

Effect of Subphase on the Formation and Properties of Langmuir–Blodgett Films of Cellulose Acetates¹

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Abstract—The formation of monolayer films and Langmuir–Blodgett films of cellulose diacetate and triacetate on the surface of water and subphases containing different concentrations of I_2 , CdI_2 , $CdCl_2$, and $BaCl_2$ was studied. The effect of the subphase composition on the molecular, surface, structural, and optical properties of the mono- and multilayers was determined. It was shown that the subphase components were adsorbed onto the polymer monolayer surface. The adsorption of $CdCl_2$ and $BaCl_2$ is determined by physical forces, whereas I_2 and CdI_2 form a complex with polymer molecules in a monolayer to contain one adsorbate molecule per two glucose units. Iodine exerts a plasticizing effect, promotes the formation of an equilibrium monolayer, and facilitates the transfer of monolayer films onto substrates.

The growing interest shown by contemporary science in materials with a complex molecular structure, such as Langmuir–Blodgett (LB) films that possess nontrivial structural features and a unique set of physical properties [1], is largely due to the possibility of studying intermolecular interactions under conditions when the distance between molecules and their mutual orientation are strictly fixed.

A great deal of attention has been given to polymer monolayers and LB films, which is associated with the possibilities of assembling and studying two-dimensional high-molecular-weight systems with controlled orientation, interchain distance, and distance between chain elements in view of the potential use of these materials in modern technology [2]. The investigation into the specifics of the behavior of macromolecules at the liquid–gas interface not only makes it possible to realize the merits of polymer LB films (thermal and mechanical stability and resistance to corrosive media) but also allows them to be employed as matrices for immobilization of low-molecular-mass compounds bearing a certain function [3].

Systematic studies on the monolayers of polymers, in particular cellulose esters, have been reported in a few papers [4–7]. However, in some cases there is disagreement between the data obtained by different investigators. For example, the limiting area for cellu-

lose triacetate, as determined by measuring the surface pressure through the Wilhelmy technique in the horizontal and vertical modes, ranges from 40 to 137 Å² per unit [4–6]. However, the properties of monolayers of hydroxyalkyl cellulose derivatives formed by spreading from solution and adsorption from the subphase were identical [7].

In this work, we studied the formation of monolayers and Langmuir–Blodgett films of cellulose diacetate (CDA) and cellulose triacetate (CTA) on the surface of water and subphases containing I_2 , CdI_2 , $CdCl_2$, and $BaCl_2$ and the mechanism of interaction of macromolecules in a monolayer with subphase components. In addition, the influence of the subphase composition on the molecular, surface, and optical properties of the mono and multilayers was evaluated for the purpose of constructing stable mono- and multilayer structures. Original CDA ($M = 2.3 \times 10^5$) and CTA ($M = 2.7 \times 10^5$) specimens were purified by repeated precipitation from a chloroform solution in a large excess of methanol.

Monolayers were formed from polymer solutions in chloroform (at a concentration of ~0.02 wt %) on the surface of doubly distilled water and subphases containing I_2 , CdI_2 , $CdCl_2$, and $BaCl_2$ [8]. Preliminary experiments showed that the monolayers formed by applying two-component CTA– I_2 and CDA– I_2 solutions onto water were identical to those prepared by deposition of a CTA or CDA solution, respectively, over the I_2 -containing subphase.

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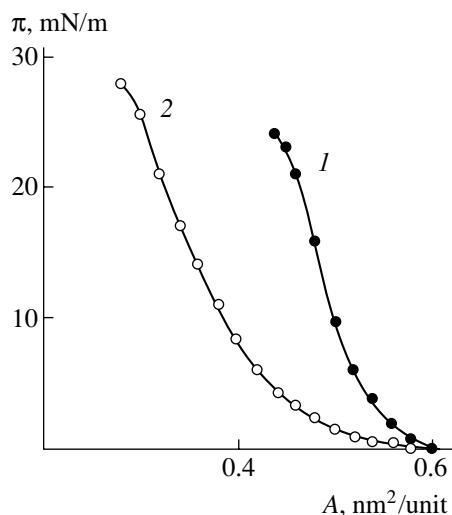


Fig. 1. Compression isotherms of cellulose (1) triacetate and (2) diacetate.

