ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 9, pp. 1533–1541. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.N. Krasovskii, S.A. Lopato, M.G. Potashev, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 9, pp. 1436–1444.

PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Surface Tension of Solutions of Low-Molecular Epoxy Resins in Monoglycidyl Ether on the Interface with Air and Production of Filled Epoxy Compositions

A. N. Krasovskii, S. A. Lopato, and M. G. Potashev

St. Petersburg State University of Cinema and Television, St. Petersburg, Russia

Received April 16, 2008

Abstract—The surface tension of solutions of epoxydiane resin (M_n ~400) in versatic acid monoglycidyl ether (Cardura) at the interface with air in the range of concentrations c = 5–60% in the presence of non-ionic surfactants was studied. The effect of concentration of epoxydiane resin in solution on the rate of dispersion of pigment particles (filler) was revealed. The structural parameters of aggregates of the epoxydiane resin molecules and pigment particles in the composition, as well as the optimal concentration of oligomeric resin, corresponding to the maximum rate of dispersion of pigments in solution were determined in the approximation of the model of fractal clusters.

DOI: 10.1134/S1070427209090067

Investigation of structure and surface properties of epoxydiane oligomers (EO) in solutions at a liquid–air and liquid–solid phase boundary is of particular interest because of the extensive use of the filled epoxide compositions in protection and anticorrosive coatings on metals [1, 2]. Such sys-tems include, in particular, filled compositions based on low molecular weight EO (M_n = 400–650) and versatic acid monoglycidyl ether (Cardura) [1], as well as pigments and fillers [2, 3].

In the study of concentration dependence of the relative viscosity and the intensity of the quasi-elastic light scattering in solutions of EO was found [4, 5] that these solutions form discrete associates and an infinite cluster of EO molecules [6, 7]. The minimum on the curve of intensity of light scattering in solutions of epoxydiane resin ED-20 (M_n ~ 380) in Cardura according to [4, 5] is defined by the formation of an infinite EO cluster at the threshold concentration $c^{\neq}$. Note that passing from the dilute ($c < c^{\neq}$) to concentrated ($c > c^{\neq}$) solutions of EO leads to a change in the fractal dimension D and the lattice density of EO aggregates near the threshold value $c^{\neq}$ [3].

Completing of construction of an infinite EO cluster in solution occurs at the critical lattice density of the aggregates of EO molecules. This conclusion is confirmed [3, 8] by the existence of a global minimum on the concentration curves of surface tension σ in the EO solutions (M_n = 400–3600) at the liquid–air interface [9]. Minimum on the curves σ(c) coincides in the scale of concentration with the threshold $c^{\neq}$ value calculated from viscosity data [8, 9], and is connected with the equality to zero of the second derivative of Gibbs free energy on the concentration, d^2F/dc^2 [10].

The spatial structure of filled polymers obtained by curing epoxy compositions with amines [2] can be represented as discrete areas with different densities of nodes of the chemical cross-linked polymer and the aggregates of pigment particles (filler) [3]. Strength and protective properties of filled polymers depend on the density of the chemical net nodes, concentrations c_p of pigment particles, type of distribution and size of particles in the polymer matrix.

It was shown previously [3] that the degree of aggregation s of pigment particles in the filled epoxy compositions increases sharply near the critical $c_p^{\neq}$. The

Table 1. Molecular characteristics[a] of oligomeric samples, 298 K

Sample no.	Oligomer	Epoxide number, %	M_n ±5%	$M_\mathrm{w}/M_\mathrm{n}$ ±10%	r_0, nm	[η], cm^3 g^{-1}	η, Pa s	s, mN m^{-1}
1	YD-128S	20.9	410	1.4	0.84	2.5	22.2	52.4
2	Cardura E-10P	17.2	250	–	–	–	0.035	30.2

[a] M_n and M_w are respectively number-average and weight-average molecular weights, r_0 is hydrodynamic radius of the molecules, [η] is intrinsic viscosity of YD-128S in solution in Cardure, η is viscosity, σ is surface tension of the samples at the liquid–air interface.

lattice density of aggregates (clusters) of particles reaches a maximum near $c_\mathrm{p}^{\neq}$ and falls in the region of $c_\mathrm{p} > c_\mathrm{p}^{\neq}$, that determines the shape of the concentration curves of viscosity $\eta(c_\mathrm{p})$ of filled compositions. The respective state of the compositions near $c_\mathrm{p}^{\neq}$ resembles a dense solution of hard spheres at the percolation threshold [11].

According to the cluster model [12], the process of dispersing aggregates (clusters) of solid particles in liquid occurs in two stages. The decay rate of large aggregates into small aggregates in the first stage of the process should be lower than in the second stage, and the number of particles formed *n* in the last stage of the process should be higher than in the initial stage.

It can be assumed that the rate of change of average radius <*R*> of the particles aggregates at the dispersing in a fluid should depend on the concentration of EO in solution, which in turn determines the surface tension of the liquid on the boundary with air and wetting of the particles with the fluid [9, 13]. A relationship between the number *n* of the particles and the current average radius <*R*> of the particles aggregates can be represented as follows: $n(t) = (R/\langle R\rangle)^D$ [7], where *R* is the initial radius, *D* is fractal dimension of the particle, *t* is duration of the process of dispersion [14].

In order to test the predictions of the cluster model [7, 12], we studied the surface tension of low molecular weight epoxydiane resin in a solution in Cardura at the interface with air in a wide range of EO concentrations and at the adding of nonionic surfactant into solutions of EO. Practical aspect of this work is to study the relationship between the structural and thermodynamic parameters of EO in the solution and the rate of dispergation of the pigment particles in the liquid.

