

## Phase Separation of Polymer Solutions on a Solvent Surface

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**Abstract**—Study of the dynamics of liquid droplets of dilute and semidilute polymer solutions on the surfaces of liquid subphases representing solvents for corresponding polymers has shown that a spot of a rather stable layer is formed on an air–liquid interface. The spot spreads over a liquid subphase surface to yield a monomolecular polymer layer. At the same time, the solvent passes into the solution, so that the polymer or its concentrated solution remains on the subphase surface. The polymer does not dissolve in the bulk subphase for several hours. The stability of the polymer spot has been explained under the assumption that the interfacial surface possesses elastic properties and hinders the penetration of macromolecules into the bulk subphase. Desolvation of macromolecules followed by phase separation occurs on the surface. The initial rate of the phase separation of the solution is rather high, while the time dependence of the diameter of the spreading spot is described by a scaling law with an exponent almost equal to 2/3.

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### INTRODUCTION

Processes of wetting and spreading of liquids over surfaces are among the main phenomena that are investigated in colloid and physical chemistry, because they are associated with the fundamental thermodynamic characteristics of both surfaces and liquid phases. Numerous studies devoted to this scope consider the processes of wetting and spreading occurring on either solid or liquid surfaces. In the first case, the processes are analyzed on the basis of the Young law; in the second case, adsorption of poorly soluble surfactants on an interfacial surface is commonly considered. It is the adsorption that predetermines the scale of a reduction in the surface tension of a liquid phase in the presence of a specific surfactant.

The general physical regularities and generalization of available experimental facts relevant to the physicochemical interactions between a liquid and a solid surface have, in particular, been considered in [1, 2], later reviews [3, 4], and monograph [5].

For the purposes of this work, the main interest is in the spreading of a liquid over a liquid, which has been studied to a much lesser extent. This is mainly due to the fact that two liquids, as a rule, interact with each other; in particular, they may miscible. Moreover, a substrate (subphase) may be deformed, while another liquid spreads over it.

As has, for a long time, been known, oil poured onto a water surface damps waves. This phenomenon has been qualitatively explained on the basis of Reyn-

olds' earlier studies in the classic monograph by Lamb [6]. This explanation is based on the fact that oil spreads over a water surface into a thin film with a nanosize thickness. When the film is stretched, its thickness decreases and the stress increases. Upon wavy motion of water, tangential and normal stresses arise in the film and the rate of energy dissipation in the viscoelastic film increases; i.e., the waves are damped. If the substrate surface area is infinite, a droplet may spread until a monomolecular layer is formed. This explanation implicitly implies that, as the thickness of the liquid film decreases, its longitudinal viscosity increases and/or elasticity begins to manifest itself, so that the film behaves as a thin elastic film.

The appearance of elasticity in thin interfacial layers on liquid subphases has recently been described in [7]. The problem of spreading a liquid over a liquid is undoubtedly of both basic and practical interest. In particular, it is of importance for the analysis of spreading hydrocarbons over water (e.g. in the case of oil spillage). Another interesting field of application of this phenomenon is the coverage of reservoirs with liquids containing active substances for eliminating larvae of malarial mosquitoes.

In the general formulation, the motion of a liquid droplet must be described by the Navier–Stokes equations. Among the early studies of the discussed problem are communications [8–10], in which dynamic equations have been formulated, which are, in essence, analogous to those for liquid spreading over a solid surface, including the case in which the spread-

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**Table 1.** Characteristics of studied polymers

Denotation	$[\eta]$ , dL/g	$M_w$ , kDa	$c^*$ , g/dL
PEO-1	10.7	3000	0.07
PEO-2	3.1	500	0.25
PEO-3	0.6	40	1.28
PAA	105	12000	0.0073
PAA	105	12000	0.0073

ing is limited by a barrier. Some results of the solution of the problem relevant to spreading one liquid over the surface of another liquid have been obtained by numerical methods in [11, 12]. In [13], a general scaling expression with an exponent of  $2/3$  has been found for the time dependence of the spot radius upon liquid spreading over the surface of another liquid. It is essential that pairs of immiscible liquids have been considered in all the cited works.

