

## PROPERTIES OF MODIFIED GELATINS AT AN INTERFACE

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UDC 541.182.02+547.96.541.183

*The influence of a chemical modification (hardening) on the behavior of photographic gelatins at an interface has been investigated. It has been established, using the Langmuir monolayer method, that the properties of the surface layers of a modified gelatin change at the water–air interface and the depth of modification influences the surface activity of the gelatin. The surface properties of gelatin gels were investigated by the method of wetting depending on the hardener nature and the gelatin molecular-mass composition. It has been established that the hydrophilicity of gelatin gels increases with increase in the content of  $\alpha$ -chains and the surface of gelatin gels is additionally hydrophilized as a result of their modification.*

**Introduction.** The main method of chemical modification of gelatins in the production of light-sensitive layers is their hardening, involving chemical reactions between the functional groups of the polypeptide chain and the multi-functional organic and inorganic compounds. The effectiveness of a hardener is determined by the number of cross links formed by it. The larger the number of functional gelatin groups interacting (under identical conditions) with a hardener, the higher its effectiveness [1].

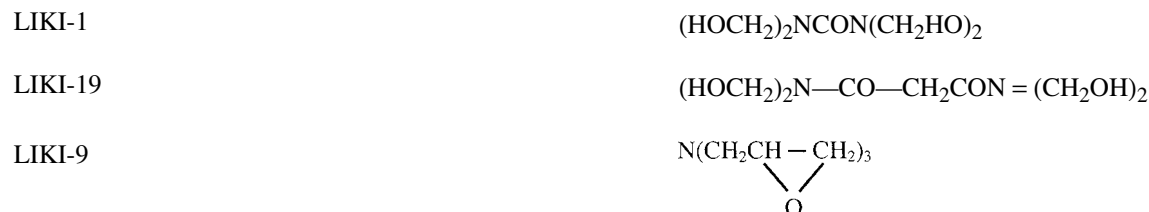
An important parameter influencing the properties of photographic materials is the molecular-mass composition of a gelatin [2]. The main components of a gelatin are  $\alpha$ -,  $\beta$ -, and  $\gamma$ -polypeptide chains with a molecular mass of 95, 190, and 285 kDa respectively; the last two components mentioned are chemically cross-linked  $\alpha$ -chains.

Modern light-sensitive materials represent multilayer systems. To obtain these systems, it is necessary to well wet emulsive gelatin layers, because, in this case, a uniform contact between the layers is formed and a high quality of treatment of the upper layer of the material can be attained. In this connection, the aim of the present work was to investigate the change in the surface gelatins in the process of hardening and the influence of the hardening and the molecular-mass composition of gelatins on the surface properties of their gels.

For the purpose of formation of light-sensitive materials and control of their properties, it is important to investigate systems exhibiting the properties of gelatins and photographic layers.

**Objects and Methods of Investigation.** We investigated two gelatin samples differing in molecular-mass composition (Table 1). The molecular-mass composition of the gelatins was determined using a high-efficiency liquid chromatography.

In our investigations, we used the formaldehyde hardeners tetrahydroxy methyl urea (LIKI-1) and tetrahydroxy methyl diamide of malonic acid (LIKI-19) and the epoxide hardener triglycidylamine (LIKI-9 or TGA):



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TABLE 1. Molecular-Mass Composition of Gelatins, %

Number of sample	Content of fractions with a definite molecular mass, kDa				
	>285	285	190	95	<95
1	—	—	—	61.5	38.5
2	7	17.5	17.5	47	11

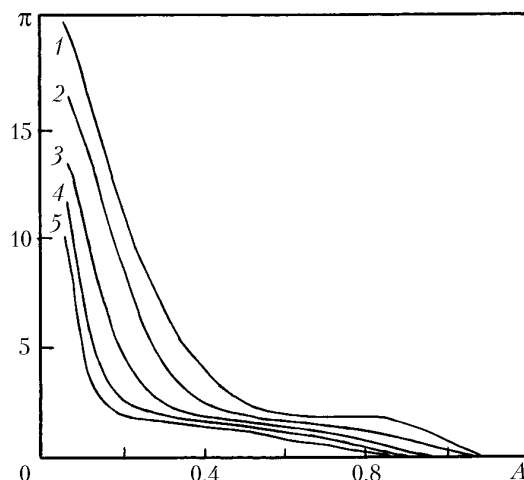


Fig. 1. Influence of the hardener LIKI-1 on the two-dimensional compression isotherms  $\pi$ - $A$  at different hardener (1 mole):gelatin (100 g) ratios: 1) non-modified gelatin; 2)  $1 \cdot 10^{-4}$ ; 3)  $1 \cdot 10^{-3}$ ; 4)  $1 \cdot 10^{-2}$ ; 5)  $1 \cdot 10^{-1}$ ; the concentration of  $(\text{NH}_4)_2\text{SO}_4$  in the aqueous subphase is 0.4 M; pH 5.33;  $t = 20^\circ\text{C}$ .

