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ПОЛУЧЕНИЕ МЕМБРАН ИЗ ДИАЦЕТАТА ЦЕЛЛЮЛОЗЫ ДЛЯ ТВЕРДОФАЗНОЙ ФЛУОРЕСЦЕНЦИИ ПОЛИЦИКЛИЧЕСКИХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ

Исследование посвящено разработке состава формовочного раствора для приготовления мембран из диацетата целлюлозы (ДАЦ) с целью их последующего применения в качестве матриц для твердофазной флуоресценции (ТФФ) полициклических ароматических углеводородов (ПАУ). Мембраны готовили в стандартных условиях сухим методом из 1,2 – 8,0 масс.% растворов ДАЦ в ацетоне и смеси ацетон : вода в соотношении компонентов от 99 : 1 до 93 : 7. В качестве модельного ПАУ был взят пирен, который сорбировали на мембране и определяли его ТФФ-сигнал. Наилучшая сорбция наблюдалась на мембранах ДАЦ, приготовленных из раствора состава ацетон : вода (95 : 5 по объему) с концентрацией полимера 3,6 масс.%. Полученные мембраны сравнили с коммерческим образцом ДАЦ по эффективности сорбции пирена. В диапазоне концентраций пирена в сорбате 10^{-6}–10^{-8} М ТФФ сигнал был получен только на лабораторном образце. Исследование энергетических характеристик и морфологии поверхности лабораторной и коммерческой мембран показали, что образцы имеют большие различия в размерах пор и

морфологии поверхности. Мембрана ДАЦ, полученная в лаборатории, имеет «кружевную» структуру с размером пор 100-500 нм, коммерческая мембрана, менее плотная и более проницаемая, имеет поры размером на порядок больше, заполненные небольшими включениями. Был сделан вывод о том, что для получения флуоресцентного сигнала пирена в фазе сорбента мембрана должна быть мелкопористой, гладкой и непрозрачной. Лабораторные мембраны ДАЦ также были модифицированы мицеллярными растворами поверхностно-активного вещества ТХ-100. Наибольший ТФФ-сигнал пирена был получен при содержании модификатора в формовочном растворе 0,26 масс.%. Такая модификация позволила снизить предел определения пирена методом ТФФ до концентрации 10^{-9} М. Разработанные матрицы могут применяться для мониторинга ПАУ в водных средах.

Ключевые слова: диацетат целлюлозы, мембрана, полициклические ароматические углеводороды, твердофазная флуоресценция

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PREPARATION OF CELLULOSE DIACETATE MEMBRANES FOR SOLID-STATE FLUORESCENCE OF POLYCYCLIC AROMATIC HYDROCARBONS

The investigation is devoted to the development of molding composition for cellulose diacetate (CDA) membranes preparation in order to use them as matrices for solid-surface fluorescence (SSF) of polycyclic aromatic hydrocarbons (PAH). Membranes were prepared under standard conditions by a dry method from CDA solutions with concentrations of 1.2–8.0 wt. % in acetone and a mixture of acetone and water (99:1 to 93:7). Pyrene was taken as a model PAH. It was adsorbed onto the membranes from water-ethanol solutions and its SSF was recorded. The best pyrene sorption and fluorescence was obtained with the CDA membranes made from the acetone-water (95:5 vol.) mixture with a polymer content of 3.6 wt. %. These membranes were compared with commercial filtering hydrophilic CDA membranes by the efficiency of pyrene sorption and SSF. In the range of pyrene concentrations in sorbate of 10^{-6}–10^{-8} M the SSF signal was observed only for the laboratory sample. The surface energy characteristics and the morphology of membranes were examined. It was shown that laboratory CDA membranes have the structure of

a continuous, "lacy" polymer network with pore sizes within 100–500 nm, the commercial membranes are less dense and more permeable to solution, they have the pores by an order of magnitude greater, filled with a set of nodules. It was concluded that in order to get a pyrene fluorescence signal in the sorbent phase, a membrane should be finely porous, smooth, and not transparent. Laboratory CDA membranes were also modified by micellar solutions of surfactant TX-100. The highest SSF signal of pyrene was obtained with the modifier's content in the forming solution of 0.26 wt. %. This modification allowed reducing the limit of pyrene detection by SSF down to a concentration of 10^{-9} M. These matrices can be used to monitor the presence of PAH in aqueous media.