Recently, an analytical study has been published devoted to the equilibrium states of a liquid on a liquid surface [14]. It has been shown that a liquid/liquid contact may be accompanied by the existence of an equilibrium state specific for liquids. It consists in the formation of a droplet having the shape of a macroscopic lens, which deforms the smooth surface of a subphase and is at equilibrium with a thin film that covers the substrate.

The goal of this work is to study the spreading of a more complex object, i.e., a polymer solution, over an air–liquid interfacial surface, with the subphase being a solvent for the studied polymer; i.e., in contrast to the previous communications, both media are actually formed by the same liquid. Both the equilibrium state

of a formed layer and the kinetics of the solution spreading over the air–liquid–subphase boundary are considered.

## EXPERIMENTAL

### Objects

Aqueous solutions of poly(ethylene oxide) (PEO) with molecular masses  $M_w = 40, 500, \text{ and } 3000 \text{ kDa}$  and polyacrylamide (PAA) with  $M_w = 12 \text{ MDa}$  were used as main objects of the study. The variations in the concentration covered two orders of magnitude: 0.005, 0.05, and 0.5%.

For infinitely diluted PEO and PAA solutions, the values of intrinsic viscosity  $[\eta]$  were measured and crossover concentrations ( $c^*$ ), which corresponded to the formation of macromolecular contacts (entanglements) in the solutions, were calculated (to some extent, conventionally) as follows [15]:

$$c^* = 0.77 \frac{1}{[\eta]}. \quad (1)$$

In all cases, distilled water was used as a solvent. All measurements were performed at  $20 \pm 1^\circ\text{C}$ . The corresponding characteristics of the samples are presented in Table 1.

The surface tensions of all solutions were measured by the maximum bubble pressure method. Surface tension  $\sigma_s$  of the studied samples was determined from the ratio between pressures of gas bubble detachment for a solution  $p_s$  and water  $p_{\text{H}_2\text{O}}$  [16]:

$$\sigma_s = \sigma_{\text{H}_2\text{O}} \frac{p_s}{p_{\text{H}_2\text{O}}}, \quad (2)$$

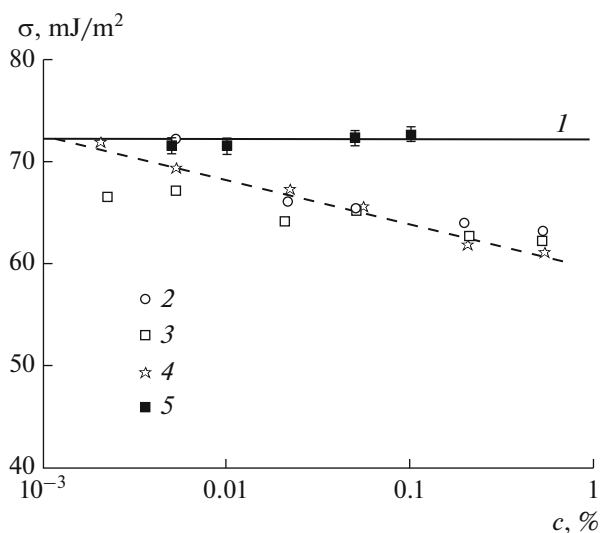
where  $\sigma_{\text{H}_2\text{O}}$  is the surface tension of the reference liquid (water). The error of the method was 1%.

The measured values of the surface tension (mJ/m<sup>2</sup>) and corresponding concentration dependences for PEO and PAA solutions are presented in Fig. 1.

The results obtained show that PEO exhibits surface activity, since the surface tension of its solutions monotonically decreases with an increase in the polymer concentration (Fig. 1). For PAA solutions, the surface tension is independent of the concentration and almost equal to that of water (72.5 mJ/m<sup>2</sup>). Thus, two water-soluble polymers have been used as objects for the study, with one polymer (PEO) being surface-active and another one (PAA) not.

### Experimental Setup

To visualize the spreading of the polymer solutions over the solvent, a setup was designed (Fig. 2), which consisted of light-protective housing 1, Teflon-coated dish 2 (3 cm in diameter) located in the housing,



**Fig. 1.** Concentration dependences of surface tension for (1) water; aqueous solutions of PEO with  $M_w =$  (2) 40, (3) 500, and (4) 3000 kDa and (5) PAA.

opaque light-scattering cone 3, light-emitting illuminators 4, and camera 5. Before an experiment, the Teflon dish was thoroughly degreased with acetone and ethanol, washed, and dried with compressed air. Then, the solvent (distilled water) was poured into the dish.

