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Коэффициент преломления воды и водных растворов вблизи ионо-обменной мембраны

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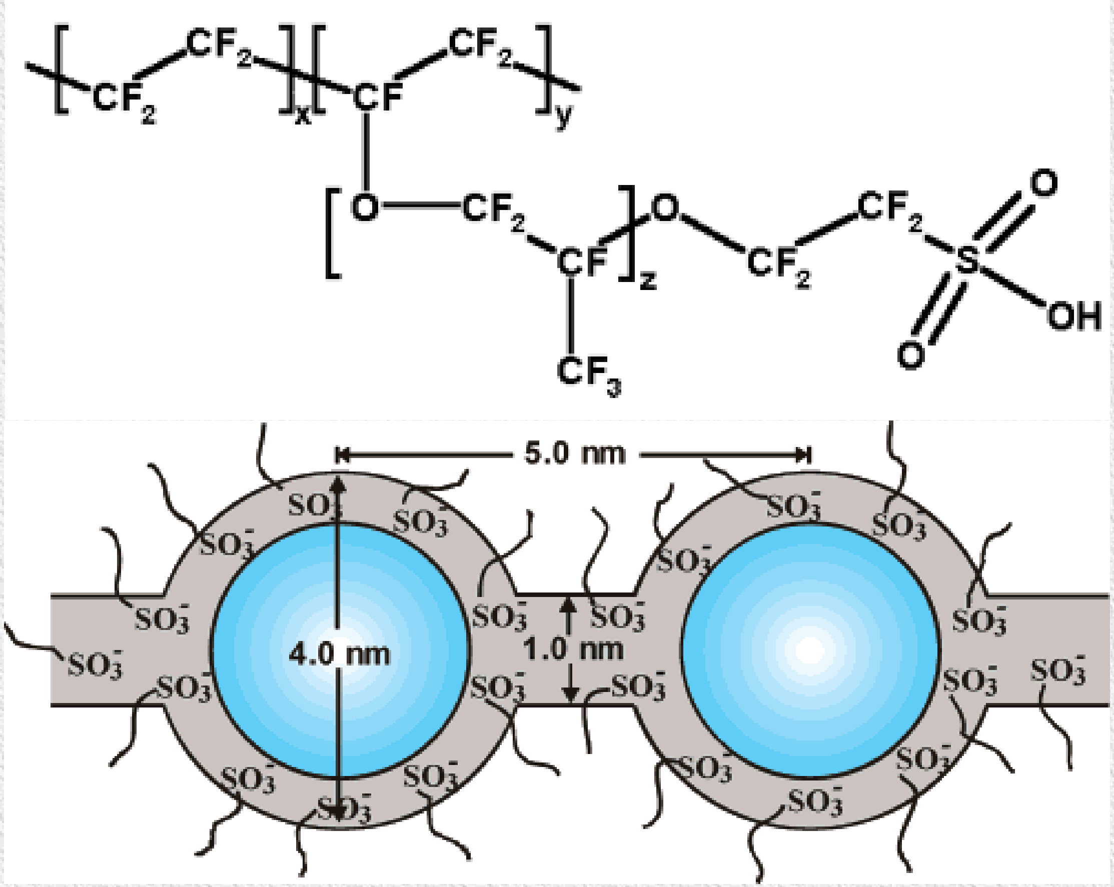
Формулировка проблемы (1)



Структура Нафиона

Формулировка проблемы (2)

B.Chai, J.Zheng, Q.Zhao, G.H.Pollack, Spectroscopic Studies of Solutes in Aqueous Solution, J. Phys. Chem. A 2008, 112, 2242-2247

B.Chai, G.H.Pollack, Solute-Free Interfacial Zones in Polar Liquids, J.Phys.Chem.B 2010, 114, 5371-5375

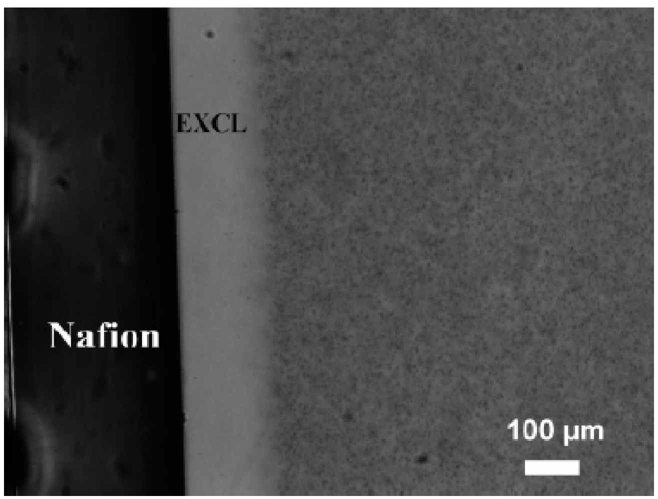


Figure 1. Solute-free aqueous zone ("EXCL") adjacent to the Nafion surface. The zone to the right of the exclusion zone (darker) contains 1 μm carboxylate microspheres.[24] The width of the exclusion zone, extending from the Nafion surface to the boundary of the microsphere zone, is approximately 150 μm.

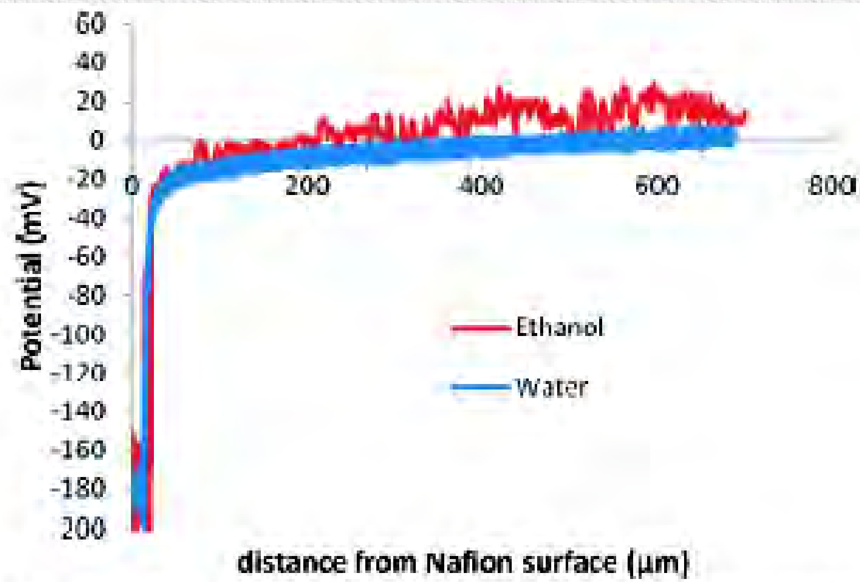


Figure 6. Average potential distributions adjacent to the Nafion surface in water and ethanol ($n = 6$).

Формулировка проблемы (3)

J.Zheng, G.H. Pollack, Long-range forces extending from polymer-gel surfaces, PHYSICAL REVIEW E 68, 031408 (2003)

B.Chai, G.H.Pollack, Solute-Free Interfacial Zones in Polar Liquids, J.Phys.Chem.B 2010, 114, 5371-5375

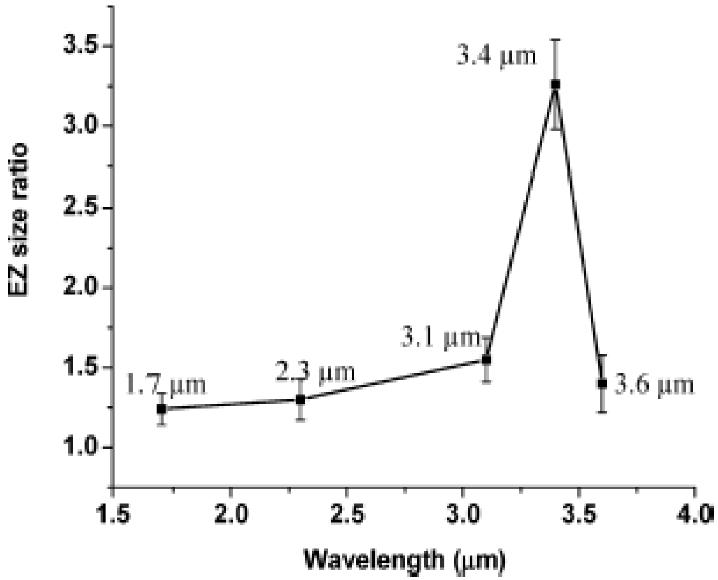


Figure 5. EZ-expansion ratios in ethanol as a function of wavelength ($n = 5$ experiments).