Key words: cellulose diacetate, membrane, polycyclic aromatic hydrocarbon, pyrene, solid-surface fluorescence

INTRODUCTION

Cellulose acetates belong to the class of artificial polymers produced from renewable resources in large scale. By their valuable properties and scale of applications in various industries, they are second only to cellulose and starch [1]. Cellulose acetates are traditionally used to produce fibers and filaments, films and membranes, filters of various functional purposes, plastics, etc. Absorbent materials made of cellulose acetates are used in nanofiltration processes [2, 3], in estimating the fermentation degree of industrial waste water [4], in separation of high-molecular-weight carbohydrates from low-molecular-weight sugars [5], etc.

High sorptive capacity of cellulose acetates and the possibility to form solid films with a smooth surface their from make these materials promising for using as matrices in solid-surface fluorescence (SSF). This technique combines sorption concentration of a substance on a solid matrix followed by its fluorescent analysis in the sorbent phase, excluding the step of desorption, which provides a significant increase in the sensitivity and selectivity of this analysis [6].

SSF has been successfully applied for trace quantification of organic and inorganic compounds in various media [7-9]. Of particular interest is the SSF analysis of polycyclic aromatic hydrocarbons (PAH), which are carcinogenic and mutagenic toxicants. The ability of various PAHs to accumulate in the environment causes the need to control their content in drinking water, waste water, air, soil, and food [10]. As PAHs are found in various media in very small quantities, their quantitative analysys is impossible without prior concentrating, which makes the SSF method promising for the design of test systems for environmental monitoring. The possibility of luminescent PAH analysis in aqueous media using various solid-phase matrices has been established for silica gel [11], zeolites [12], fiberglass with silica particles [13], foamed polyurethane [14], nylon membranes [15], and cellulose [16].

Earlier we tested cellulose diacetate (CDA) fibers and membranes as matrices for the SSF of pyrene taken as a model PAH. Both were shown to be good sorbents for pyrene from water-micellar surfactant media of various types [17, 18]. CDA membranes were characterized as the most promising matrices for SSF.

The aim of this study was to compare commercial CDA membranes with our laboratory samples by the efficiency of pyrene sorption and SSF, to optimize the composition of the molding mixture for the preparation of CDA membranes, and to estimate the sensitivity of pyrene detection in an aqueous medium by SSF on designed CDA membranes.

EXPERIMENTAL METHODS

CDA membranes were made using polymer with the following characteristics: a viscosity-average molecular weight M_η of 77 kDa, an acetylation degree of 55%, and 3% moisture, used to produce acetate filaments of textile purposes (Technofilter Ltd., Vladimir, Russian Federation). To prepare membranes, CDA solutions with concentrations C_{CDA} = 1.2-8.0 wt. % in acetone (analytical grade, 99.75%) and a mixture of acetone and water (99:1 to 93:7) were used. Membranes were prepared under standard conditions by a dry method.

CDA membranes were also prepared with addition of a modifier into the process, namely, the nonionic surfactant polyoxyethylene(10)mono-4-isooctylphenyl ether, TX-100 (ACROS ORGANICS, USA). The concentrations of TX-100 in micellar solutions were: $0.23\cdot10^{-3}$, $1.4\cdot10^{-3}$, $7.0\cdot10^{-2}$, 0.14, 0.50 M.

Commercial filtering hydrophilic CDA membranes manufactured by JSC STC "Vladipor" (Russia) were also used.

Water-ethanolic solutions of pyrene (Fluka, Germany) with concentrations of 10^{-6}-10^{-9} M were used in experiments. Pyrene stock solution was prepared by dissolving an accurate weight in ethanol and stored in a dark place to prevent photochemical destruction. Water-ethanolic pyrene solutions for tests were made by diluting the stock solution with distilled water immediately prior to use.

Surface morphology was examined by scanning electron micrographs (SEM) on a MIRA \\ LMU electron scanning microscope (Tescan, Czech Republic) at a voltage of 8 kV and a conductive current of 60 pA. A gold layer of 5 nm thickness was sprayed onto the samples with a K450X carbon coater device (Germany); the spraying current was 20 mA, the spraying duration 1 min. The surface potential (ξ, mV) of matrices was measured with a surface potential sensor (Nima KSV, Finland).