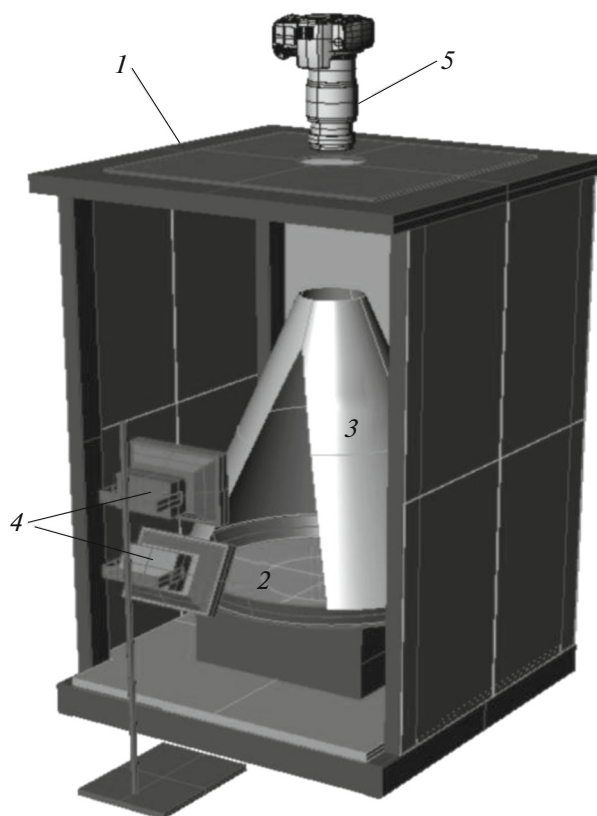
When preparing to the main experiment, light-reflecting tracers were applied onto water surface. Aluminum powder, the particles of which were used as the tracers, was sprayed onto the water surface in amounts so small that the particles could be seen and recorded with the camera.

The used aluminum powder particles contained 2% of grease, and there were no additional stabilizers. After the powder particles were sprayed over the surface, no flows in the form of microscopic streams, which would cause rotation or displacement of dispersed particles, were observed. Aluminum powder particles were selected as tracers, because particles with high reflecting power were necessary for obtaining high-quality images. A possible influence of the particles on the character of polymer solution spreading over the surface was specially estimated. For example, independent experiments were performed to detect the boundary of a spreading spot from the displacement of dust particles, which had been deposited onto the surface from air, and microscopic foamed-polystyrene particles, which were also used as tracers. The results of these experiments appeared to be identical. The data obtained have led us to conclude that particles of aluminum powder (deposited in small amounts as dust set onto the surface) can be used as tracers that do not disturb the results of experiments on polymer solution spreading.

The water surface with deposited aluminum powder particles was uniformly illuminated with light scattered by the opaque cone. This was realized by directing the luminous flux of light-emitting diodes inside the cone avoiding the direct exposure of the surface. The light-scattering cone had an orifice at its vertex for photographing and video filming. A Sony NX-5N camera equipped with an SEL30M35 macroobjective was used as a photo and video recorder.

The experiment was performed as follows. A polymer-solution droplet with a preset volume was placed onto the center of the dish with a microsyringe, while moving a needle to the surface as closely as possible to avoid the impact of the droplet on the surface. Droplets of PEO solutions did not mix with the aqueous subphase, but rather spread over its surface, thus "pushing aside" the tracers (Fig. 3).

The spreading kinetics was recorded by filming at the HD quality and a frequency of 30 frames per second. The frame-by-frame processing of initial data (measurements of the spot diameter) resulted in the quantitative description of the spreading process. All time dependences of the spot diameter presented and



**Fig. 2.** Setup for visualization of the spreading process: (1) housing, (2) dish, (3) light-scattering cone, (4) illuminators, and (5) camera.

discussed below were normalized with respect to a fixed solution volume of 10  $\mu\text{L}$ .