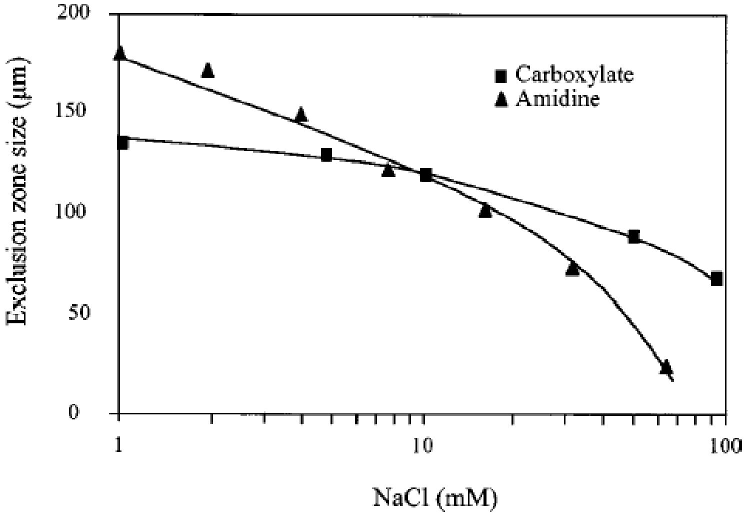


FIG. 7. Effect of salt on the exclusion-zone size with 2-µm carboxylate and 1.5-µm amidine microspheres suspended in aqueous solutions at pH 2.5 and pH 10, respectively.

ЧТО ТАКОЕ КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ В ОПТИЧЕСКОМ ДИАПАЗОНЕ ЧАСТОТ?

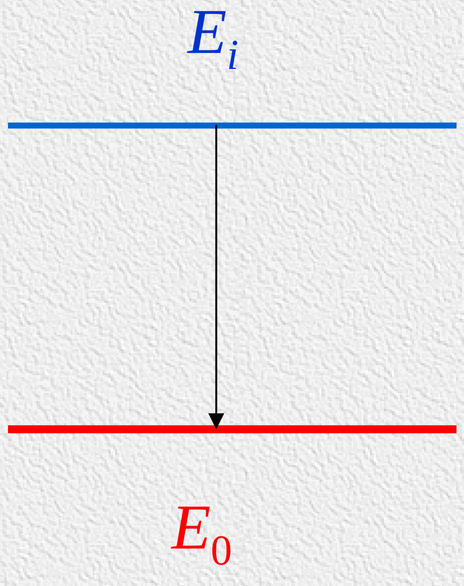
F = 10^{15} Hz

$$\frac{n^2-1}{n^2+2}=\frac{1}{3}\alpha_e N$$

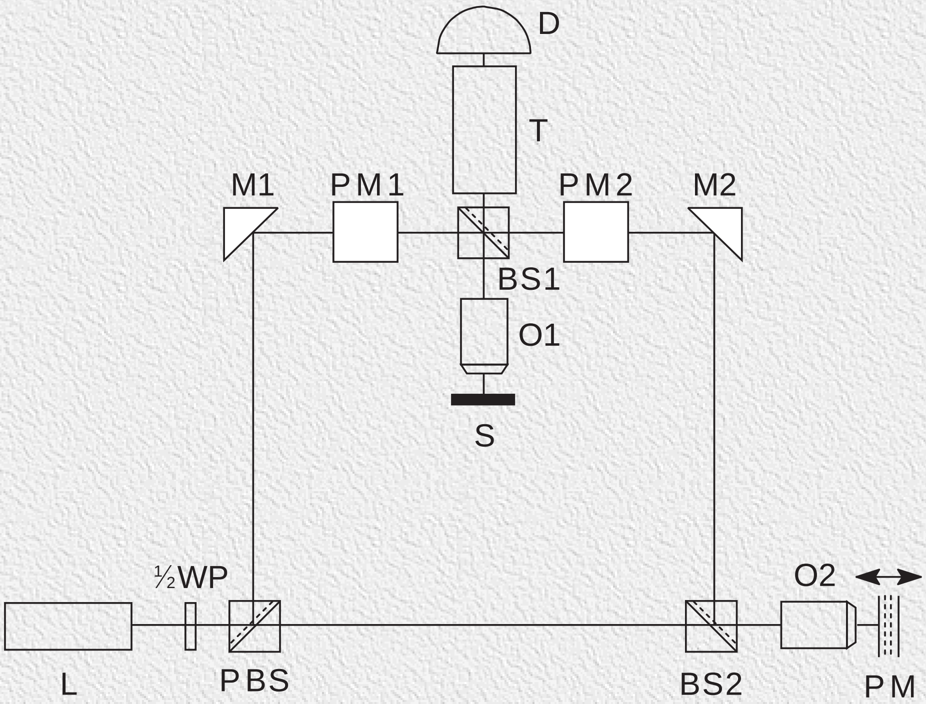
$$\alpha_e=\frac{2}{3\hbar}\sum_i \frac{\omega_{i0}}{\omega_{i0}^2-\omega^2}\left|\mathbf{P}_{i0}\right|^2$$

$$E_i - E_0 = \hbar\omega_{i0}$$

$$\omega \neq \omega_{i0}$$



ЭКСПЕРИМЕНТ ПО МОДУЛЯЦИОННОЙ ИНТЕРФЕРЕНЦИОННОЙ МИКРОСКОПИИ



$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\delta + I_{str}$$

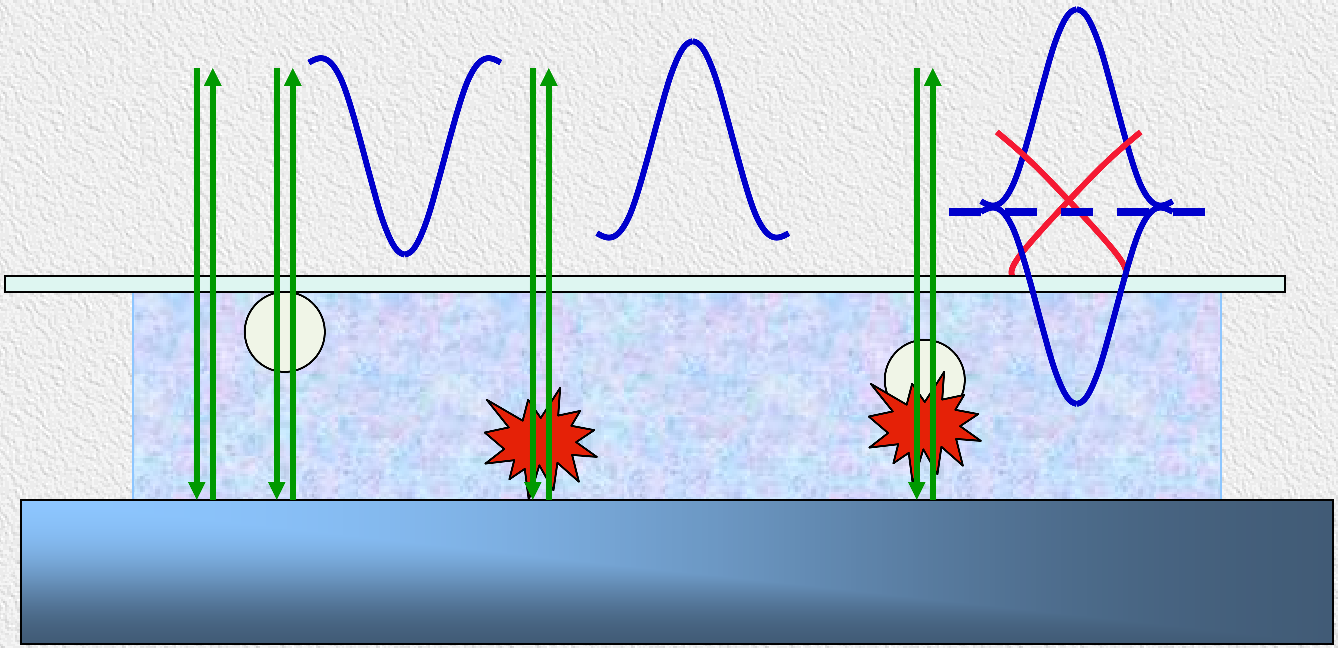
$$I(1) = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\left(\delta + \Delta_1\right) + I_{srt}$$

$$I(2) = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\left(\delta + \Delta_2\right) + I_{str}$$

$$I(3) = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\left(\delta + \Delta_3\right) + I_{str}$$