Note that the development of physico-chemical principles of the construction of filled epoxy compositions with an active solvent [1–3], based on the concepts of the model of fractal clusters [7, 11], is important for a reliable prediction of the resin composition. This approach includes selecting the optimal concentration of EO in solution for the effective dispersion of fillers, which is relevant to the improvement of technology of the filled compositions [15].

EXPERIMENTAL

We studied industrial samples of epoxydiane resin YD-128S (Kykdo Chemicals) and Cardura E-10P, versatic acid monoglycidyl ether, with the total number of carbon atoms equal to 10 (Shell Chemicals) [1]. Chatarteristics of the samples nos. 1 and 2 are shown in Table 1.

Surface tension σ at the interface of solutions of YD-128S in Cardura with air was studied by the ring detachment method with the use of a du Noiiy tensiometer [10], graded on standard liquids (isooctane, ethanol, cellosolve, toluene, benzyl alcohol, water) in the range of σ from 18.4 to 72 mN m^{-1} at 25°C [16]. The relative error of 15 parallel measurements of σ is ±0.3%. Concentration curves of surface tension σ(*c*) obtained in the range of concentrations of YD-128S in Cardura $c = 5 – 60\%$ at the increment $\Delta c = 1–5\%$ (Figs. 1–3).

In the study of the effect of surfactants on the surface tension of YD-128S solutions in Cardura at the interface with air were used nonionic oligomeric siloxane surfactants Byk-A530 (Byk Chemie) and Troysol S-366 (Troy, Eurochime) [17], which were widely used as dispersant additives in the technology of processing filled epoxy compositions [15]. To the solutions of YD-128S in Cardura was added 0.2–0.4% of Byk-A530 or 0.15–0.45% of Troysol S-366. These concentrations of surfactants, according to [15, 17] are optimal for effective dispersion of pigment particles in solutions of low molecular weight epoxy resins in active solvents.

The kinetics of the process of dispersion of pigment particles in solutions of YD-128S in Cardura in the range of concentration c = 10–60% was studied on the example of three filled compositions: on the basis of iron minium (Arbolit), microtalc (GSHM, Talkon) [18], and a mixture of microtalc with anticorrosive pigments [19] chromium oxide (Terrhell, Germany) and zinc phosphate (SZC, France) in the mass ratio 5:3:2. Mass concentration of the pigments and fillers in the compositions was 40%. For example, to a solution containing 24 g of YD-128S and 36 g of Cardura was added 40 g of iron minium, or microtalc, or its mixture with chromium oxide and zinc phosphate. The volume concentration of a pigment in the compositions is about 31 vol %, which coincides with the critical concentration $c^{\neq}$ of particles in the infinite cluster in the case of simple cubic lattice (SCL) [3, 7].

The dispersion of pigments in solutions of YD-128S was carried out in a bead mill at a rotation 560 rpm. Number of beads (diameter of particles 1.8 mm) in the compositions was maintained equal to the pigment or a mixture of pigments mass fraction. The average radius <R> of the aggregated particles of pigments at their dispersion was found by the wedge method [19, 20] with a relative error ~10%. Initial average radius R of aggregated particles of iron minium and microtalc was 48 and 40 μm, respectively, the final particle radius <R> = 6–7 μm.

Dispersion component ε^d of the total surface energy ε, determining the pigment wetting [10], was calculated from the values of the surface tension σ on the boundary of solutions YD-128S with air and the value of σ_{12} (indices 1 and 2 refer to the liquid and solid states, respectively) at the solution–pigment interface by the method described in [13].

The global minimum on the concentration curve of surface tension σ(c) at the interface of solutions of YD-128S in Cardura with air corresponds to the threshold concentration of YD-128S $c^{\neq}$ = 40% and surface tension $\sigma_{\min}$ = 24 mN m^{-1}, which is significantly lower than the value of σ_l = 30.2 mN m^{-1} on the Cardura–air border (Fig. 1, Table. 1, 2). The minimum on the σ(c) curve is defined by the formation of a continuous fluctuating net of YD-128S links in the surface phase of solution [8]. According to light scattering data [3, 5], it practically coincides on the concentration scale with the minimum of the

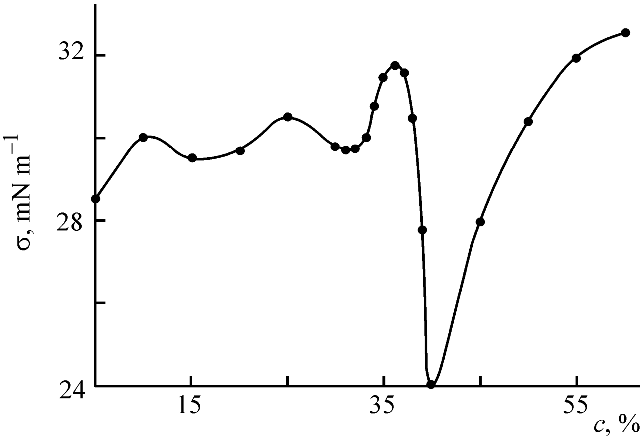

Fig. 1. Concentration curve for the surface tension σ at the interface of solutions of YD-128S in Cardura with air in the range of c = 5–60%; T = 298 K.