## RESULTS AND DISCUSSION

### *Characteristics of Resulting Equilibrium Spot*

The main qualitative result of the performed experiments was the finding that, when a droplet of a polymer solution in a liquid was applied onto the surface of the same liquid, the droplet integrity and spreading over the subphase surface were observed rather than the dissolution of the polymer. It is of significance that the spreading over the surface was observed throughout the studied concentration range. As can be seen from the data in Table 1, the experiments were performed with both dilute ( $c < c^*$ ) and moderately concentrated ( $c > c^*$ ) solutions, because it was not clear in advance if the behaviors of dilute and moderately concentrated PEO solutions would be different. It appeared that the spreading over the surface rather than the dilution of a solution droplet with the solvent up to complete dissolution took place for solutions of all concentrations, including the most diluted ones. The same phenomenon of spreading rather than dis-

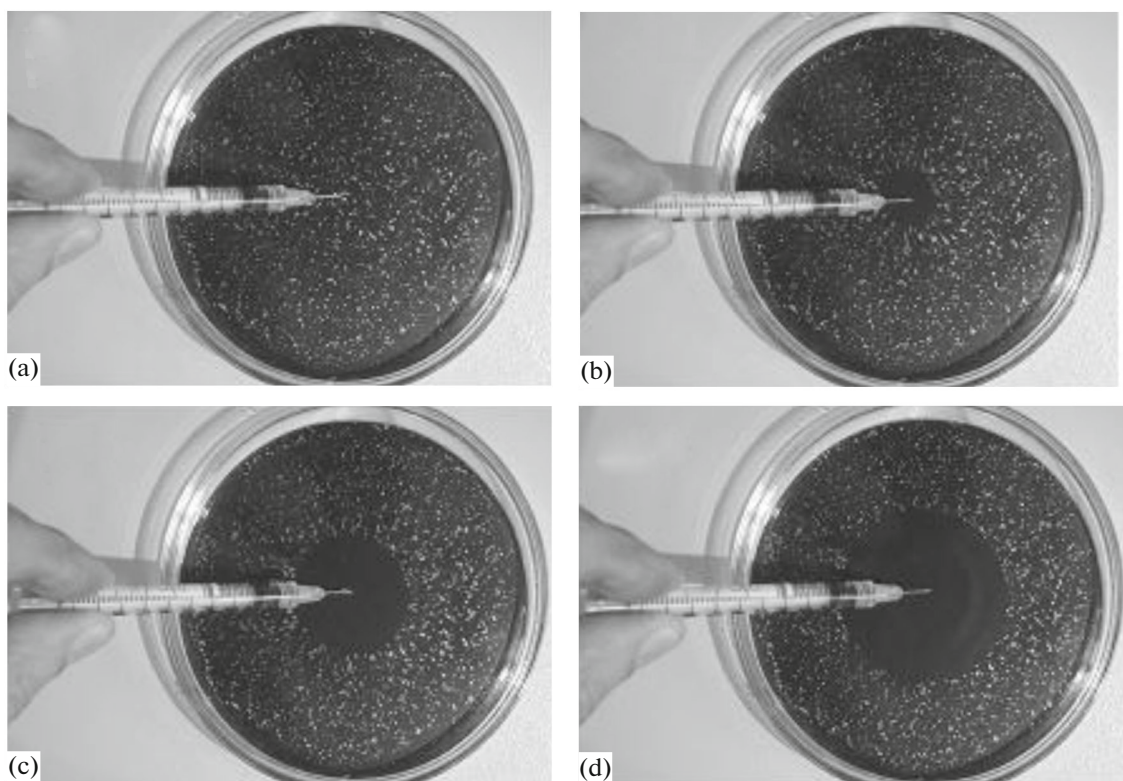


Fig. 3. Successive (a)–(d) stages of PEO solution spreading over a water surface.

solution was observed for not only the studied PEO and PAA solutions, but also in qualitative control experiments with dilute aqueous solutions of hydroxypropyl cellulose and gelatin, as well as with solutions of polyacrylonitrile and a different solvent—dimethyl sulfoxide—used as a subphase.

Thus, the discussed phenomenon of the spreading of dilute and semidilute solutions over an air–solvent interfacial surface was observed for both surface-active and surface-inactive polymers.