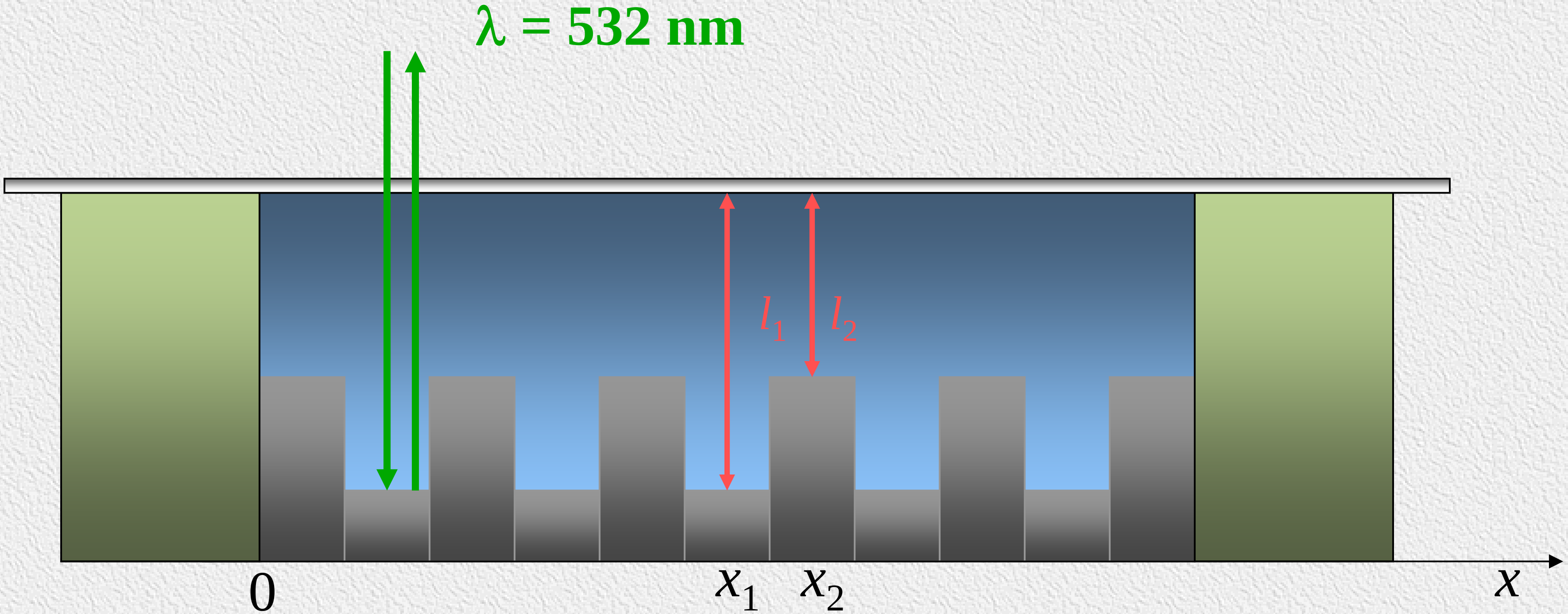
$$I(4) = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos\left(\delta + \Delta_4\right) + I_{str}$$

ПРИНЦИП РАБОТЫ ФАЗОВОГО МИКРОСКОПА



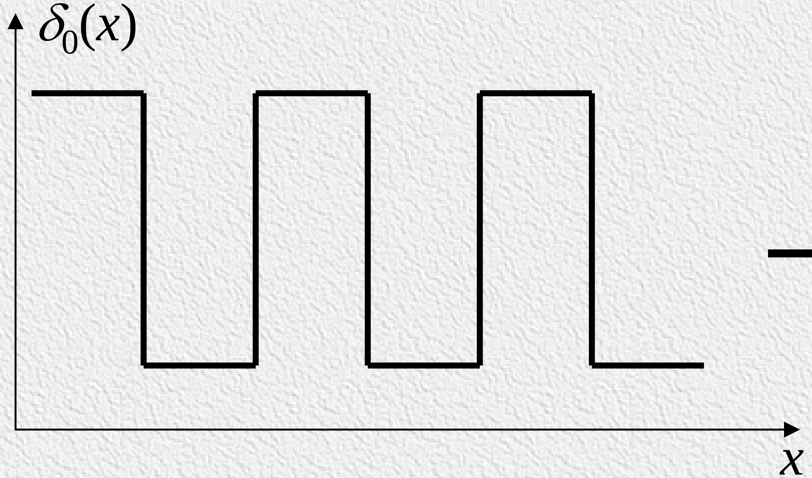
$$\delta(x,y,z)=\frac{4\pi}{\lambda}\left(n(x,y,z)-n_0\right)l(x,y)$$

КЮВЕТА С ЖИДКИМ ОБРАЗЦОМ (1)



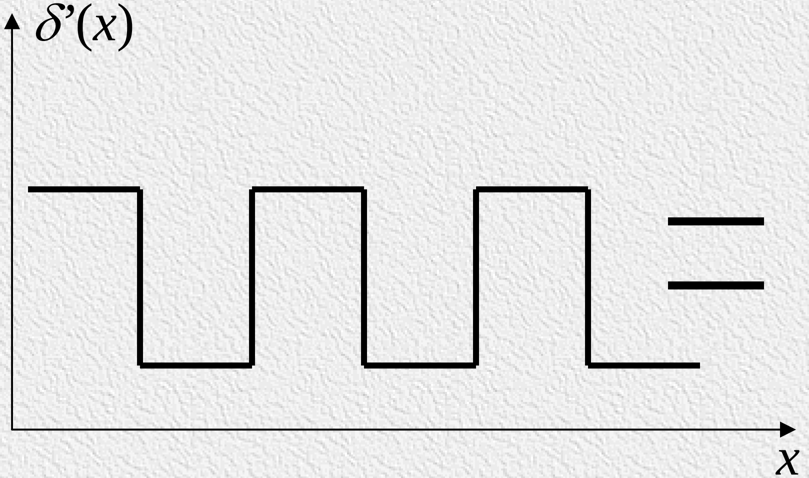
$$\delta_1(x_1) = \frac{4\pi}{\lambda} n(x_1) l_1 \qquad \delta_2(x_2) = \frac{4\pi}{\lambda} n(x_2) l_2$$

АЛГОРИТМ ОБРАБОТКИ ДАННЫХ



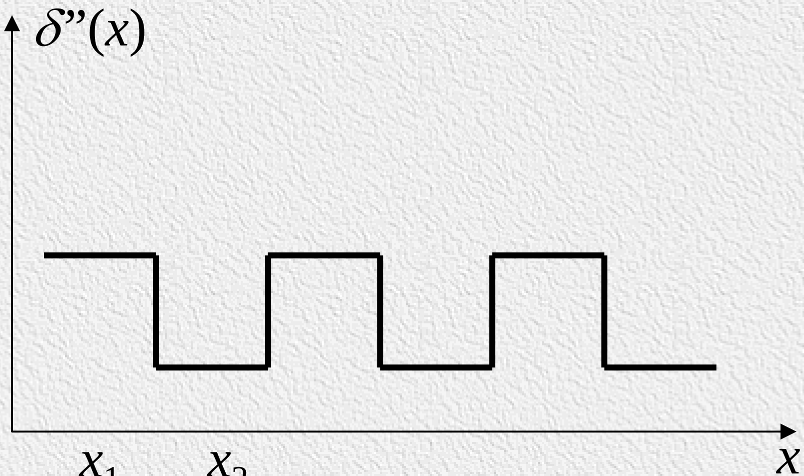
The profile of optical phase for the cell with liquid

$-$



The profile of optical phase for the empty cell

$=$



The profile of optical phase for pure liquid

$$\left.\begin{aligned} n(x_1) &= \frac{\lambda\delta''(x_1)}{4\pi l_1} \\ n(x_2) &= \frac{\lambda\delta''(x_2)}{4\pi l_2} \end{aligned}\right\} \Rightarrow n(x)$$

КЮВЕТА С ЖИДКИМ ОБРАЗЦОМ (2)

Photo of golden diffraction grating, which was used as a substrate for the cell with the liquid sample.