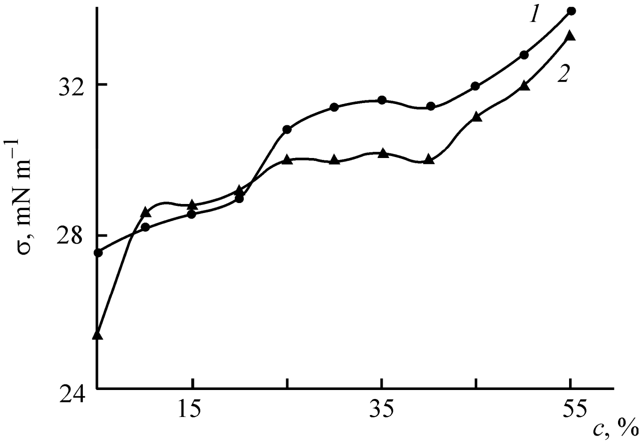

Fig. 2. Concentration curves for the surface tension σ at the interface of solution of YD-128S in Cardura with air in the range of c = 5 – 55% in the presence of surfactants. Concentration of Byk-A530, %: (*1*) 0.2 and (*2*) 0.4

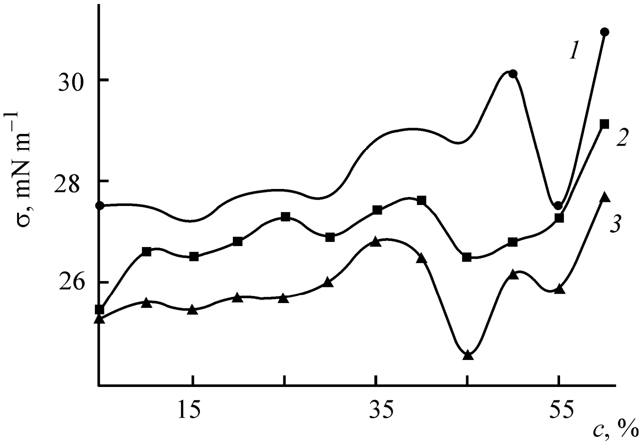

Fig. 3. Concentration curves for the surface tension σ at the interface of solution of YD-128S in Cardura with air in the range of c = 5–60% in the presence of surfactants. Concentration of Troysol S-366, %: (*1*) 0.15, (*2*) 0.3, and (*3*) 0.45.

Table 2. Characteristics[a] of the molecules aggregates in the surface phase, surface tension σ at the interface with air of solutions YD-128S in Cardura near the threshold concentration $c^{\neq}$ (experiments 1–3), and after adding to the solutions of 0.2% of Byk-A530 (experiments 4–6) and 0.3% of Troysol S-366 (experiments 7– 9), $T = 298$ K

Sample no.	c, %	σ	$\Delta\sigma = \sigma - \sigma_1$	D ±10%	ω, nm^2	$\Delta F(c)\times 10^3$, J mol^{-1}	ε^d, mJ m^{-2}
		mN m^{-1}					
1	35	30.8	0.6	1.1	5.4	0.5	15.7
2	40	24.0	–6.2	2.0	2.2	–2.4	10.3
3	45	28.0	–2.2	2.8	1.4	–0.6	14.5
4	35	31.8 (31.1)	1.6 (0.9)		4.6 (5.3)	1.1 (0.7)	16.2(15.7)
5	40	31.7(31.0)	1.5 (0.8)	1.2	5.6 (6.5)	1.5 (1.0)	16.1(15.3)
6	45	32.0 (31.6)	1.8 (1.4)	(1.1)	6.5 (8.2)	2.3 (2.3)	16.3(16.0)
7	35	27.4 (26.8)	–2.8 (-3.4)		3.5 (5.3)	–1.4 (–2.7)	13.2(12.9)
8	40	27.6 (26.5)	–2.6 (3.7)	1.4	4.0 (6.5)	–1.8 (–4.4)	13.4(12.7)
9	45	26.5 (25.8)	–3.7 (-4.6)	(1.1)	4.4 (8.2)	–3.3 (–7.2)	12.7(11.8)

[a] σ_1 is surface tension at the Cardura–air border, D is fractal dimension of the molecules YD-128S aggregates, ω is the area per molecule in the surface phase, $\Delta F(c)$ is Gibbs free energy, ε^d is dispersion surface energy of wetting of particles microtalc with solution of YD-128S; in parentheses are the options for the concentrations of Byk-A530 and Troysol S-366 in solution, respectively, equal to 0.4 and 0.45%.

Table 3. Surface tension σ and $\sigma\, c^{\neq}_{12}$ at the interface of solutions YD-128S in Cardura with air and microtalc, rate γ_1 (γ_2) and the duration Δt_1 (Δt_2) of the process in the first and second stages of the dispersion of iron minium and microtalc in solutions of YD-128S, $T = 298$ K

c, %	$[\eta]c$[a]	σ	Δσ	σ_{12}	ε^d, mJ m^{-2}	γ_1±10%	γ_2±10%	Δt_1	Δt_2	n_1[a]	n_2[a]
		mN m^{-1}				min^{-1}		min		±10%	
10	0.3	30.0 (30.1)	–0.2 (–0.1)	40.1	14.5	0.7^b	16.5^a	13^a	7^a	7.5	84
						1.3^c (1.1)^c	8.2^c (7.2)^c	3^b (3)^c	4^b (4)^c	– –	– –
40	1.0	24.0 (31.7)	–6.2 (1.5)	35.4	10.3	1.4^a	21.5^a	11^a	4^a	10	120
						2.5^b (1.2)^c	12^b (9)^c	2^b (2)^c	3^b (3)^c	– –	– –
60	1.8	32.6 (31.2)	2.4 (1.0)	42.3	16.9	0.5^a	12^a	15^a	8^a	6.5	84
						1.2^b (1.3)^c	10^b (16)^c	5^b (5)^c	3^b (2)^c	– –	– –

[a] n_1 and n_2 are respectively the number of particles formed at the end of the first and second stages of the process of dispersing; in parentheses are the options for solutions of YD-128S in Cardura containing 0.2% of Byk-A530. [b] At dispersing iron minium in solutions of YD-128S. [c] At dispersing microtalc in solutions of YD-128S.

correlation radius of the density fluctuations in the solutions of resin ED-20 in Cardura. A local maximum on the curve σ(c) corresponds to YD-128S excesses in the surface phase of the solution with the concentration $c = 36\%$ [3, 8].