Surface pressure–area per glucose unit (π – A) isotherms were measured with a computer-controlled setup comprised of a Teflon trough, a Wilhelmy vertical film balance for measuring π , and a device for moving the substrate [8]. The accuracy of measurements of the working area and pressure was 0.1%. The multilayer films were formed by horizontal lifting onto quartz substrates. The film thickness H and the refractive index n were determined through reflectance ellipsometry [9] using an LEF-3M ellipsometer ($\lambda = 6328 \text{ \AA}$). The H and n values were calculated by the Monte Carlo method on multidimensional nets and by the Newton–Raphson method using the model of the medium–film–substrate ideal optical multilayer system.

The surface of films prepared by horizontal deposition [10] onto mica or graphite was examined by the technique of atomic force microscopy (AFM) with a Nanoscope-IIIa atomic probe microscope (Digital Instruments) in the contact mode using standard cantilevers 100 and 200 μm in length with a Si_3N_4 tip and an elasticity constant of 0.12 or 0.36 N/m (Nanoprobes, Digital Instruments). The scanning rate was selected in the range 1–2 Hz, and the data density was 512×512 points. The tip force during scanning was varied over a wide range from a few nanonewtons to tens or hundreds of nanonewtons.

The amount of components adsorbed by LB films from the subphase was determined on a Spectrace 5000 spectrofluorimeter (Tracor X-Ray, version 1.31) with preliminary construction of calibration plots, as well as by monitoring changes in the monolayer molecular mass [2].

The coefficient of static elasticity of the monolayer, K_s^{-1} , the two-dimensional analogue of the second virial coefficient B , was calculated as described in [8].

CDA and CTA form monolayers at the water–air interface (Fig. 1). A change in the slope of isotherms at a pressure above 20 mN/m is partly due to the expulsion of the Wilhelmy plate because of the higher rigidity of the film; therefore, K_s^{-1} was calculated below this pressure. The experimental values of limiting area per glucose unit A_0 obtained through extrapolation of an isotherm from the regions of a densely packed monolayer to zero surface pressure are 0.47 and 0.53 nm^2 for CDA and CTA, respectively. These values are smaller than the projected area of the trisubstituted glucose ring [11]. Monolayers of CDA have a higher compressibility and elasticity in different phase states as compared to CTA (Table 1).

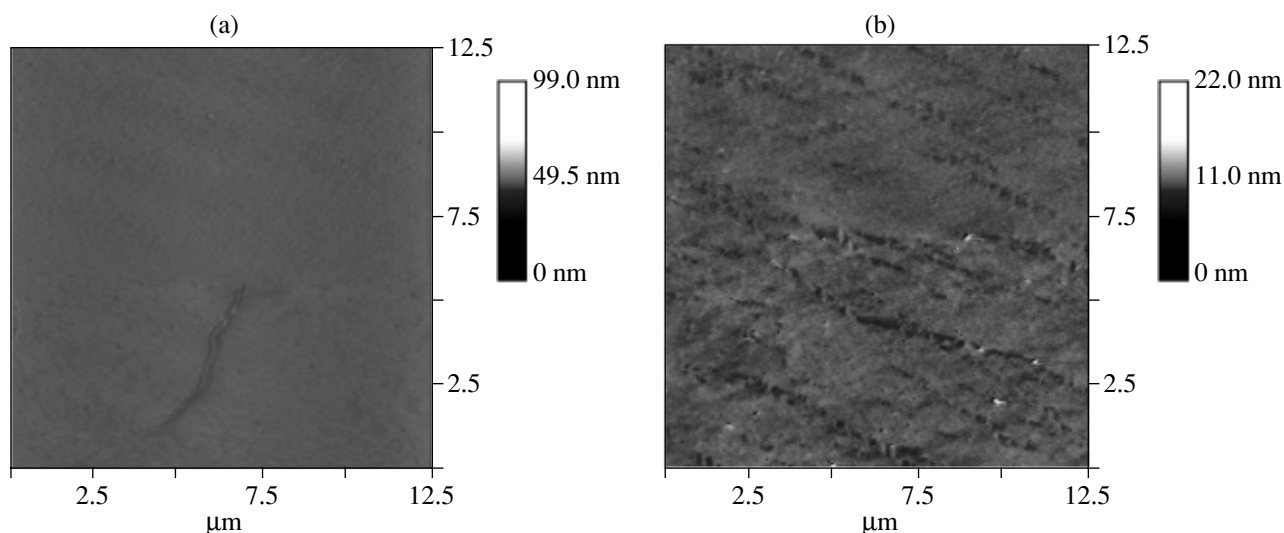


Fig. 2. Surface morphology of (a) CDA and (b) CTA monolayer films formed on the water surface and transferred onto mica: $\pi = 20 \text{ mN/m}$.

