34.6	38.9	4.30	5.31	5.95
B-8	40	20	39.3	64.5	7.28	1.79	2.13
		40	43.4	54.8	4.42	3.61	4.13
	60	20	25.6	28.9	21.0	1.54	1.63
		40	28.9	29.5	12.0	2.68	2.87
B-9	60	20	45.9	59.2	11.3	1.02	1.26
		40	34.4	42.8	11.2	1.57	1.87
B-10	60	20	23.0	20.9	18.0	2.55	2.71
		40	19.5	22.6	13.0	3.21	3.32
B-11	60	20	17.8	18.4	29.0	1.82	1.90
		40	10.6	11.9	33.0	2.49	2.56
B-12	60	20	29.3	24.4	80.0	0.48	0.51
		40	11.0	8.60	128.0	0.91	0.91

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Table 4. Kinetic parameters of sorption of reactive dyes B-13 to B-17 derived from orthanilic acid.

Dye symbol	Temperature of sorption, °C	Content of NaCl, g/dm ³	t _{0.5} , min		k' ₂ × 10 ³ , kg · g ⁻¹ · min ⁻¹	C _w ^{5h} , g · kg ⁻¹	C _{theor.} ^h , g · kg ⁻¹
			exper.	theor.			
B-13	40	20	23.4	27.4	5.15	6.46	7.09
		40	28.7	33.4	3.26	8.24	9.17
	60	20	20.2	18.7	8.10	6.24	6.59
		40	22.3	22.2	5.50	7.59	8.20
B-14	40	20	26.3	30.0	6.13	4.98	5.43
		40	20.1	21.4	7.57	5.89	6.17
	60	20	20.1	19.7	12.0	3.98	4.22
		40	15.6	10.2	20.0	4.72	4.89
B-15	60	20	27.1	30.3	75.0	0.42	0.44
		40	37.6	40.9	22.0	0.99	1.11
B-16	40	20	48.3	72.1	1.86	5.96	7.46
		40	47.6	58.2	1.96	7.23	8.77
	60	20	32.0	78.2	2.20	5.16	5.81
		40	31.4	37.7	3.40	6.98	7.81
B-17	60	20	28.9	28.9	4.60	6.86	7.52
		40	24.9	25.8	4.70	7.69	8.26

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