The following experiments were also performed. A droplet of a solution was extruded from the needle (of the microsyringe) located under the surface of a subphase at a depth of 1–3 mm. When the experiment was performed rather carefully without a jet flow in the bulk, no spots were formed on the surface. A spot arose only when the tip of the needle led up to the surface from below touched the interface. Thus, it may be believed that, irrespective of the manner in which a solution is introduced (from the side of a liquid or a gas), the spreading phenomenon arises when the interface is accessed.

The spreading of dilute polymer solutions results in the formation of a spot with a finite size. Assuming that, in this case, monolayers are formed in which dense packing of coils takes place with concentration  $c^*$ , measured spot area ( $S$ ), droplet volume ( $V$ ), and solution concentration ( $c$ ) normalized with respect to

crossover concentration ( $c^*$ ) may be used to determine thickness  $h$  of the formed layer as follows:

$$hS = \frac{c}{c^*} V. \quad (3)$$

The performed experiments have enabled us to calculate the thickness of the adsorption layer for PEO with each molecular mass by formula (3).

Root-mean-square radius of inertia  $\langle R^2 \rangle^{0.5}$  of macromolecular coils under theta-conditions is known to be related with molecular mass via the following relation [17]:

$$\langle R^2 \rangle^{0.5} = AN^{0.5}, \quad (4)$$

where  $N$  is the number of segments, which is proportional to the molecular mass of a polymer, and  $A$  is a coefficient.

This makes it possible to compare the thicknesses of the layers and the diameters of the coils (Table 2). It can be seen that the layer thicknesses and macromolecular coil sizes calculated for the theta-conditions coincide, at least in order of magnitude, with each other; i.e., a layer of a polymer or its concentrated solution is formed. This comparison leads us to suggest that PEO monolayers are present in the formed adsorption layers, with the interfacial surface, in con-

**Table 2.** Thicknesses of layers of PEO solutions

MM, kDa	$c^*$ , dL/g	$\langle 2R \rangle$ , nm	Concentration, mL/g	$V$ , $\mu\text{L}$	$D$ , cm	$h$ , nm
40	1.14	24	0.005	7	6.6	11
				15	7.3	20
			0.05	10	20	17.5
			0.5	1.5	27.6	14
				2.0	31.9	14
500	0.23	85	0.005	10	6.8	77
				2	2.8	89
			0.05	5	15.5	74
				3	13.1	62
			0.5	1.0	27.3	47
				1.5	27.8	58
3000	0.07	208	0.005	5	8.2	87
				10	10.5	105
			0.05	10	24.1	199
				5	15.6	239
			0.5	2	31.7	231
				1	24.3	196

trast to the bulk subphase, playing the role of a bad solvent or even a precipitant.

The linear (in the logarithmic coordinates) dependence of the layer thickness on molecular mass  $M_w$  offers additional experimental confirmation that polymer monolayers are formed. This dependence (Fig. 4) may be described by a formula analogous to the Mark–Houwink equation

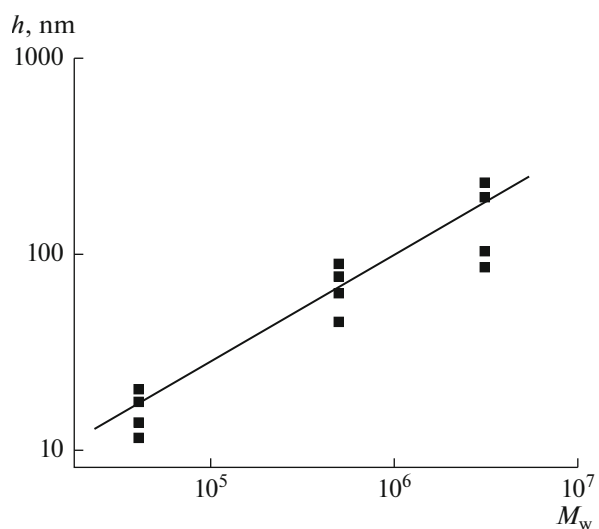
$$h(M) = 0.046M_w^{0.52}. \quad (5)$$

The exponent of this dependence is equal to 0.52, which, taking into account the scatter of the points, almost coincides with the exponent corresponding to the theta-conditions. The error in the determination of the adsorption layer thickness (corridor of data scattering) may be judged from the scattering of values obtained in a series of measurements (see Table 2).