Table 1. Effect of subphase composition on the properties of cellulose acetate monolayer films

Cellulose acetate	$c_{\text{sol}}^* \times 10^5$, mol/l	A_0 , nm ² /unit	B , mN/m	K_s^{-1}		
				$\pi = 0-5$	$\pi = 0-10$	$\pi = 0-20$
				mN/m		
CDA	–	0.47	0.59	26.5	53.3	76.6
			BaCl ₂			
	10	0.52	0.64	40.0	58.9	66.2
	50	0.55	0.66	61.1	132.5	151.4
	100	0.65	0.70	85.3	132.3	144.4
			I ₂			
	0.27	0.65	0.75	26.4	61.8	95.7
	0.40	0.67	0.74	29.2	56.1	92.0
	0.55	0.67	0.73	28.8	48.0	83.7
	1.10	0.68	0.76	25.0	45.0	65.5
CTA	–	0.53	0.77	49.1	72.5	176.0
			I ₂			
	0.27	0.61	0.89	52.5	78.7	127.0
	0.40	0.62	–	45.0	71.8	118.1
	0.55	0.66	0.88	28.1	67.0	81.0
	0.81	0.70	0.86	28.9	60.8	76.2
	1.10	0.71	0.87	29.6	56.9	66.4
			CdI ₂			
	1	0.53	0.58	42.8	64.4	96.3
	5	0.54	0.63	49.1	68.7	96.4
	10	0.54	0.65	42.8	64.4	80.0
	50	0.55	0.62	33.3	63.3	80.6
	100	0.57	0.62	34.1	53.3	81.0
			CdCl ₂			
	1	0.52	–	49.6	71.0	120
	5	0.54	0.51	53.0	83.3	115.3
	10	0.55	0.51	51.0	83.2	109.9
	50	0.56	0.50	53.0	84.3	112.3
	100	0.55	0.51	53.1	85.0	111.1

* The concentration of I₂, CdI₂, CdCl₂, or BaCl₂ in the subphase.

According to the AFM data, a characteristic feature of the surface of CDA and CTA monolayer films formed on the water surface and transferred onto mica or graphite is their fairly high uniformity and the absence of noticeable discrete inclusions of imperfect regions (Fig. 2), which have been observed in films

obtained through the spreading method [12]. The roughness of monolayer films is somewhat higher in the case of CTA; the height difference is ~0.4 nm, which is much smaller than the monolayer thickness. These monolayer films are extremely stable to the action of the tip force, as the formation of an artificial