The sorption of pyrene from solution was performed in dynamic mode. To this purpose, the solutions (V = 10 ml) were passed through the membrane five times, using a disposable sterile syringe Master UNI "PharmLine Limited" (Cornwall Buildings, Great Britain). The mass of the sorbents was 0,05±0,01 g. Then the matrices were dried at room temperature until constant weight. The sorption degree (R, %) was calculated as [17]:

$$R = \frac{I'_{\max} - I''_{\max}}{I'_{\max}} \cdot 100\%,$$

where I'_{max} и I''_{max} are the fluorescence intensity of pyrene at 394 nm in the source solution and after sorption on the membrane, respectively.

The fluorescence spectra of pyrene in a solution and an adsorbed state on solid matrices were recorded on a spectrofluorimeter Fluorat-02-Panorama (Lumex, Saint-Petersburg, Russia) with a holder for solid samples. The fluorescence intensity of pyrene (I_{SSF}) was measured within the spectral range of 350-450 nm, the excitation radiation wavelength being 320 nm. The spectrum always has two peaks at λ = 374 and 394 nm.

RESULTS AND DISCUSSION

It is known that to produce porous CDA membranes by a dry method, a mixture of a volatile solvent, typically acetone, with a porogene modifier not dissolving the polymer, e.g. water, should be used [19]. The significant differences in the boiling temperatures and surface tensions of water and acetone and the high incompatibility degree of water with the solvated polymeric component lead to water's slower evaporation from the polymeric system, in comparison with acetone, whereby pores are formed in the film structure. In addition, the main factors determining the porosity and spatial characteristics of the pores in the membranes obtained by dry spinning are the polymer concentration in the forming solution and the solvent : porogene volume ratio.

To select CDA membranes with the best ability to adsorbed pyrene luminescence, a series of samples was prepared by casting from a polymer solution in acetone and water-acetone mixtures with several component ratios. Pyrene was adsorbed onto the matrices prepared, and the SSF spectra were recorded.

The membrane formed from the CDA solution in acetone was found to give a weaker pyrene fluorescence signal as compared to that prepared from the mixture of acetone and water. Addition of more than 5 vol. % of water into the system reduces the solubility of the polymer, while that of less than 5 vol. % makes the membrane sample more transparent, which hinders to get a high-quality pyrene fluorescence signal. Introduction of 5 vol. % of water to the solution leads to a decrease in its viscosity, an increase in the number of microgel particles of the dispersed phase of the polymer system, and increased membrane permeability and porosity. Thus, the optimal acetone : water ratio is 95:5 vol.

Further, an optimum CDA concentration in the forming solution was selected. Air-dry polymer powder was introduced into a water-acetone (95:5 vol.) mixture in amounts from 1.2 to 8.0 wt. %. Pyrene was adsorbed onto the membranes and its SSF was recorded. To compare the sorption capacities of our matrices, the pyrene extraction degrees (R, %) were estimated. Experimental results are presented in Table 1, which shows that the best pyrene sorption and fluorescence is obtained with the CDA membrane made from the acetone-water mixture with a polymer content of 3.6 wt. %. We used these matrices in further studies.

Table 1

Pyrene sorption degree (R, %) and SSF intensity (ISSF) on the CDA membranes prepared from acetone-water (95:5 vol.) mixtures with several polymer concentrations

Таблица 1. **Степень извлечения пирена (R, %) из водно-этанольной среды и интенсивность ТФФ пирена (ISFF) на ДАЦ мембранах, полученных из смеси ацетон-вода (95:5 об. %) с различной концентрацией полимера**

C_{CDA}, wt. %	R, %	I_{SSF}, a.u.
1.2	28 ± 2	41 ± 5
3.6	84 ± 1	122 ± 5
5.9	63 ± 2	93 ± 6
8.0	24 ± 1	35 ± 4

It was interesting to compare our matrix with commercial CDA membranes used in industry to filter aqueous media and biological fluids. Pyrene was adsorbed on both samples from water-ethanol solutions with concentrations of 10^{-6}-10^{-8} M.