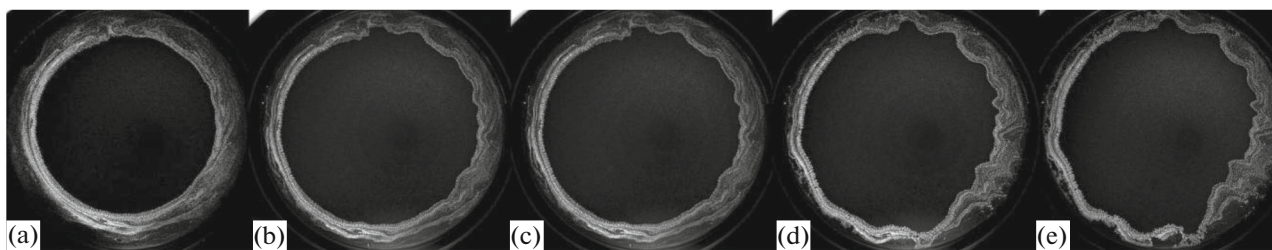
PEO monolayers are time-stable; their lifetime is no shorter than several tens of minutes. In the course of time, the contour of a circular spot begins to be deformed (Fig. 5). A distortion that has occasionally appeared in one place begins to propagate along the contour. In essence, the contour instability may be considered as an analog of ordinary capillary instability for the two-dimensional case. The amplitude of these distortions increases with time, and an initial single spot is, in the long run, disintegrated into smaller spots to yield a two-dimensional emulsion of polymer monolayers.

Although large spots are (on a large time scale) unstable, it may be concluded that macroscopically large adsorbed polymer monolayers remain preserved at the interface at room temperature and are not ruptured by the thermal motion.

The phenomenon considered in this work is similar to the well-known phenomenon of the formation of



**Fig. 4.** Layer thickness of a stable spot resulting from solution spreading as a function of polymer  $M_w$ .



**Fig. 5.** Temporal development of contour instability of a PEO monolayer on a water surface. The time intervals between separate (a)–(e) photographs are equal to 3 min.

stable monolayers of water-soluble proteins on an aqueous surface. Such monolayers may exist for a long time at a water–air interface without passing to the subphase [18]. At the same time, proteins forming stable monolayers possess surface activity, which is, however, not a decisive factor in the discussed experiments. Moreover, when performing such experiments, salt solutions are commonly used rather than pure water, with the solutions degrading the solubility of the proteins.

#### *Kinetics of PEO Solution Spreading*

When a droplet touches the subphase surface, a circular spot is formed on the latter, with the circle diameter rapidly increasing. On reaching a certain size, the growth of the circular spot dramatically decelerates and a stable spot is formed. At the stage of the passage from the spot growth to its stabilization, damped self-oscillations of the spot diameter are observed in some cases. The formation time of a relatively stable spot is 5–20 s. On a time scale of approximately 1 min and more, the spot diameter slightly increases or (sometimes) decreases.

The kinetics of the spot diameter growth (i.e., the rate of variations in the diameter at the stage of rapid growth) is of significance. The data on time variations in the rate of spreading are shown in Fig. 6.

It can be seen that the spreading kinetics is characterized by two regions: in a wide time interval, the diameter gradually increases; then, it rather abruptly reaches a constant value. Initial values of the rate of spreading (at  $t \approx 0$ ) can be estimated only rather approximately. For 0.5% solutions of the studied polymers with all molecular masses under consideration, the initial rate is nearly 40–60 mm/s. Figure 7 illustrates the time dependences of spot diameters  $D$  for 0.5% solutions of the polymers with different molecular masses. The spreading kinetics of the spot (until the equilibrium state is reached) is quite adequately described by a power law of the following form:

$$D \propto t^n. \quad (6)$$

Figure 7 indicates that, for three different molecular masses, the exponents are close to each other;

hence, a general scaling dependence with exponent  $n = 0.65 \pm 0.05$  or  $n = 2/3$  may be used. Reliable quantitative time dependences of the spot diameter can hardly be obtained for solutions with lower concentrations.