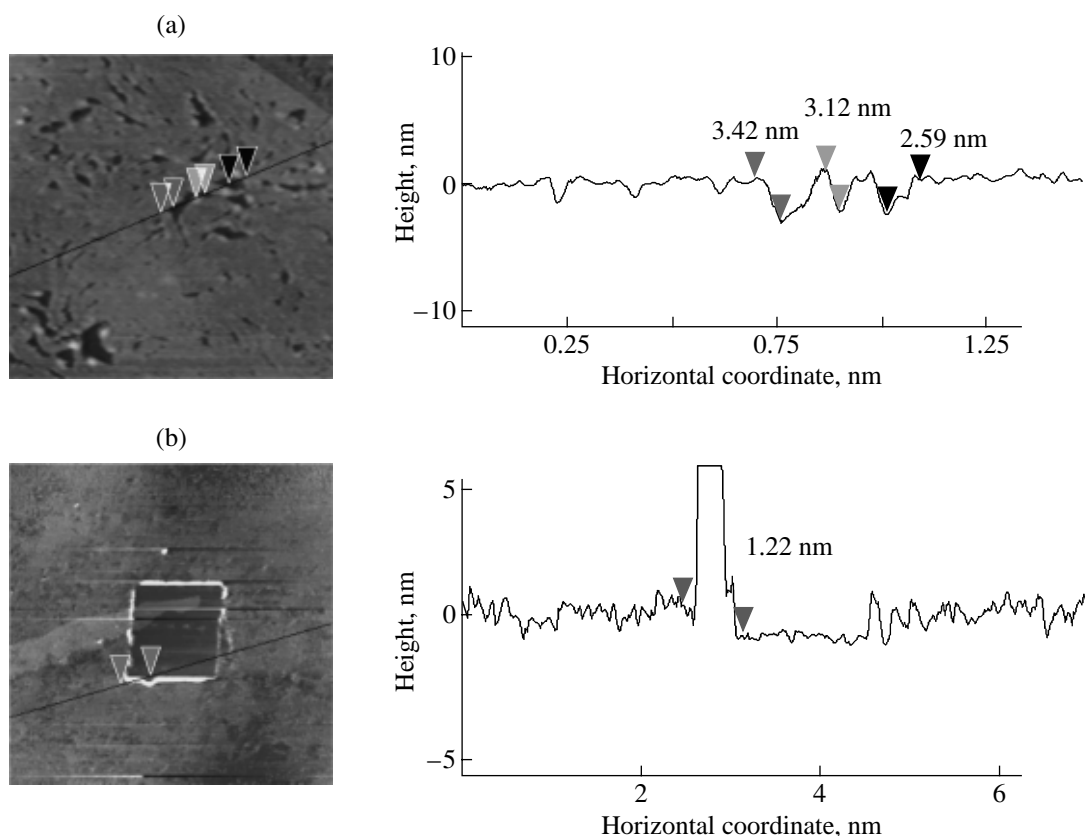


Fig. 3. Height assessment for surface elements of CTA monolayer films: (a) H_2O , graphite, $\pi = 20$ mN/m and (b) $[\text{CdCl}_2] = 6 \times 10^{-4}$ mol/l, mica, $\pi = 20$ mN/m.

defect in them turned out to be a rather complicated problem. After transfer of a monolayer from the water surface to mica and graphite simultaneously, the CTA monolayer thickness was 1.7 ± 0.3 nm on mica as estimated from the depth of an artificial defect of the film and 3.0 ± 0.4 nm on graphite as found by measuring the pore depth (Fig. 3a). For the sake of comparison, note that the ellipsometrically determined thickness of CDA and CTA films was 1.7 and 1.6 nm per monolayer, respectively [13] (transfer ratios of 0.65 and 0.44, $\pi = 10$ –20 mN/m, horizontal lifting). The difference in the experimental data can be due both to the difference in conformations of polymer helices at different pressures and to the complexity of transfer of multilayer films onto substrates determined by their high rigidity and fragility [6].

By the Alchemy-II routine, the polymer chain thickness of these cellulose esters in the fully extended conformation has been estimated at a value that does not exceed 1 nm.

Most likely, CDA and CTA form, on the water surface, a monolayer film from helical, densely packed molecular chains (similar to the amylose esters of identical structure [14]).

When CDA and CTA are deposited on the subphase containing I_2 , CdI_2 , CdCl_2 , or BaCl_2 , a significant

change in the physicochemical characteristics of the monolayers is observed (Table 1). An increase in the concentration of components in the subphase leads to the expansion of the monolayer, so that the limiting area per glucose unit in the presence of iodine approaches the A_0 value defined by the high-polymer model for the parallel arrangement of glucose units with respect to the aqueous surface [11, 15]. Barium chloride reduces the elasticity of the monolayer film (Table 1). A similar effect of divalent ions (Ca^{2+} , Ba^{2+} , Pb^{2+} , etc.) acting as crosslinking agents on cellulose esters in the liquid phase was reported earlier [16]. The presence of CdI_2 , CdCl_2 , and I_2 results in the reduction of monolayer rigidity, the most profound effect being exerted by I_2 .

The two-dimensional analogue of the second virial coefficient that characterizes intermolecular attraction in a monolayer somewhat increases in the presence of BaCl_2 and I_2 and slightly decreases when cadmium salts are introduced into the subphase (Table 1).