The surface properties of the materials studied were investigated using model systems: monolayers at the water-air interface and gels. Monolayers were formed and investigated in a round Langmuir tank. The apparatus allowed us to measure the surface tension in the process of changing the area of the film applied on the liquid-air interface [3].

In experiments we used a 0.1% aqueous solution of a gelatin prepared by a standard method (bloating of the gelatin for 0.5 h and its dissolution at  $40^\circ\text{C}$ ). In the process of modification, the hardener (LIKI-1)-gelatin ratio in solutions was  $1 \cdot 10^{-2}$ - $1 \cdot 10^{-4}$  mole of the hardener to 100 g of the air-dried gelatin (a.d.g.). The hardening was conducted at a temperature of  $60^\circ\text{C}$  for 1-3 h.

The influence of the hardening on the wetting of the surface of a gel was investigated by the method developed and described in [4-6]. A hardener solution was introduced into an aqueous gelatin solution ( $c_g = 1.5\%$ ,  $t = 35^\circ\text{C}$ ) under mixing. The pH level of the solution was brought to 6.0, and then the system was mixed for 1.5 h until the viscosity was constant (viscosimetry control). The gelatin solution studied was applied, using a pipette, in amount of  $0.7 \text{ cm}^3$  on object carriers (size  $25 \times 70 \text{ mm}$ ) cleaned in advance. The layers were dried at room temperature for 24 h and then were held in a humid air (humidity of 90%) as long as 5 days and heated for 1 h. For each sample of a gelatin layer we determined the wetting angles at  $20^\circ\text{C}$  (no less than 30 measurements). The measurement error was  $\Delta\theta = \pm 2^\circ$ .

**Results and their Discussion.** A gelatin represents a hydrophilic biopolymer that is well dissolved in water; therefore, an important condition for formation of monolayers is the prevention of the dissolution of protein in the bulk phase (including repeated cycles of compression-extension of the surface film). In this connection, we considered the influence of the ionic strength of a substrate on the shape of the  $\pi$ - $A$  isotherms. Monolayers in the subphase with a gelation content of 0.4 mole/liter of ammonium sulfate were investigated. In our experiments, quasiequilibrium two-dimensional compression isotherms of a gelatin were obtained only at low rates of compression of the surface film —  $0.01309 \text{ m}^2/\text{min}$  and lower. Investigation of the cyclic hysteresis of the  $\pi$ - $A$  isotherms has shown that a hysteresis loop appears in the process of compression-expansion of a gelatin monolayer. This loop is well reproduced — the hysteresis is reversible, which indicates that a gelatin in the subphase is insoluble.

TABLE 2. Influence of the Chemical Modification of a Gelatin with the Hardener LIKI-1 on the Parameters of the Two-Dimensional Compression Isotherms of Monolayers (subphase 0.4 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; pH 5.4; *t* = 20°C)

Content of hardener, mole per 100 g of the a.d.g	<i>A</i> <sub>0</sub> , m <sup>2</sup> /mg	$\pi_c$ , mN/m	$\epsilon_1$ , mN/m	$\epsilon_2$ , mN/m	$\gamma$ , kJ/mole
Free of hardener	1.09	20.0	6.8	12.1	550
10 <sup>-4</sup>	1.03	17.1	4.5	12.6	379
10 <sup>-3</sup>	0.91	13.2	3.4	10.6	314
10 <sup>-2</sup>	0.85	11.8	2.6	11.1	193
10 <sup>-1</sup>	0.81	10.2	2.1	12.6	147

TABLE 3. Angles ( $\theta$ , deg) of Wetting of Modified Gelatin Gels by Water (*c<sub>g</sub>* = 1.5%, *c<sub>h</sub>* = 10<sup>-3</sup> mole per 100 g of a.d.g)

Content of sample (gel)	<i>t</i> = 20 °C		<i>t</i> = 40 °C		<i>t</i> = 60 °C		Humidity 90%	
	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2	No. 1	No. 2
Gelatin	58	57	60	58	44	45	43	43
Gelatin + LIKI-1	40	70	45	52	48	55	38	43
Gelatin + LIKI-19	65	38	43	45	47	49	40	36
Gelatin + TGA	30	40	37	43	45	47	—	—

Note. No. 1 and No. 2 are gelatin samples.