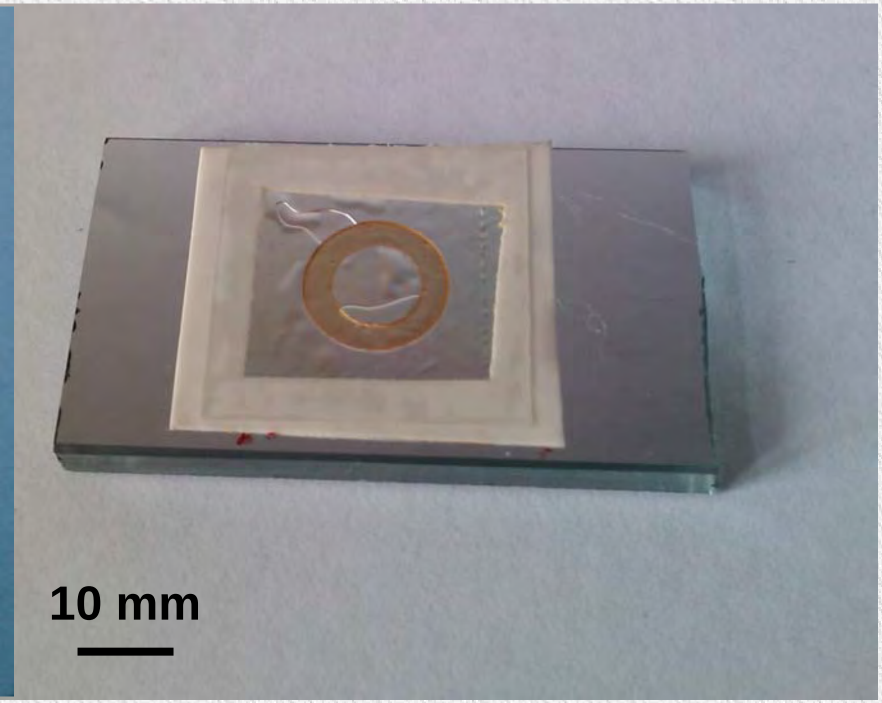
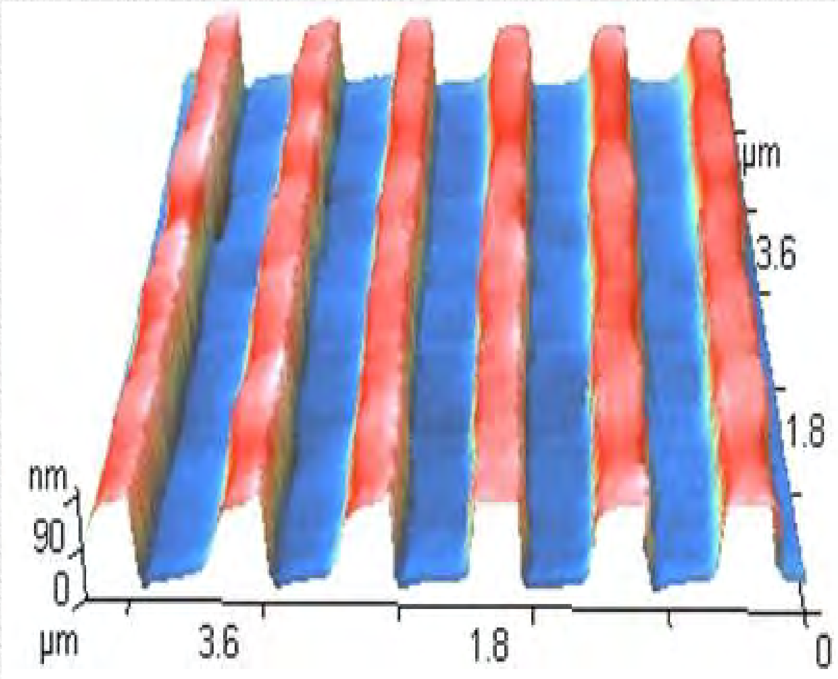
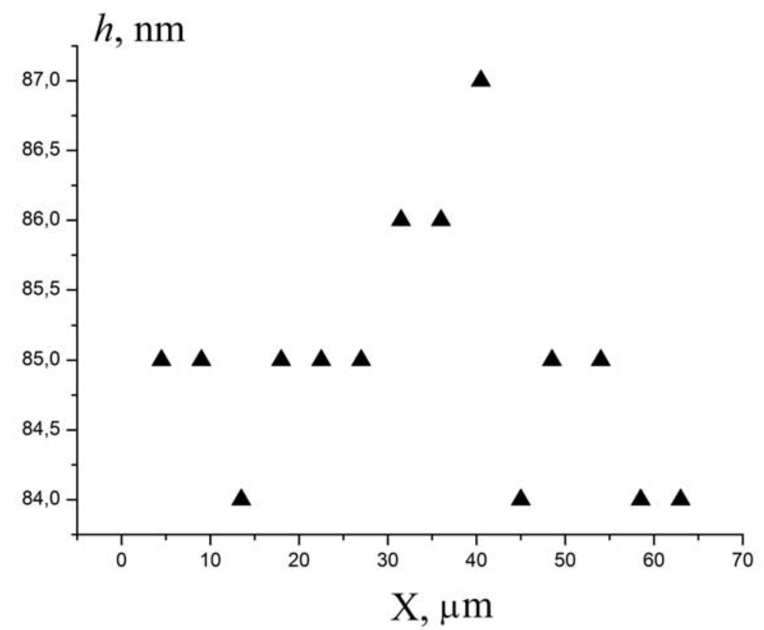


Photo of the cell with water sample based on aluminic diffraction grating. The nafion ring is in the center of the cell. The resistivity of water was 7 MΩ·cm. The thickness of Nafion and Teflon film was 170 μm.