The initial rates of spreading depend on solution concentration (the higher the concentration, the higher the rate), although this dependence is not very strong.

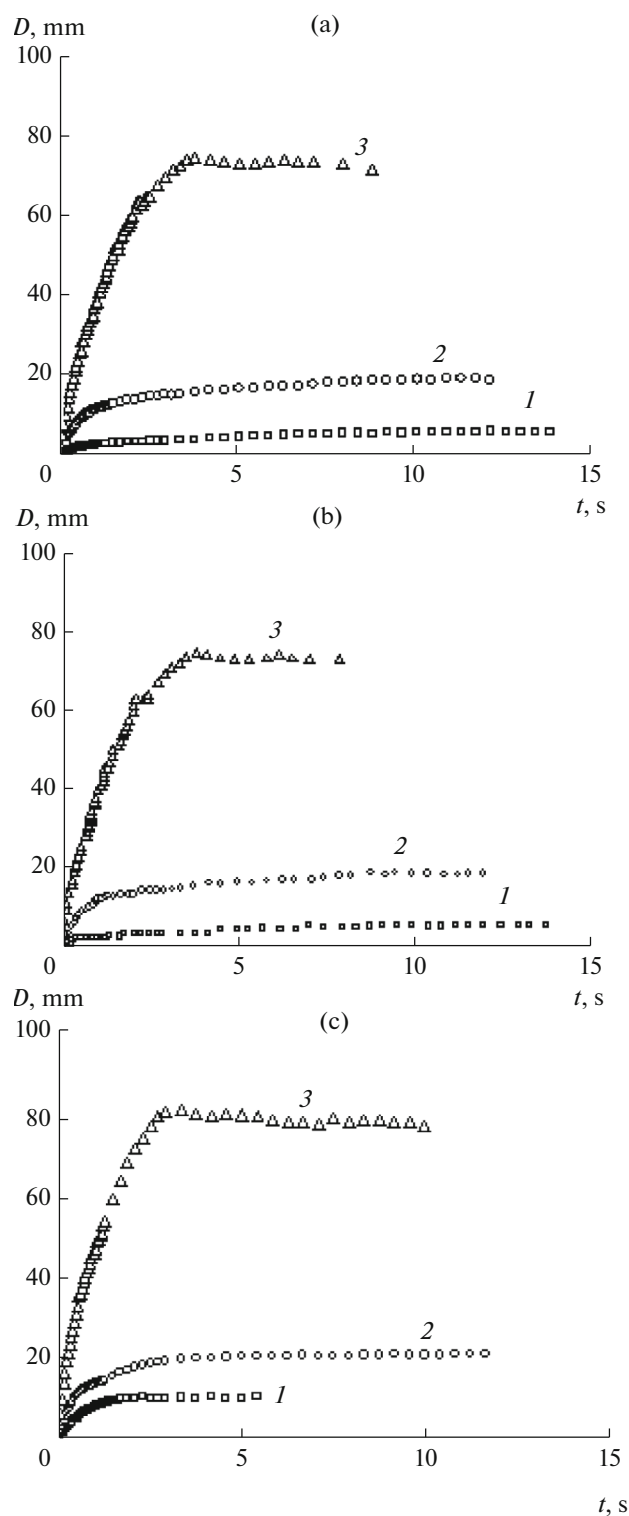
According to the results of some well-known studies, the dependence of the diameter of a droplet spreading over a solid surface on time  $t$  is also described by power law (6). Depending on a model used for calculations,  $n$  lies between 1/4 and 1/10 (see, e.g., [19, 20]). These data are incommensurable with the obtained result  $n \approx 2/3$ . Hence, the mechanism (driving force) of droplet spreading differs from that considered in the cited works. Indeed, the driving force of immiscible liquid spreading over a liquid subphase is the Marangoni effect [10, 13]. According to our experimental data, the exponent in formula (6) appears to be lower than the value of 0.75 that was obtained for immiscible liquids.

Thus, some novel experimental data have been obtained in the above-described experiments.