In dilute solutions of YD-128S in Cardura in a region of $c < c^{\neq}$ discrete aggregates are formed of YD-128S molecules, while in concentrated solutions with $c > c^{\neq}$ lyotropic liquid crystal phase appears [4, 5].

Adding Byk-A530 and Troysol S-366 to the solution of YD128S leads to a drastic change in the form of the curve σ(c). The global minimum on the σ(c) curve disappears completely (Fig. 2, 3). Surface tension σ in the range of c = 35–45% becomes higher than 24 mN m^{-1}, corresponding to the global minimum on the curve σ(c) at the threshold concentration $c^{\neq}$ in the absence of a surfactant (Table 2). Adding the surfactant to dilute ($c < c^{\neq}$) and concentrated ($c > c^{\neq}$) solutions of YD-128S led to minor changes in the surface tension σ (Table 3).

Concentration curves of surface tension σ(c) can be quantitatively described using the expression relating the value Δσ with the dimensionless parameter x = [η] (where [η] is characteristic viscosity, c is concentration of YD-128S in the solution, g dl^{-1}) [9]:

$$\Delta\sigma(c) = \sigma - \sigma_1$$
$$= kT\pi^{-1}w^{(2-D)/D}x^{(D-2)/D}r_0^{-2}[\ln(1 - \varphi_2^{\text{surface}})/(1 - \varphi_2^{\text{volume}})], \quad (1)$$

where σ and σ_1 are the surface tension of the solution and the solvent, respectively (Tables 1, 2), k is Boltzmann constant, w = 0.637 is a coefficient of random packing of hard spheres, $\varphi_2^{\text{surface}}$ and $\varphi_2^{\text{volume}}$ are volume fraction of the molecules YD-128S in the surface and bulk phases of the solution [7, 10].

In the region of global minimum on the curve of surface tension σ(c) near $c^{\neq}$: $d\sigma/dc = 0$, $\Delta\sigma(c) < 0$ and $D = 2$, for $c > c^{\neq}$ $d\sigma/dc > 0$ and $D > 2$. In the local maximum of the curve σ(c) for $c < c^{\neq}$ are just the conditions $d\sigma/dc < 0$, $\Delta\sigma(c) > 0$ and $D < 2$ are valid (Fig. 1, Table 2). The maximum on σ(c) curve corresponds, according to [3, 9], to the minimum of the lattice density ρ of the aggregates of molecules YD-128S in solution, and the minimum of the σ(c) curve to the maximum density of agree near $c^{\neq}$.

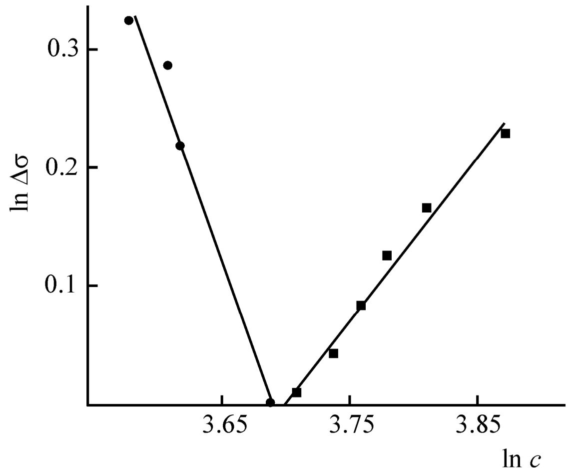

Fig. 4. The increment of surface tension $\Delta\sigma = \sigma - \sigma_{\min}$ on the boundary of solutions of YD-128S in Cardura with air as a function of concentration c (%) of YD-128S near the threshold value $c^{\neq}$. The fractal dimension D of the aggregates of YD-128S molecules in the solution calculated with Eq. (2) equals to 1.1 ($c < c^{\neq}$), 2 ($c = c^{\neq}$), and 2.8 ($c > c^{\neq}$).

Assuming that ln $(1 - \varphi_2^{\text{surface}})/(1 - \varphi_2^{\text{volume}})$ = const in the area close to $c^{\neq}$, from the expression (1) a relation can be obtained for finding the fractal dimension D of YD-128S aggregates from the change in the surface tension $\Delta\sigma(c) = \sigma - \sigma_{\min}$:

$$(D - 2)/D \sim (\ln\Delta\sigma/\ln c). \quad (2)$$

The data obtained confirm the predictions originating from the cluster model [7, 9] (Fig. 4). The minimum on the σ(c) curve for solutions of YD-128S in Cardura near $c^{\neq}$ is associated with the fact that the second derivative of the free Gibbs energy $d^2F/dc^2 = 0$, and the fractal dimension D of YD-128S aggregates is close to 2. Free Gibbs energy $\Delta F(c) = \Delta\sigma\omega\varphi_2^{\text{surface}}N_{\text{A}}$ (N_{A} is the Avogadro's number) [10] is minimum when $c = c^{\neq}$ and increases with deviation from the threshold