A change of the subphase also substantially affects the monolayer morphology. Films formed on the surface of CdI_2 , CdCl_2 , or I_2 solutions become more elastic and are rather easy to destroy by the microscope tip (Fig. 3b); the degree of imperfection of the surface

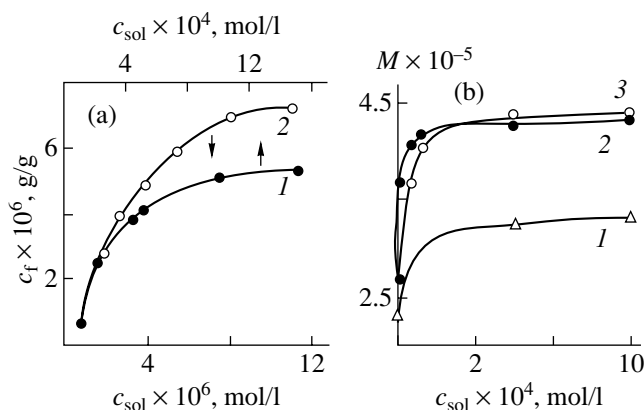


Fig. 4. Plots of (a) (1) cadmium and (2) iodine uptake by LB films of CTA upon adsorption from CdI_2 and I_2 solution, respectively, and (b) the change in molecular mass of (1) CDA and (2, 3) CTA in the adsorption for (1) BaCl_2 , (2) CdI_2 , and (3) CdCl_2 solutions: c_f and c_{sol} are the adsorbate concentrations in the film and solution, respectively.

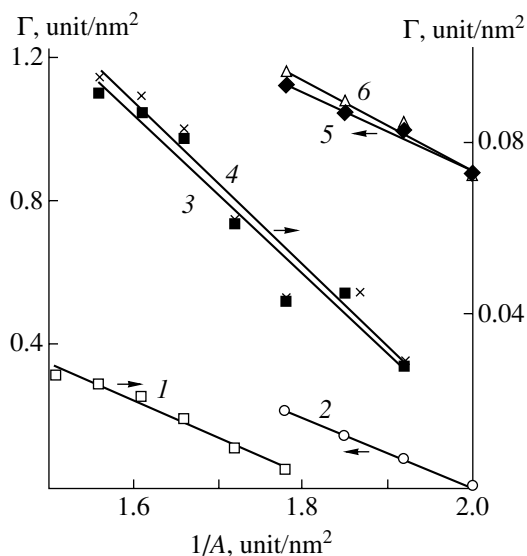


Fig. 5. Plots of Γ vs. $1/A$ for the adsorption of (1, 3, 4) CdI_2 on CTA and (2, 5, 6) I_2 on CDA at $k =$ (3, 5) 2 and (4, 6) 3.

somewhat increases. The thickness of monolayer films transferred onto mica was 1.7 nm (CDA, CdI_2), 1.2 nm (CTA, CdCl_2), and 1.0 nm (CTA, I_2). This result agrees with the π - A plots; when ionogenic compounds are introduced into the subphase, the slope of the isotherms for cellulose esters decreases; i.e., the monolayer expands.

Most probably, the insertion of subphase ions into cellulose molecular helices is accompanied by unfolding and extension of polymer chains in such a manner that glucose units arrange themselves parallel or nearly parallel to the subphase and occur in contact with it.

The observed changes in the properties of CDA and CTA monolayer films can be associated with the adsorption of subphase components on the monolayer surface followed by their interaction with polymer molecules in the monolayer film. Previously [13], we showed that I_2 , CdI_2 , CdCl_2 , and BaCl_2 form associates with CDA and CTA molecules. The curves of iodine and cadmium uptake by LB films, as well as the curves that reflect a change in the CDA and CTA molecular mass in their monolayers due to the adsorption of ions from the subphase, tend to saturate, which is characteristic of complexation reactions (Fig. 4). However, the van der Waals adsorption of subphase components on polymer molecules in the monolayer cannot be ruled out.

In the general case, the absorption Γ of a low-molecular-weight compound from the subphase to a monolayer film can be described by the equation [17]

$$\Gamma = \Gamma_w - a_m \Gamma_w (1/A), \quad (1)$$

where a_m is the cross-sectional area of the glucose unit and Γ_w is the adsorption on the monolayer-free surface.