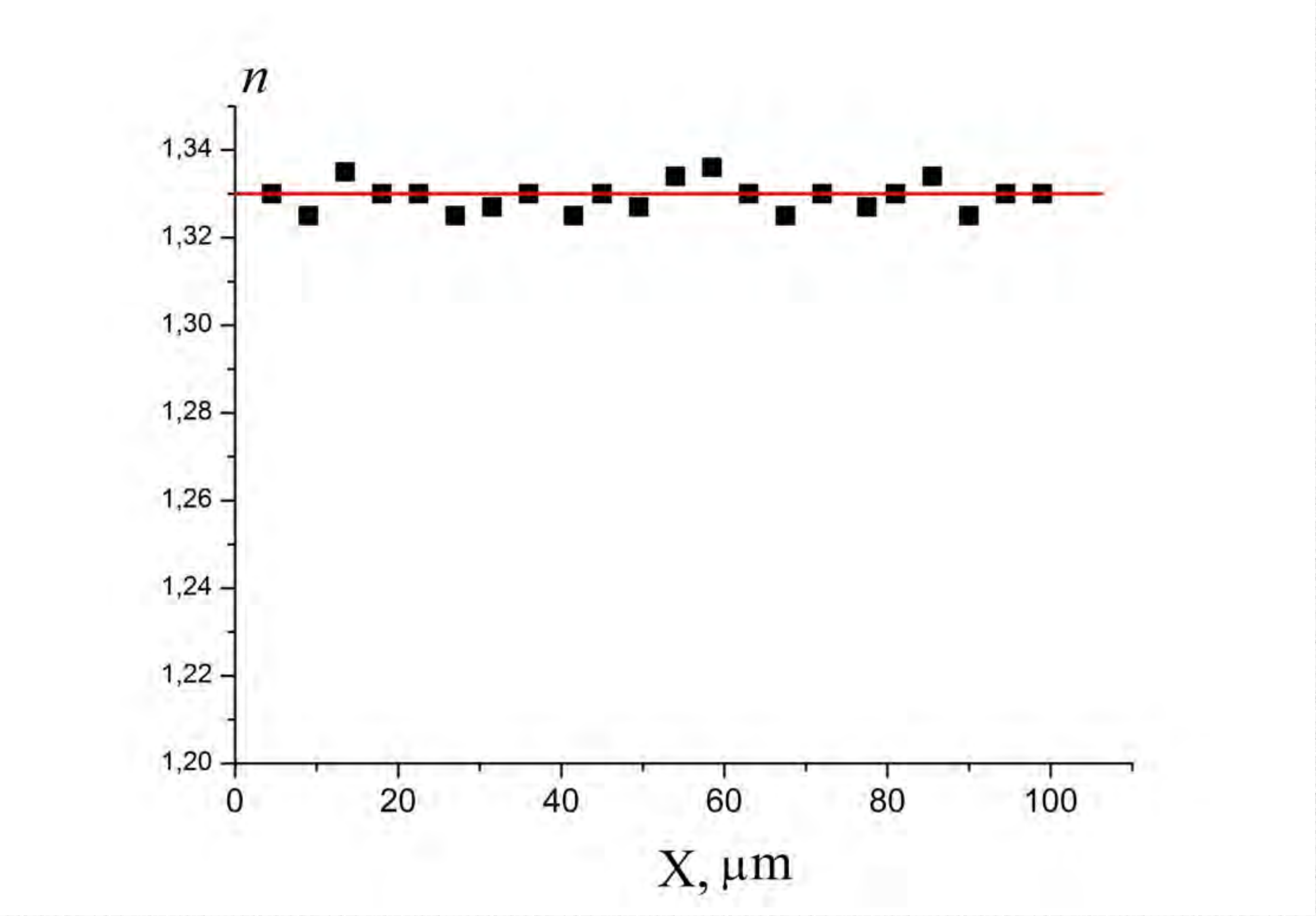
ДИФРАКЦИОННАЯ РЕШЕТКА





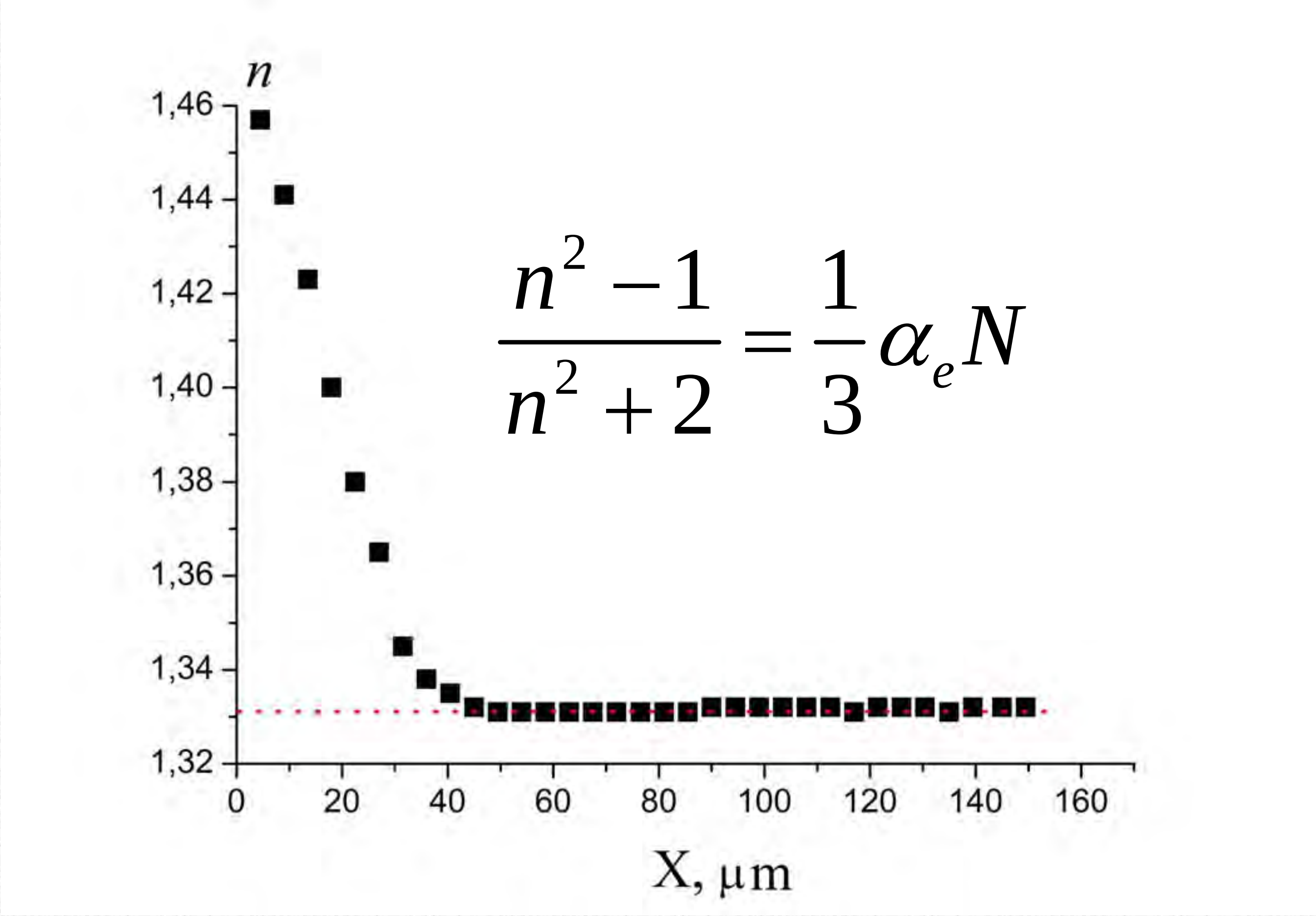
The profile of aluminic diffraction grating and scatter of heights of the grating lines. The grating spatial period was 0.9 μm.

ИЗУЧЕНИЯ КОЭФФИЦИЕНТА ПРЕЛОМЛЕНИЯ ВОДЫ (1): НАФИОН ОТСУТСТВУЕТ



Distribution of the refractive index in the cell with liquid without Nafion; the zero of X axis was chosen arbitrarily.