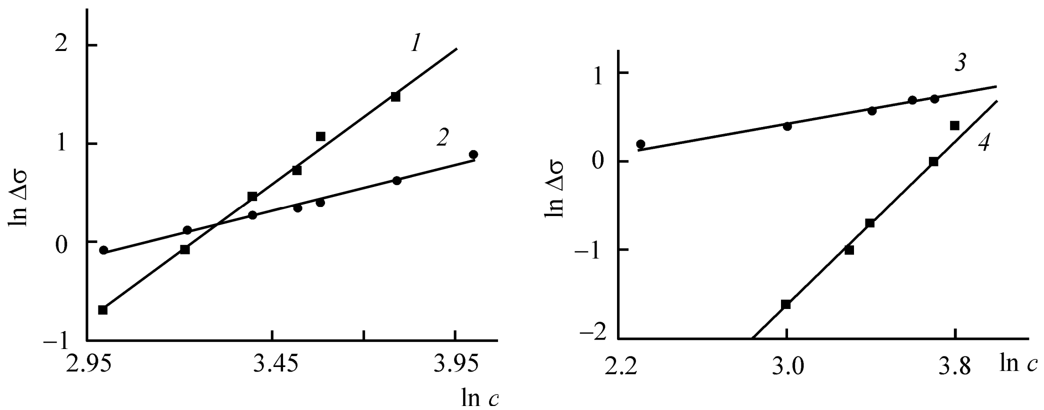
(a) (b)

Fig. 5. Dependences of the increment of surface tension $\Delta\sigma = \sigma - \sigma_1$ for the solutions of YD-128S in Cardura at the border with the air on the concentration c (%) of YD-128S in solution in the range c = 30-50% in the presence of (a) Byk-A530 and (b) Troysol S-366. Concentration, %: Byk-A530 (*1*) 0.2, (*2*) 0.4; Troysol S-366 (*3*) 0.3, (*4*) 0.45.

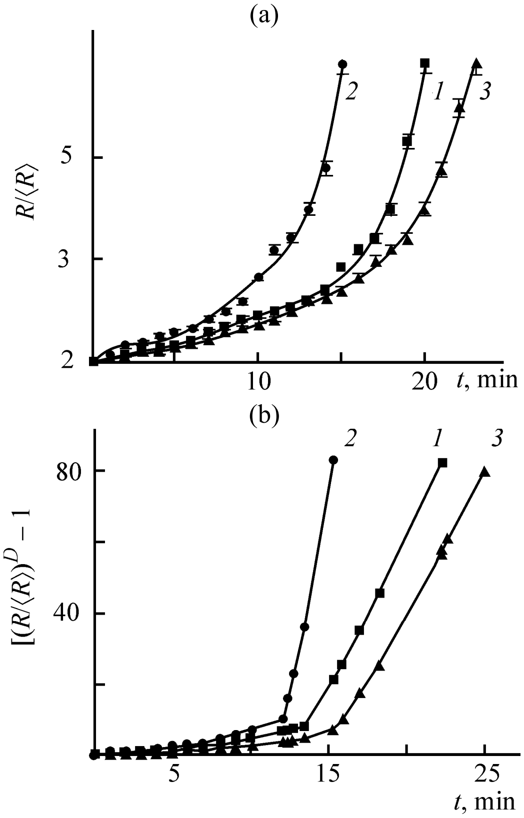

Fig. 6. Kinetic curves of the change in the ratio of initial radius R to the current average radius $<R>$ of particles aggregates (a) and anamorphoses of the kinetic curves in the coordinates $[(R/<R>)^D - 1] - t$ (min) (b) for iron minium dispersed in solutions of YD-128S. Concentration, %: YD-128S (*1*) 10, (*2*) 40, and (*3*) 60.

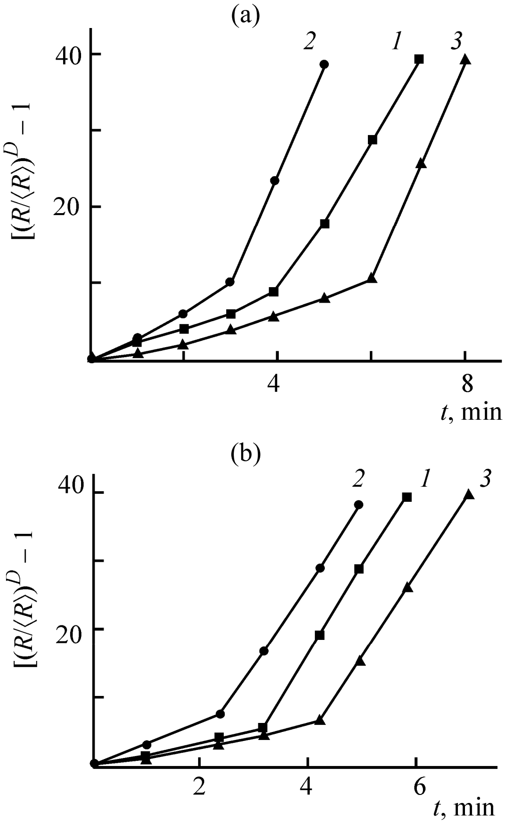

Fig. 7. Anamorphoses of the kinetic curves of dispersing the microtalc particles in solutions of YD-128S in the coordinates $[(R/<R>)^D - 1] - t$ (min). Concentration of YD-128S (%): (*1*) 10, (*2*) 40, (*3*) 60; the same for Fig. 8. Concentration of Byk-A530 (%) (a) 0, (b) 0.2; the same for Fig. 8.

$c^{\neq}$ value, which is consistent with the thermodynamic criterion of stability of multicomponent systems [11]. In the region of $c < c^{\neq}$, $\Delta F(c)$ has a local maximum, which coincides with a maximum concentration of discrete units YD-128S in a solution with $D \sim 1.1$ [8]. When $c > c^{\neq}$, the fractal dimension D of aggregates is equal to 2.8, the value $\Delta F(c) > \Delta F(c^{\neq})$ (Table 2, Fig. 4).

According to the cluster model [7–9], the area ω per one molecule of YD-128S in the surface phase near the threshold concentration $c^{\neq}$ is $\pi<r>^{2-D}r_0$, where r_0 and $<r>$ are radii of the molecule and the aggregate. The fractal dimension D of EO aggregates in solution near the $c^{\neq}$ is approximately equal to 2 [8, 9], so $\omega > \pi r_0^2$.