The Γ value was calculated in two fashions. The first suggested the absence of complexation in the interaction of I_2 , CdI_2 , CdCl_2 , and BaCl_2 with macromolecules in a monolayer. The adsorption of subphase components at certain A values was determined from experimental π - A plots obtained on subphases containing different concentrations of substances using the equation [18]

$$d\pi = \Phi QRT \Gamma d \ln c \quad (2)$$

(c is the concentration of components in a subphase). The factor Φ that takes account of the presence of a monolayer on the subphase surface is defined by

$$\Phi = A/(A - A^p), \quad (3)$$

where A^p is the partial molar area of the glucose unit in a mixed monolayer of a cellulose ester with adsorbed small molecules. The quantity Q , which takes account of the presence of solutes in the subphase, was taken to be 2 [17]. Calculating the A^p value, we assumed that A^p in the mixed polymer-adsorbate monolayer at a given surface pressure is equal to the area of the glucose residue of a cellulose ester on water at the same π value.

In the second case, we assumed the formation of a complex between polymer molecules and I_2 , CdI_2 , CdCl_2 , or BaCl_2 . The Γ value was determined using the equation [19]

$$\Gamma = \frac{1}{2RT} \left(\frac{kA - A_c^p}{kA} \right) \frac{d\pi}{d \ln c}. \quad (4)$$

Here, A_c^p is the partial area of the complex, which is equal to the difference between the area of the glucose unit of a cellulose ester with adsorbed molecules and the partial area of the CDA or CTA glucose unit, and k is the ratio of the number of glucose units to that of adsorbed molecules. The k value, as calculated from experimental data, turned out to vary from 1.8 to 2.7.

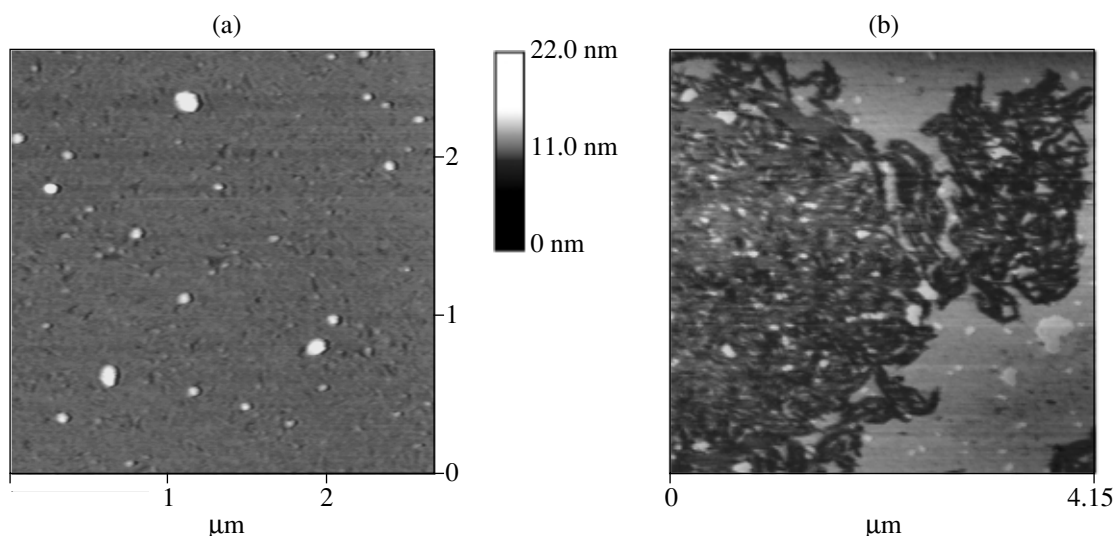


Fig. 6. Surface morphology of CTA films formed on the surface of (a) water and (b) iodine solution and transferred onto mica: (a) height, (b) friction; $[I_2] = 8 \times 10^{-6}$ mol/l, $\pi = 20$ mN/m.

Based on this finding, to determine Γ with allowance for complexation, we took k to be equal to 2 or 3.

The dependence of Γ on $1/A$ calculated in both manners is linear (Fig. 5) and allows the values of a_m and Γ_w to be determined (Table 2).