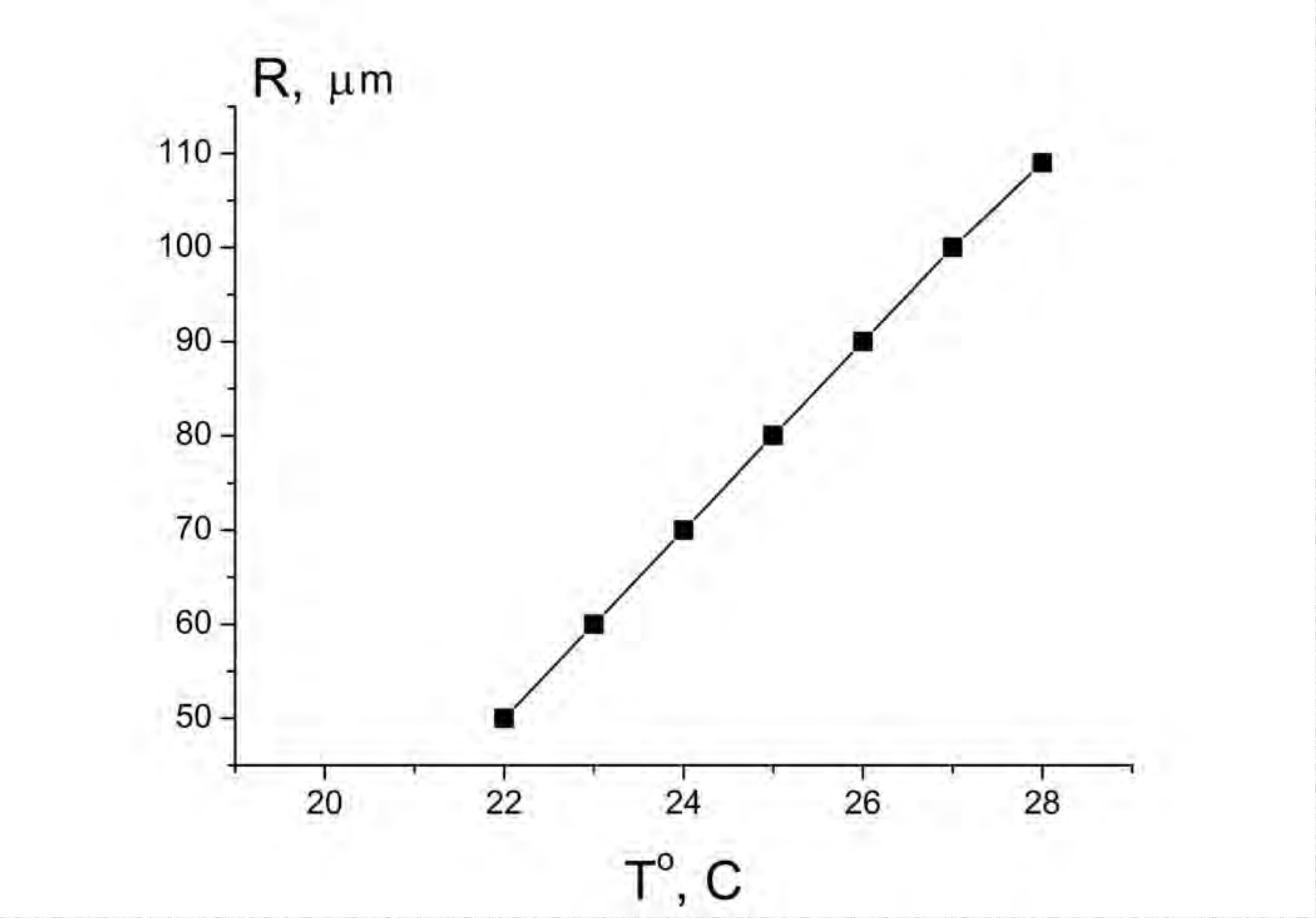
ИЗУЧЕНИЯ КОЭФФИЦИЕНТА ПРЕЛОМЛЕНИЯ ВОДЫ ВБЛИЗИ ГРАНИЦЫ С НАФИОНОМ



$$\frac{n^2-1}{n^2+2}=\frac{1}{3}\alpha_e N$$

The refractive index profile close to the Nafion – water interface. The red dotted line is the level of refractive index for non-disturbed water.

ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ РАДИУСА ВЛИЯНИЯ НАФИОНА



ИНТЕРПРЕТАЦИЯ РЕЗУЛЬТАТОВ

$$\varepsilon = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_T \approx 5.1\cdot 10^{-5}$$ **(1/Атм)**

$$\boldsymbol{n = 1.46 \approx 1.1 n_0}$$

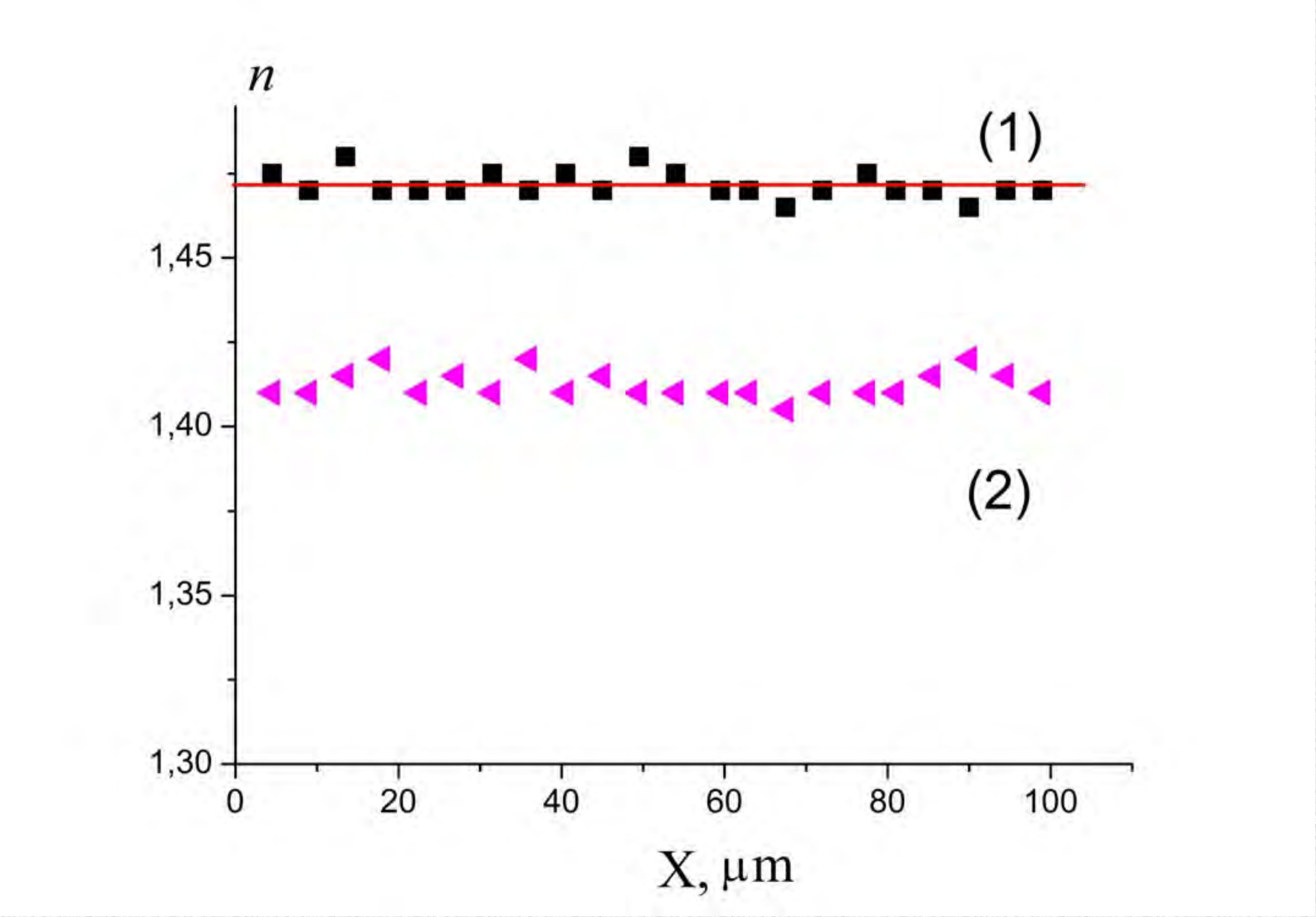
$$\frac{\Delta\rho}{\rho} \sim \frac{\Delta N}{N} \sim \frac{\left(1.1^2 - 1\right) n_0^2}{n_0^2 - 1} = 0.27.$$

$$\boldsymbol{\Delta p \approx 5.3\cdot 10^3}$$ **Атм.**

ТАБЛИЦА ПАРАМЕТРОВ ВОДЫ И ГЛИЦЕРИНА

	M, g/mole	n	μ, D	ΔH_{evap}, kJ/mole	T_{boil}, C
water	18	1.33	1.84	40.66	100
glicerol	92.09	1.47	0.28	88.12	290