As in the region of $c < c^{\neq}$ the fractal dimension of aggregates $D < 2$, hence $\omega = \pi<r>^{2-D}r_0^D$ and exceeds the value of πr_0^2. In the region of $c > c^{\neq}$ at $D \sim 3$ the value $\omega = \pi<r>^{-1}r_0^3$, or less than the value πr_0^2 (Table 2).

It is presumable that surfactant molecules are localized in the surface phase of the solution YD-128S in Cardura [10]. According to the concepts [7], adding a surfactant to the solution of YD-128S should cause a decrease in the volume fraction $\varphi_2^{\text{surface}}$ of YD-128S in the surface phase and disintegration of the continuous fluctuation net of YD-128S links into discrete EO domains [10].

As follows from the data obtained (Fig. 5, Table 2), on adding of Byk-A530 (Troysol S-366) to a solution of YD128S near the threshold value $c^{\neq}$ the fractal dimension D of YD-128S aggregates decreases from 2 to 1.2 (1.4). With increasing Troysol S-366 concentration in the solution the value of D decreases further from 1.4 to 1.1. Decrease in the fractal dimension of YD-128S aggregates in solution in the presence of surfactants compared with solutions containing no surfactant leads to an increase in the area ω of the surface phase per one molecule of YD-128S and to decrease in the density ρ of the aggregates, which is undoubtedly connected with the decomposition of the continuous fluctuating net of links into the discrete domain [11].

The quantitative estimation of the effects of the concentration regimes of YD-128S resin in a solution on the rate of dispersion of pigment particles in liquid was carried out using an expression which relates the ratio of the initial radius *R* to the current average radius <*R*> of the aggregate particles with the reduced time $\tau = \gamma t$ of the process [7]

$$n(\tau) = (R/\langle R\rangle)^D = 1 + \gamma t, \qquad (3)$$

where γ is the process rate, *t* is duration of dispersion.

The rate γ of the pigments dispersion in various stages of the process was determined from the change the radius <*R*> of the particles aggregates with the fractal dimension $D = 2.3$ [14]. Note that, according to [3], fractal dimension *D* of microtalc particles aggregates dispersed in solutions of EO in Cardura in the region of $\langle R\rangle = 6–40$ μm is 2.0–2.5.

Kinetic curves of the change in the ratio of the initial *R* to the current average radius <*R*> of the particles aggregates in the coordinates $[(R/\langle R\rangle)^D - 1] - t$ consist of two linear plots, as follows from the data on the dispersion of pigments in solutions of YD-128S in Cardura (*c* = 10, 40 and 60%, Figs. 6–8).

The rate of the particles aggregates dispersion in the first and the second stages (γ_1 and γ_2, respectively) determines the length of the respective zones Δt_1 and of Δt_2 of the kinetic curve on the time scale *t*; the number *n* of the formed particles is proportional to the reduced time *t* (Table 3).

The rate of dispersing iron minium (Fig. 6), microtalc (Fig. 7) and the mixture of microtalc with chromium oxide and zinc phosphate (Fig. 8) is maximal at the threshold concentration $c^{\neq}$ of YD-128S in the solution. In this case the surface tension σ_{12} at the border of YD-128S solution with, for example, microtalc, like the dispersion surface energy ε^d of the microtalc wetting with solution, are minimal at $c^{\neq}$ = 40% (Tables 2 and 3).

Quantitative relationship between the ratio of rates γ_2/γ_1 of the first and second stages of the particles aggregates dispersion and the ratio $\Delta t_1/\Delta t_2$ can be represented by the expression

$$\gamma_2/\gamma_1 = \Delta t_1/\Delta t_2\,(e^D + 1). \qquad (4)$$

According to Table 3, the rate γ_2 of conversion of large particles aggregates of pigments and fillers into small aggregates in the second stage of the process of dispersion was approximately by an order of magnitude higher than the rate γ_1 of dispersion of particles in the first stage, which is consistent with the expression (4) and theoretical expectations [7, 12].

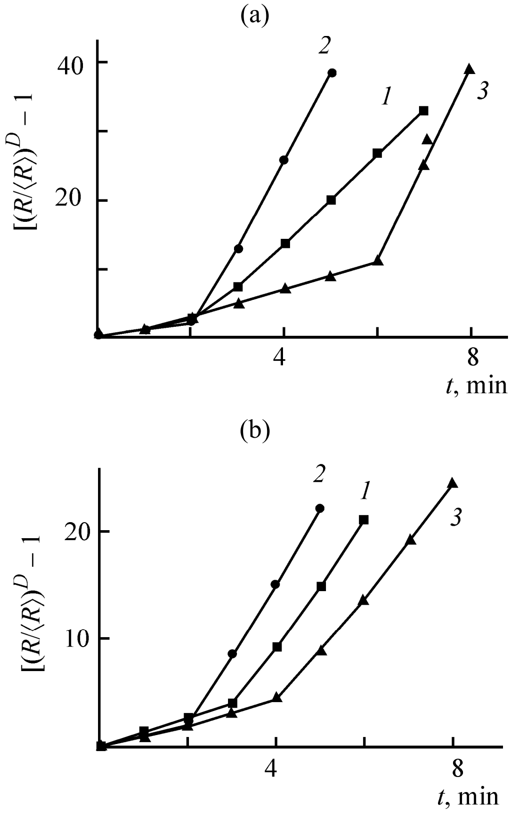

Fig. 8. Anamorphosis of the kinetic curves of dispersion of the mixture of particles of microtalc, chromium oxide and zinc phosphate (mass ratio 5:3:2) in solutions of YD-128S in the coordinates $[(R/\langle R\rangle)^D - 1]–t$ (min).