An SSF signal was only observed for the CDA membrane obtained in the laboratory (Fig. 1). The commercial sample of the CDA membrane gave no SSF signal in this range of fluorophore concentrations.

In order to clear up such differences we examined surface energy characteristics and the morphology of the membranes. The surface potential (ξ) of both laboratory and commercial membranes was negative: -32.0±2.0 and -18.6±2.0 mV, respectively. The surface potential of the laboratory sample is almost twice higher by the absolute value.

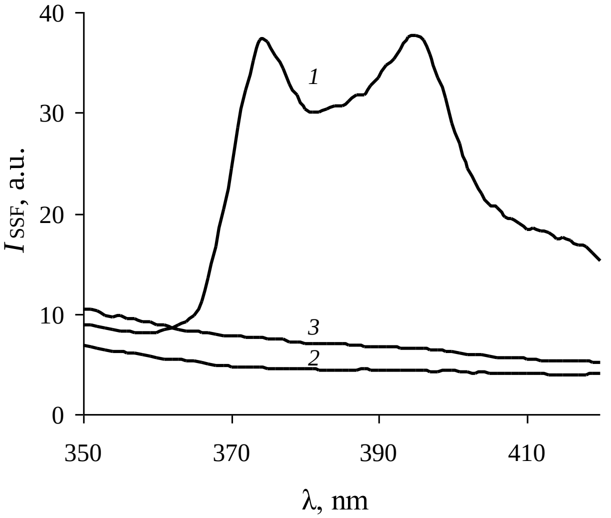
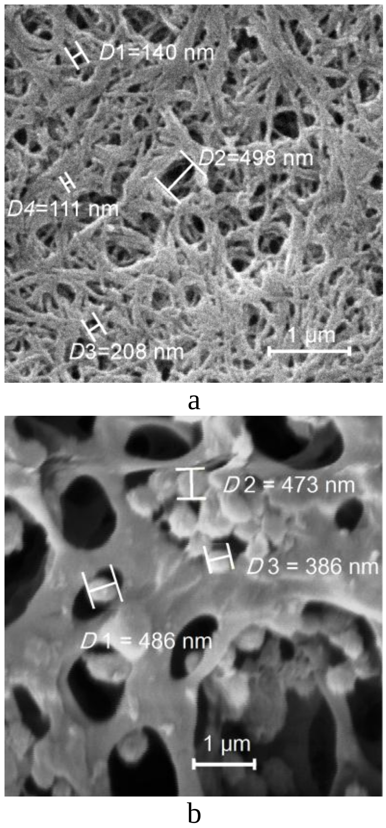


Fig. 1. Fluorescence spectra of pyrene (10^{-7} M) adsorbed on the laboratory (1) and commercially CDA membrane (2), and that of the laboratory CDA membrane alone (3)

Рис. 1. Спектры флуоресценции пирена (10^{-7} М), сорбированного на лабораторной (1) и коммерческой (2) ДАЦ мембранах, спектры флуоресценции лабораторной мембраны ДАЦ (3)

The SEM data show that our laboratory CDA membranes have the structure of a continuous, ‘‘lacy’’ polymer network with pore sizes within 100-500 nm (Fig. 2a). The modal pore diameter was d = 0.12± ±0.03 μm, the porosity P = 0.2±0.1 rel. units.

The commercial CDA sample also had a porous structure, but the pores were by an order of magnitude greater: d = 1.8±0.5 μm, P = 0.6±0.1 rel. units. The pores of the commercial sample were filled with a set of nodules with diameters within 350-500 nm. In general, the commercial membrane was less dense and more permeable to solution than that obtained in the laboratory.



a

b

Fig. 2. SEM images of the surface morphological structure of the laboratory samples (a) and commercial CDA membrane (b), D (1–4) is the pore diameter

Рис. 2. СЭМ-фотографии поверхности образцов лабораторной (a) и коммерческой (b) мембран ДАЦ, D (1–4) – диаметр пор

Apparently, the ability of pyrene to fluoresce in the sorbent phase depends on the surface morphology of the membrane, which should be finely porous, smooth, and not transparent.