The comparison of the cross-sectional areas of glucose units determined according to Eqs. (2) and (4) with their values at collapse (A_c), which should be equal to one another from the standpoint of the closed-packed cluster model [17], enables us to propose a mechanism

Table 2. Values for parameters a_m , Γ_w , and A_c

Cellulose acetate	Subphase component	Γ_w , unit/nm ²	a_m	A_c
			nm ² /unit	
No complexation				
CTA	I ₂	1.150	0.504	0.46
"	CdI ₂	0.155	0.557	0.42
"	CdCl ₂	0.156	0.464	0.46
CDA	I ₂	1.570	0.490	0.35
"	BaCl ₂	0.42×10^{-2}	0.393	0.39
2 : 1 complex				
CTA	I ₂	2.630	0.458	0.46
"	CdI ₂	0.442	0.421	0.42
"	CdCl ₂	0.471	0.414	0.46
CDA	I ₂	3.070	0.346	0.35
"	BaCl ₂	0.115	0.739	0.39
3 : 1 complex				
CTA	I ₂	2.830	0.477	0.46
"	CdI ₂	0.450	0.453	0.42
"	CdCl ₂	0.542	0.450	0.46
CDA	I ₂	3.330	0.372	0.35
"	BaCl ₂	0.127	0.847	0.39

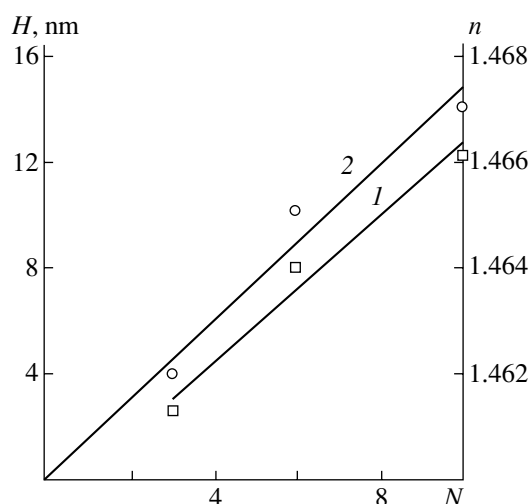


Fig. 7. (1) Refractive index n and (2) film thickness H as a function of the number of transfer cycles N : $[I_2] = 8 \times 10^{-6}$ mol/l, $\pi = 15$ mN/m.

for the interaction of cellulose esters with subphase components. As follows from the data presented in Table 2, the adsorption of $CdCl_2$ and $BaCl_2$ on the cellulose ester monolayers is due to physical forces; I_2 and CdI_2 , being adsorbed on a monolayer film, form a complex with polymer molecules, in which the ratio of the number of glucose units to the adsorbed molecules of a low-molecular weight compound is equal to two.

The most profound effect on the properties of CDA and CTA monolayer films is exerted by iodine, for which the spontaneous complexation process is the most feasible [13]. In penetrating into a monolayer, iodine is located between polymer units and leads to their extension, altering the crystal structure of the polymer and rendering the monolayer film more elastic, which, in our opinion, indicates its plasticizing effect. The complex formation is accompanied by electron transfer from the oxygen of a polymer unit to iodine molecules [20] and by the binding of the latter to one another [21]. As a result, I_2 microcrystals are formed in the cellulose ester films compressed to a pressure of 20 mN/m, as has been detected with the AFM technique (Fig. 6).

As has been mentioned above, CDA and CTA monolayer films are difficult to transfer onto solid substrates. In the case of cellulose tridodecanoate, the use of the horizontal lifting technique [11] made it possible to reach a transfer ratio equal to unity (with increasing the number of transfer cycles). The formation of multilayer films of CDA and CTA through this technique showed that the diacetate with a higher elasticity as compared to the triacetate is somewhat easier to transfer onto quartz substrates from the water surface. The formation of multilayer structures from the cellulose acetates is improved by introducing I_2 into the subphase and, at concentrations above 6×10^{-6} mol/l in the subphase, almost linear dependences of the film thickness and refractive index on the number of layers are realized (Fig. 7).

In summary, I_2 , CdI_2 , $CdCl_2$, or $BaCl_2$ introduced into the subphase are adsorbed on the surface of a cellulose diacetate or triacetate monolayer, altering its surfactant, molecular, structural, and optical properties. The adsorption of $CdCl_2$ and $BaCl_2$ is due to physical forces, whereas I_2 and CdI_2 form a complex with polymer molecules in a monolayer film in a 2 : 1 ratio of glucose units to adsorbed molecules. The limiting area of the polymer unit of cellulose acetates almost reaches the area defined by the high-polymer model with the glucose ring planes arranged parallel to the water surface. The monolayer elasticity increases, and the formation of multilayer structure is facilitated.

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