It is easy to show [3] that for the lattice density of particles aggregates the expression $\rho = w^{D-3}(R/\langle R\rangle)^{D-3}$ is valid. At the second stage of dispersion of pigments and fillers in a solution, the lattice density ρ reaches a critical value (~0.31), corresponding to an infinite cluster (SCC, *D* = 2.5) [7]. The correlation radius ξ of the particles aggregates, equal to $\langle R\rangle e^D$ [11], is about 70 μm, and near the threshold value $c^{\neq}$ the fractal dimensions *D* of aggregates of molecules YD-128S in solution and the aggregates of pigment particles (filler) are identical [3].

In the first stage Δt_1 of the dispersion of iron minium at the threshold concentration $c^{\neq}$ the average radius of particles aggregates decreases from the initial value 48 μm to $\langle R\rangle = 17\pm2$ μm or, approximately, *e* times. Number n_1 of the particles in this stage of dispersion is increased by approximately an order of magnitude (Fig. 6, Table 3).

In the second stage Δt_2 of the dispersion of iron minium ($c^{\neq}$ = 40%) the average radius <R> of the particles aggregates decreases from 17 to 6 μm, or about e times. Consequently, in the final stage of dispersing iron minium the average radius <R> of the particles aggregates decreases approximately e^2 times compared to the initial average radius R of the particles aggregates equal to 48 μ, which is also consistent with the expressions (3) and (4).

At the deviation of concentration from the threshold value $c^{\neq}$ the rate of the particles aggregates dispersion sharply decreases both in the first and in the second stages of the process (Figs. 6–8). For example, in the second Δt_2 stage the dispersing of the iron minium in a solution of YD-128S (c = 60%) the rate γ_2 of the process falls 2 times relatively to c = 40% (Fig. 6). Note that the maximum increase in the σ value was found in going from the semidilute ($[\eta]c = 1$) to the concentrated solution of YD-128S ($[\eta]c = 1.8$) (Table 3).

The rate γ_1 of disintegration of large aggregates into smaller aggregates in the first Δt_1 stage of the dispersing iron minium in a dilute solution of YD-128S in Cardura ($[\eta]c = 0.3$) is reduced approximately twofold compared to the semidilute solution of YD-128S ($[\eta]c = 1$). The rate γ_2 of the process in the second stage Δt_2 is reduced 1.5 times (Fig. 6).

In the study of dispersion of microtalc and its mixture with chromium oxide and zinc phosphate (initial average radius of the particles aggregates R = 35 μm) are found similar patterns of the change in the rate of dispersion of particles in going from a dilute ($c < c^{\neq}$) to the concentrated ($c > c^{\neq}$) solution of YD-128S (Table 3). According to our data (Figs. 7 and 8), the rate of dispersion of microtalc and the mixture of microtalc with pigments in the first and second stages of the process is also maximum at the threshold concentration $c^{\neq}$.

It should be noted that the introduction of non-ionic surfactant to the solution of YD-128S in Cardura at a threshold value $c^{\neq}$ does not increase the rate of dispersion of pigment particles [19, 20]. This is explained by the fact that at adding of surfactant to the solution ($c^{\neq}$ = 40%) the fractal dimension D of aggregates of molecules YD-128S is reduced from 2 to 1.2 (1.4). This leads to disintegration of the continuous fluctuating net of YD-128S links in the solution to the discrete domains and an increase in the dispersion of the surface energy ε^d of wetting the particles with the fluid. As $\gamma = dn/dt \sim \exp[-\varepsilon^d/kT]$ [21], in this case the rate γ of dispersing the pigments must be less than the rate γ of the process in the absence of a surfactant (Table 2).

Introduction of surfactants into a dilute solutions of YD-128S gives no noticeable effect on the rate γ of dispersing pigments in comparison with the solutions containing no surfactant (Figs. 7 and 8). Adding of 0.2% of Byk-A530 to the diluted solution of YD-128S (c = 10%) leaves the σ and ε^d values virtually unchanged, so the rate γ of dispersion of pigment particles (filler) remains the same.

In concentrated ($c > c^{\neq}$) solutions of YD-128S containing Byk-A530 and Troysol S-366, the rate of pigments dispersion depends on the surfactant concentration. For example, at the introduction of 0.2% of Byk-A530 into the solution with c = 60% is observed an increase in the rate γ_2 of dispersion at the second part of the kinetic curve of change in the radius <R> of the particles aggregates, compared with a solution of YD-128S not containing a surfactant (Table 3). However, the rate γ_1 of dispersion particles in the first Δt_1 stage of the process is about 2 times lower than at the threshold value in the absence of surfactant (Figs. 7 and 8).

At adding 0.45% of Troysol S-366 to a solution of YD-128S with the concentration c = 45%, slightly exceeding threshold $c^{\neq}$, the Gibbs free energy change $\Delta F < 0$ and larger in magnitude than ΔF at $c = c^{\neq}$. In this case, the dispersion energy ε^d at wetting particles decreases, and this can lead to an increase in the rate of the pigments dispersion [10, 13] (Table 2). However, it should be noted that the use for dispersing the pigments of a solutions of YD-128S in Cardura in which the content of a surfactant (in particular, Troysol S-366) exceeds 0.4%, is undesirable because of the sharp fall in the protective characteristics of the cross-linked epoxy coatings.