It has been shown previously that pyrene sorption onto polysaccharide matrices is improved by adding a surfactant into the sorbate, in particular TX-100 [17, 18]. In this regard, we studied the effect of this surfactant with various concentrations when added directly to the polymeric matrix during its preparation on the sorption capacity of CDA membranes. The modified membranes were used as matrices for pyrene SSF, the pyrene concentration in the sorbate being 10^{-6} M. The diagram (Fig. 3) shows that the ability of pyrene to sorption and SSF on CDA membranes depends on the surfactant content therein. The highest fluorescence signal of pyrene in the sorbent phase was obtained with the modifier’s content in the forming solution of 0.26 wt. %, and the fluorescence intensity decreased sharply with further increase of the TX-100 concentration in the matrix.

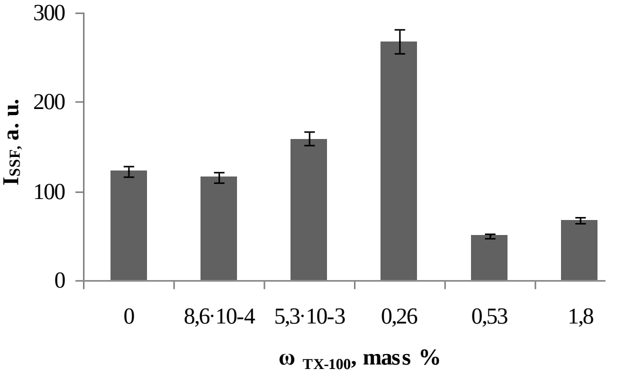


Fig. 3. Dependence of pyrene SSF on the TX-100 content (wt. %) in the CDA membranes with the pyrene concentration in the sorbate of 10^{-6} M

Рис. 3. Зависимость ТФФ пирена от содержания ТХ-100 (масс. %) в мембранах ДАЦ при концентрации пирена в сорбате 10^{-6} М

Thus, the use of TX-100 as a CDA film modifier allows obtaining a higher pyrene SSF signal.

To estimate the SSF pyrene analysis sensitivity, sorption of the substance was held from its 10^{-6}-10^{-9} M water-ethanol solutions onto our laboratory CDA membranes, including those modified with the surfactant, i.e. containing 0.26 wt. % of TX-100, and the SSF spectra of pyrene on the matrices were recorded.

Table 2 contains the values of the pyrene SSF intensity for the CDA matrices, from which it follows that such modification of the CDA membrane using the surfactant TX-100 allows one to extend the limit of pyrene detection by SSF down to a concentration of 10^{-9} M and to increase the fluorescence signal intensity.

Table 2

SSF intensities of pyrene adsorbed on CDA matrices from water-ethanol media with several concentrations of the substance

***Таблица 2*. Значения интенсивности ТФФ пирена, сорбированного на матрицы ДАЦ из водно-этанольных сред с различной концентрацией вещества**

Pyrene concentration in the sorbate, M	I_{SSF} of pyrene (λ = 394 nm), a.u.	
	CDA membrane	Modified CDA membrane
10^{-6}	122±5	269±7
10^{-7}	38±3	101±5
10^{-8}	5±1	44±3
10^{-9}	–	21±3

Thus, we have developed a molding composition to prepare CDA membranes for the purpose of their use as matrices for solid-phase fluorescence of pyrene. These matrices can be used to monitor the presence of PAH in aqueous media.

CONCLUSIONS

The ability of CDA membranes to adsorb PAH and to exhibit their SSF signals was found to depend on the composition of the forming solution. The maximum pyrene fluorescence signal in the adsorbed state was obtained on the membranes prepared by dry spinning from a water-acetone mixture (95:5 vol.) with a polymer content of 3.6 wt. %.

Comparison of our laboratory CDA membrane with a commercial sample has shown that such commercial membranes are not effective matrices for PAH SSF. The tested membranes revealed differences in the quantity and sizes of pores, surface morphology and surface potential. To get a pyrene fluorescence signal in the sorbent phase, the membrane should be finely porous, smooth, and not transparent.

Our CDA membrane was modified by a surfactant: adding TX-100 with a concentration of 0.26 wt.% into the forming solution reduced the limit of pyrene detection by SSF down to a concentration of 10^{-9} M and increased the intensity of the fluorescence signal.

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