The influence of a chemical modifier (LIKI-1) on the surface properties of a gelatin was investigated using compression isotherms with the following parameters: 1) *A*<sub>0</sub>; 2)  $\pi_c$ ; 3)  $\epsilon = \Delta\pi/\Delta \ln A$  is determined for the liquid-expanded ( $\epsilon_1$ ) and liquid-condensed ( $\epsilon_2$ ) states of a monomolecular film corresponding to the first and second portions of the dependence  $\pi = f(\ln A)$ ; and 4)  $\gamma = \Delta\pi/\Delta\Gamma$  is calculated for the initial linear portion of the isotherm  $\pi = f(\Gamma)$ .

Figure 1 presents the compression isotherms of gelatin monolayers, characterized by a different degree of modification, and the isotherm parameters (Table 2). As a result of the hardening with LIKI-1, the modulus of surface elasticity of a monolayer in the liquid-expanded state  $\epsilon_1$  decreased by approximately three times, i.e., the intermolecular interaction of the polypeptide chains in the monolayer became weaker, depending on the depth of hardening. At the same time, the modulus of surface elasticity of a monolayer in the liquid-condensed state  $\epsilon_2$  was independent of the degree of modification of the gelatin and changed insignificantly.

The effective two-dimensional surface activity  $\gamma$  decreased by approximately four times with increase in the amount of LIKI-1 in the monolayer (from 500 kJ/mole for the initial gelatin to 147 kJ/mole for the modified gelatin).

The surface of gelatin layers (gels) was investigated by the method of wetting in many works [7–9]. The wetting angle of the surface of a gelatin gel depends on the gelatin concentration, the nature of the modifier and substrate, and the temperature and time of formation of the gel [7]. Investigation of the dependence of the wetting of a gel by water on the gelatin concentration and the gel-formation temperature has shown that the wetting angle and the critical shear stress change symbately [8, 9]. The influence of the time of gelatin-gel formation on the angle of wetting of a gelatin by water is determined by its concentration. Low-concentration gelatin gels (*c<sub>g</sub>* = 1%) have an induction period of the order of 2 h. In the case where the time of formation is equal to the induction period, water drops are not held on the gel surface and rapidly penetrate into the layer. When a gel is formed for a long time, the wetting angle reaches a constant value. The surface layer of a high-concentration gelatin gel (*c<sub>g</sub>* > 10%) is formed very rapidly (for 5 min); in this case, the surface of the gel is not deformed. Thus, the wetting of gelatin gels is determined to a large extent by their rheological parameters.

Investigation of the influence of the structurization of gelatin gels on the wetting of their surface has shown that the use of the protective formaldehyde modifier LIKI-19 and the oxirane modifier triglycidylamine leads to an increase in the hydrophilicity of the gel surface and the use of LIKI-1 increases its hydrophobicity. On heating of the samples studied, the action of the hardening on the wetting of the gel surfaces was leveled (Table 3).

To determine the influence of the hardening of a gelatin in solutions on the hydrophylic-lipophilic balance of the polypeptide chains, we measured the angle of wetting of a teflon surface by gelatin solutions [10]. The chemical modification of a gelatin in solutions by the protective formaldehyde hardeners caused significant changes in the surface properties of the gelatin; this effect is similar to the effect caused by the interaction of a gelatin in a solution with low-molecular surface-active substances.

**Conclusions.** Our investigations have shown that the hardening of the polypeptide chains in a gelatin increases their hydrophilicity and decreases the surface activity of the gelatin. When the content of  $\alpha$ -chains increases, the hydrophilicity of gelatin gels increases. The change in the surface properties of a gelatin depends substantially on the structure of the modifier and the molecular-mass composition of the gelatin.

This work was carried out with financial support from the Russian Basic Research Foundation (project 04-03-32633).

## NOTATION

$A_0$ , area corresponding to the beginning of the isotherm rise,  $\text{m}^2/\text{mg}$ ;  $c_g$ , gelatin concentration, %;  $t$ , temperature, deg;  $\Gamma$ , surface concentration,  $\text{mole}/\text{m}^2$ ;  $\gamma$ , effective two-dimensional surface activity of gelatin macromolecules,  $\text{J}/\text{mole}$ ;  $\epsilon$ , modulus of surface elasticity,  $\text{mN}/\text{m}$ ;  $\theta$ , wetting angle, deg;  $\pi_c$ , maximum two-dimensional compression,  $\text{mN}/\text{m}$ . Subscripts: g, gelatin; c, critical; h, hardener; 0, initial conditions.

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