To conclude, it should be noted that at curing the studied epoxide compositions ($c = c^{\neq}$) with amines two infinite clusters are formed , one nested in the other [7, 9]. The lattice density of the clusters, which reflects the continuous small-scale chemical net of the epoxyamine polymer and uniform large-scale physical net of the pigment (filler) particles distributed in the domains with low local density of nodes of the chemical net [3, 9], is close to the critical values 0.69 and 0.31, respectively [7]. At a deviation from the threshold concentration of EO in solution in the region of $c > c^{\neq}$ the usual infinite cluster of the nodes of chemical net of cross-linked polymer and pigment particles (filler) is not formed.

CONCLUSIONS

(1) It is shown that the rate of dispersion of pigments particles depends on the concentration of low-molecular epoxydiane resin dissolved in Cardura, which determines the surface tension σ at the interface between the solutions and air, as well as dispersion energy of wetting particles with fluid and conditions of percolation of particles and aggregates of the resin molecules.

(2) The rate of dispersion of the particles aggregates of pigments and fillers in the solutions of epoxydiane resin (YD-128S) is maximal at the threshold concentration $c^{\neq} = 40\%$, corresponding to the global minimum on the $\sigma(c)$ curve and formation in the solutions of continuous fluctuating net of links. The rate of dispersion of the particles aggregates on the second stage of the process is approximately by an order of magnitude higher than in the first stage, which is consistent with the cluster lattice model.

(3) At the use of dilute or concentrated solutions of resin YD128S instead of semidiluted solution, as well as at the introduction to the resin solutions of nonionic surfactants a decrease is detected in the rate of dispersion of the particles aggregates. This effect is associated with the growth of the surface free Gibbs energy and surface dispersion energy of wetting particles with fluid, owing to the collapse of the continuous fluctuating net of links of the epoxydiane resin molecules in the solution into discrete domains.

(4) At the increase in the concentration of nonionic surfactants in concentrated solutions of epoxydiane resin the rate of dispersion of the particles aggregates increases. However, at the concentration of nonionic surfactants (dispersing additives) exceeding 0.4% the protective characteristics of cross-linked epoxy coatings are reduced, which limits the use of surfactants for dispersing pigments and fillers.

ACKNOWLEDGMENTS

The authors express their gratitude to V.I. Karaseva, S.S. Mnatsakanov, and V.D. Zaporozhets for help in experiment and discussion of results of the work.

REFERENCES

1. *Lakokrasochnye materialy i pokrytiya: Teoriya i praktika* (Painr and Varnish Materials and Films),. Lyamburn, R., Ed., Mashlyakovskii, L.M. and Frost, A.M., Eds., St.-Petersburg.: Khimiya, 1991.
2. Chernin, I.Z., Smekhov, F.M., and Zherdyaev, Yu.M., *Epoksidnye polimery i kompozitsii* (Epoxy Polymers and Compositions), Moscow: Khimiya, 1982.
3. Krasovskii, A.N., Potashev, M.G., Filippov, V.N., and Mnatsakanov S.S., *Zh. Prikl. Khim.,* 2006, vol. 79, no. 10, pp. 1693–1700.
4. Krasovskii, A.N., Kharlampiev, A.A., and Krasheninnikov, V.A., *Vysokomol. Soedin. A*, 1997, vol. 39, no. 2, pp. 250–258.
5. Krasovskii, A.N., Kharlampiev, A.A., and Plodistyi, A.B., *Zh. Prikl. Khim.,* 1997, vol. 70, no. 4, pp. 661–669.
6. Demidov, V.N., *Dokl. Akad. Nauk,* 2004, vol. 394, no. 2, pp. 218–221.
7. Feder, J., *Fractals*, New York: Plenum Press, 1988.
8. Filippov, V.N., Cand. Sci. (Chem.) Dissertation, St.-Petersburg, 2004.
9. Krasovskii, A.N., Filippov, V.N., and Novikov, D.V., *Zh. Prikl. Khim.,* 2007, vol. 80, no. 7, pp. 1190–1199.
10. Pugachevich, P.P., Beglyarov, E.M., Lavygin, I.A., *Poverkhnostnye yavleniya v polimerakh* (Surface Phenomena in Polimers), Moscow: Khimiya, 1982.
11. De Zhen, P., *Idei skeilinga v fizike polimerov* (Skeiling's Ideas in Physic of Polymers), Lifshits, I.M., Moscow: Mir, 1982.
12. Von Smoluchovski, M., *Phys. Z.*, 1916, vol. 17, pp. 557–599.
13. Wu, S., *Polymer Interfaces and Adhesion*, New-York: Marcel Dekker, 1982.
14. Avnir, D., Farin, D., and Pfeifer, P., *Nature*, 1984, vol. 308, pp. 261–263.
15. Hare, C.H., *Protective Coatings. Fundamentals of Chemistry and Composition*, London: Technology Publishing Comp., 2001.
16. Drinberg, S.A. and Itsko, E.F., *Rastvoriteli dlya lakokrasochnykh materialov* (Solvents for Paint and Varnish Materials), St.-Petersburg: Khimizdat, 2003.
17. *SERVO Coating Additives in Primary Formulations for Various Coatings*, Delden: Sasol Servo BV, 2002.
18. Kuleshov, I.D., *Lakokrasochnye materialy i ikh primenenie*, 2002, no. 12, pp. 4–8.
19. Korsunskii, L.F., Kalinskaya, T.V., and Stepin, S.N., *Neorganicheskie pigmenty: Spravochnik* (Inorganic Pigments: Handbook), St.-Petersburg: Khimiya, 1992.
20. Ermilov, P.I., Indeikin, E.A., and Tolmachev, I.A., *Pigmenty i pigmentirovannye lakokrasochnye materialy* (Pigments and Paint and Varnish Materials Pigmented), Leningrad: Khimiya, 1987.
21. Khennei, N., *Khimiya tverdogo tela* (The Chemistry of Solid), Boldyrev, V.V., Ed., Moscow: Mir, 1971.