First, the long-term absence of the solubility of a polymer, which is readily soluble in a subphase, through the solvent surface, although both liquids are miscible and the polymer may be free of surface-active properties. In this respect, the interface plays the role of a barrier. According to the data obtained, the interfacial surface may be considered to be a “theta-solvent” in contrast to a “good” bulk solvent. The existence of a polymer monolayer on the surface may be considered as an equilibrium state (although the possibility of a very slow diffusion transfer through the surface with the dissolution of the monolayer cannot be completely excluded).

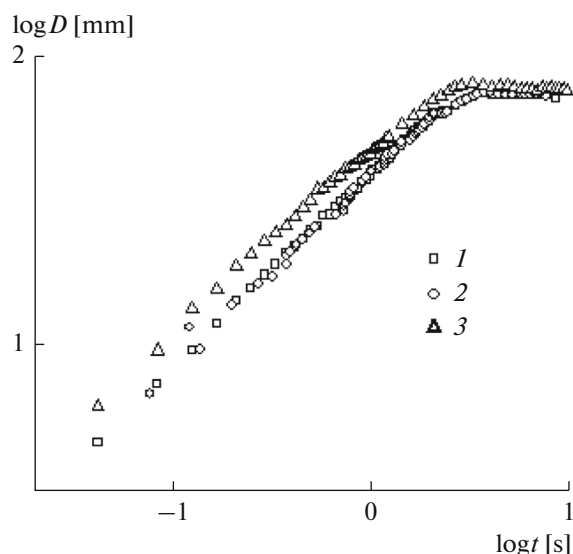
Second, a rather high initial rate of spreading.

Third, the power dependence of the spreading spot diameter on time with an exponent of 2/3, which is substantially higher than the values known for the spreading over a solid surface but somewhat lower than



**Fig. 6.** Time dependences of diameters of the spots resulting from spreading of 10- $\mu$ L droplets of solutions of PEO with  $M_w =$  (a) 40, (b) 500, and (c) 3000 kDa at polymer concentrations of (1) 0.005, (2) 0.05, and (3) 0.5%.

the exponent for the spreading of a liquid incompatible with a subphase.



**Fig. 7.** Spot-growth rates for 0.5% solutions of polymers with  $M_w =$  (1) 40, (2) 500, and (3) 3000 kDa.

Fourth, the peripheral instability of a formed monolayer, which may be interpreted as an analog of the Rayleigh instability.

It has been suggested that there are different mechanisms responsible for the discussed phenomena. In any case, the community of the observed phenomenon for both surface-active and -inactive polymers enables us to exclude surface tension as a factor playing a key role in the spreading kinetics. In our opinion, the key factor affecting the formation of a stable spot is the fact that an interfacial surface that possesses elastic properties hinders the penetration of macromolecules into the subphase. Desolvation of macromolecules followed by phase separation occurs on the surface. Therefore, the majority of the solvent passes into the subphase, so that the phases are separated, and the polymer or its concentrated solution forms a monomolecular layer on the liquid surface. This phenomenon is observed for not only very dilute solutions, but also for solutions in which entanglements arise (at concentrations higher than the crossover point). Even if the polymer dissolution takes place, it proceeds much slower than the mixing of a subphase with a dilute solution, thus leading to the long-term retention of the polymer on the surface. Moreover, a two-dimensional polymer layer may, at room temperature, be entirely insoluble in the solvent, but rather occur at the thermodynamic equilibrium with the subphase, which is evident from its thickness, which is approximately equal to the size of a macromolecular coil non-interacting with the solvent.

The same mechanism (phase separation) may be responsible for the rapid spreading of a polymer solution droplet over a surface, the driving force of which is the release of the polymer–solvent bond energy.

## CONCLUSIONS

Novel experimental data have been obtained on the behavior of polymer solutions at an air–liquid interface, with a liquid being a solvent for a polymer. It has been found that the application of a polymer solution droplet onto the solvent surface results in the formation of a stable spot, which, most likely, represents a monomolecular polymer layer. Thus, the dissolution does not occur through the interfacial surface in contrast to mixing of the same solution with the solvent in bulk. On the liquid surface, macromolecules form coils with sizes close to the sizes of macromolecules occurring in a theta-solvent. At the initial moment, the solution spreads over the liquid surface at a high rate, while the time dependence of the spot diameter is described by a scaling law with an exponent close to 2/3. The formed spot may disintegrate because of the instability of its contour boundary.

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