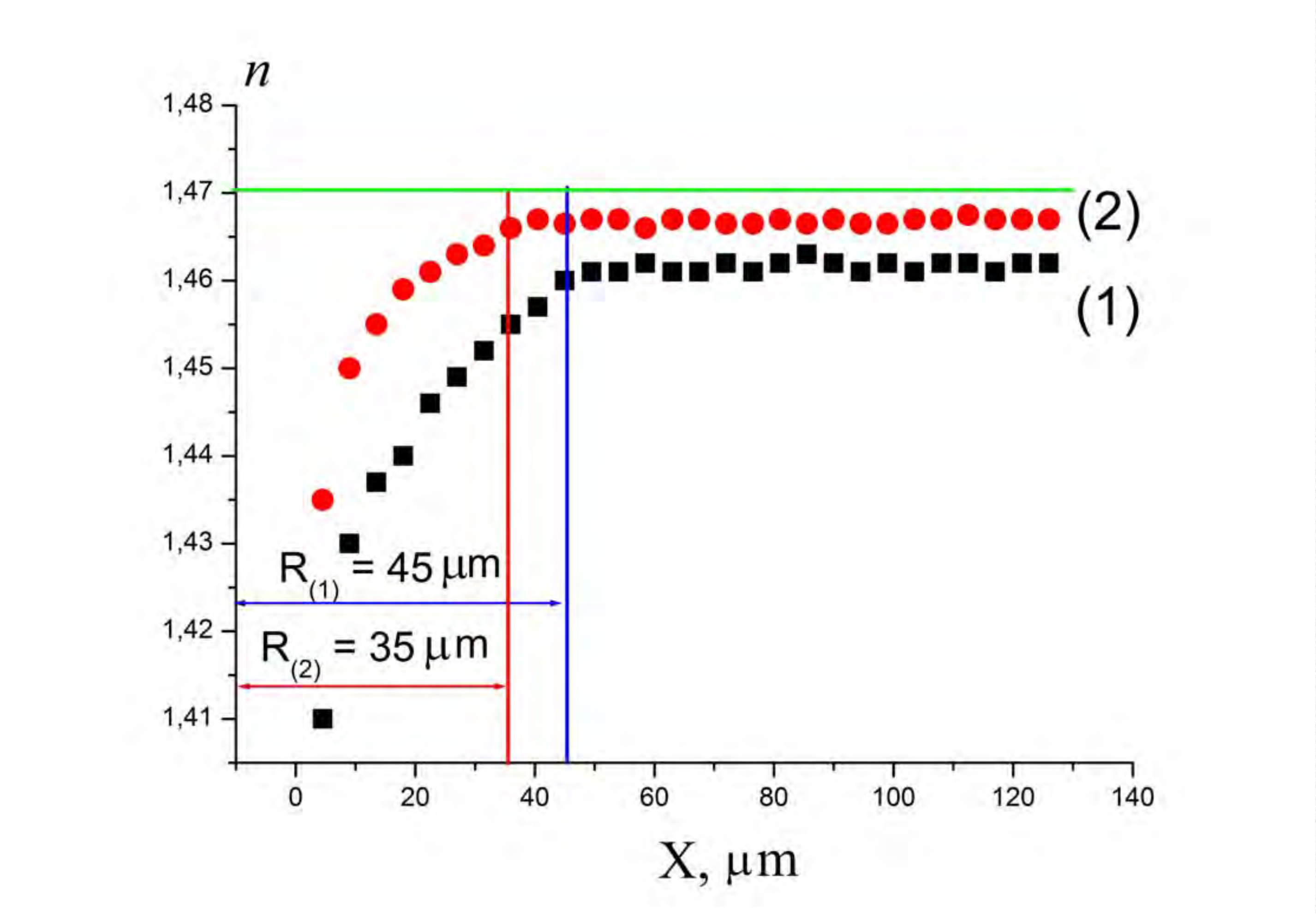
КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ СМЕСИ ВОДА - ГЛИЦЕРИН (1): НАФИОН ОТСУТСТВУЕТ



(1) – water-free (dry) glycerol; this graph have the same shape in the presence of Nafion spacer as well

(2) – water-glycerol mixture; water content is 5 M (100 g/l)

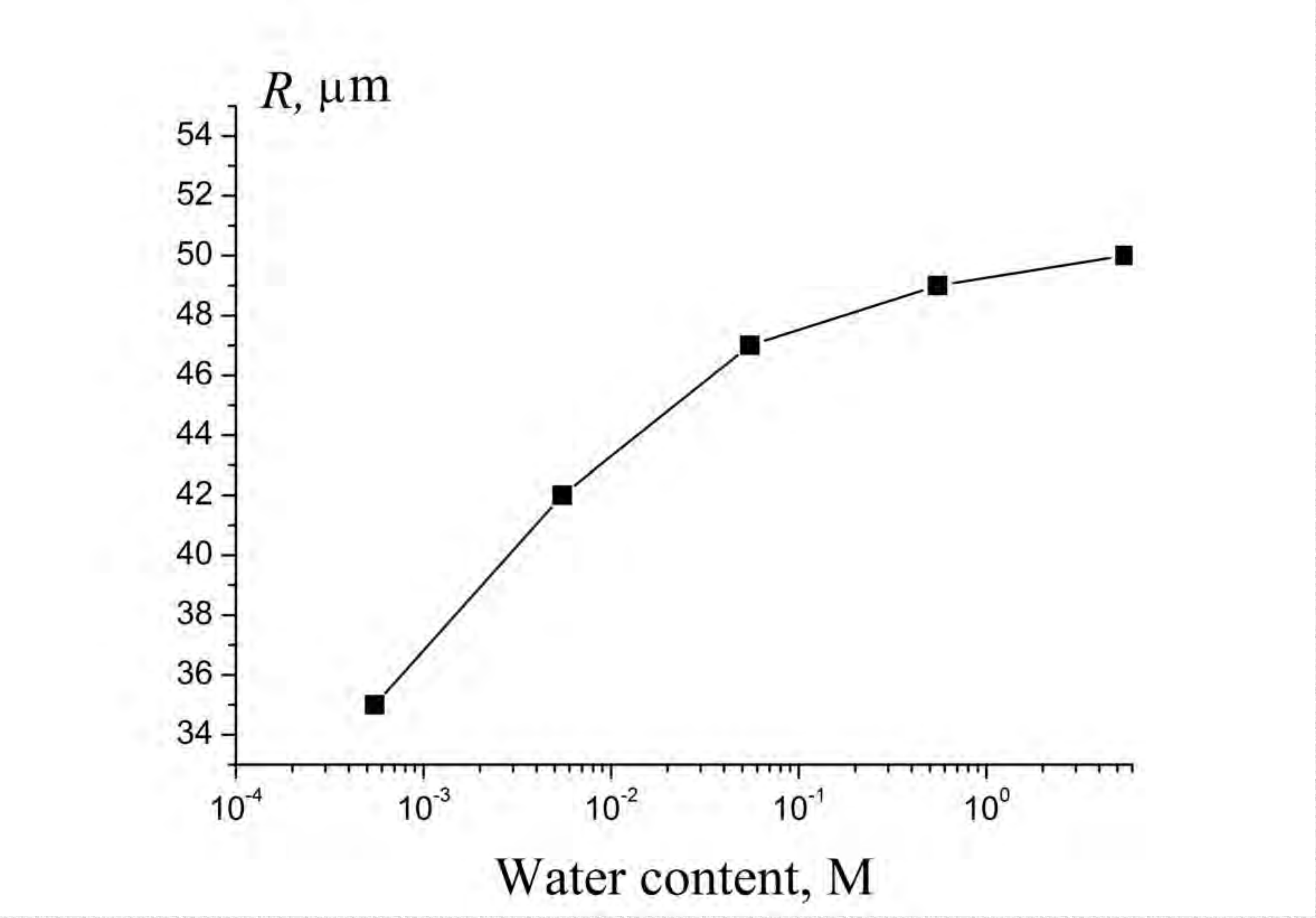
КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ СМЕСИ ВОДА - ГЛИЦЕРИН ВБЛИЗИ ПОВЕРХНОСТИ НАФИОНА (1)



(1) – **water content is $5 \cdot 10^{-4}$ M**

(2) – **water content is $5 \cdot 10^{-3}$ M**

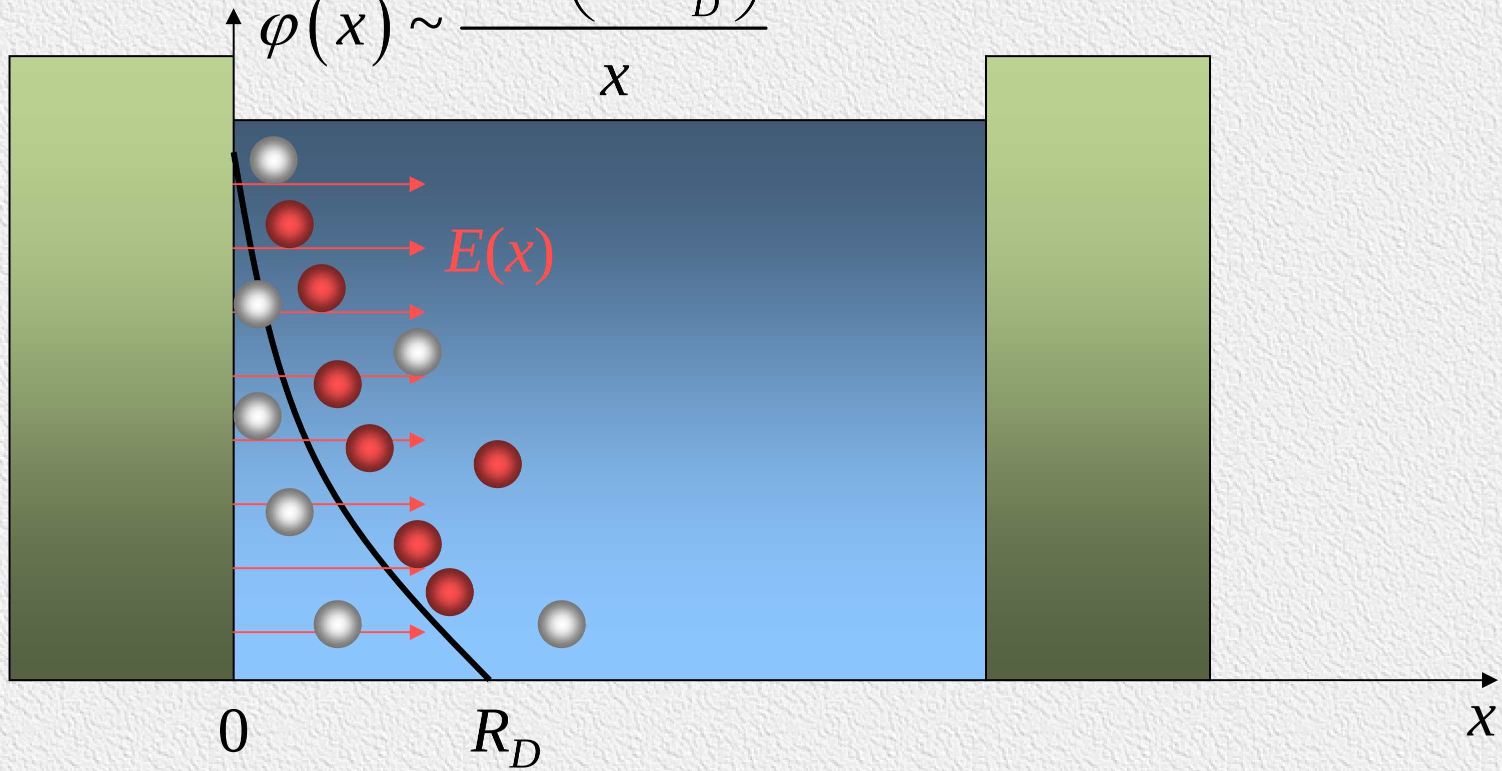
КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ СМЕСИ ВОДА - ГЛИЦЕРИН



The dependence of Nafion influence radius versus the content of water

ВОЗМОЖНАЯ ПРИЧИНА: ЭЛЕКТРОСТАТИЧЕСКОЕ ПОЛЕ?

$$\varphi(x) \sim \frac{\exp\left(-\frac{x}{R_D}\right)}{x}$$



$$R_D = \sqrt{\frac{\varepsilon kT}{8\pi e^2 N_i}}$$

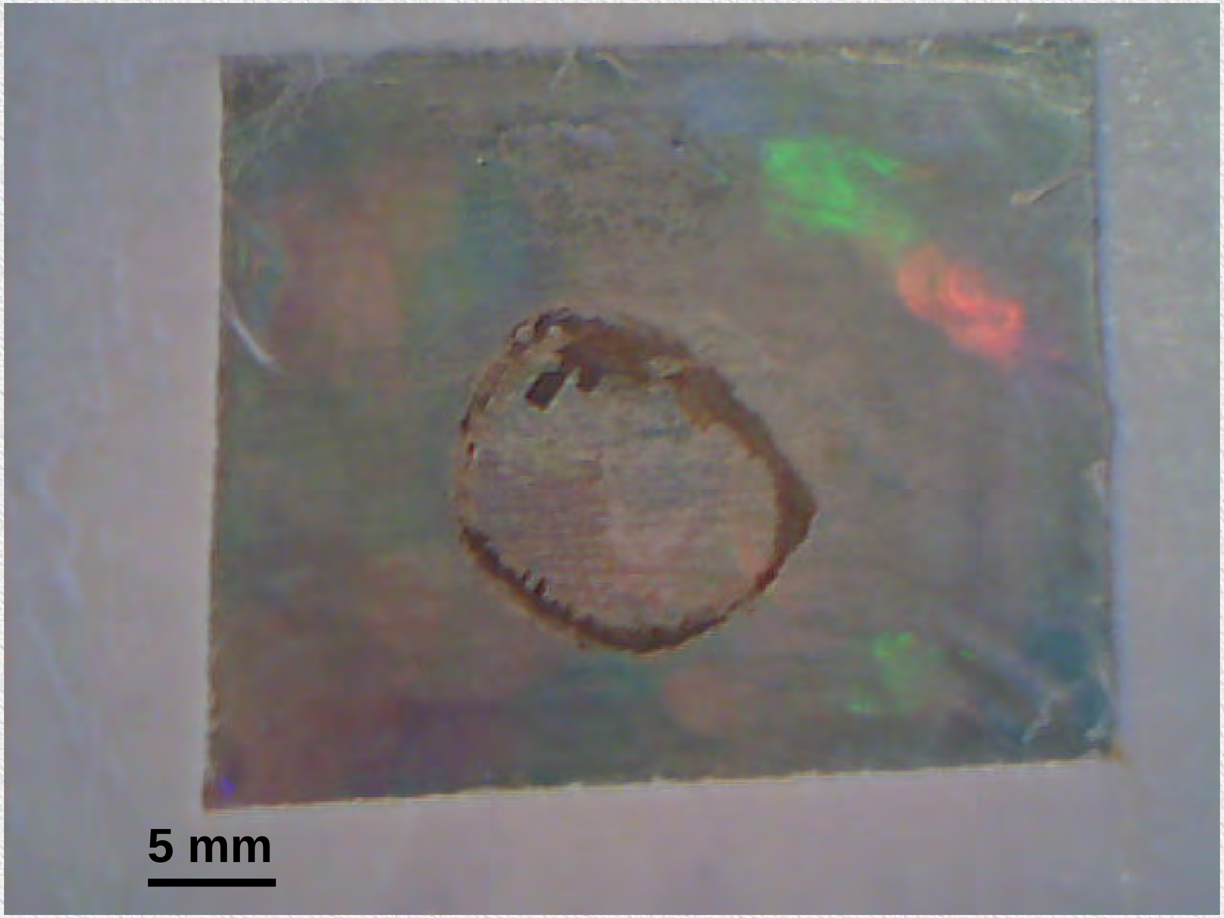
- the Debye screening radius;

N_i – the bulk density of ions

Зависимость Дебаевского радиуса от концентрации ионов

C, M	10^{-7}	10^{-5}	10^{-3}	10^{-1}
R_D, μm	1	0.1	0.01	0.001

ТРАВЛЕНИЕ ПОДЛОЖКИ; NaCl (1)

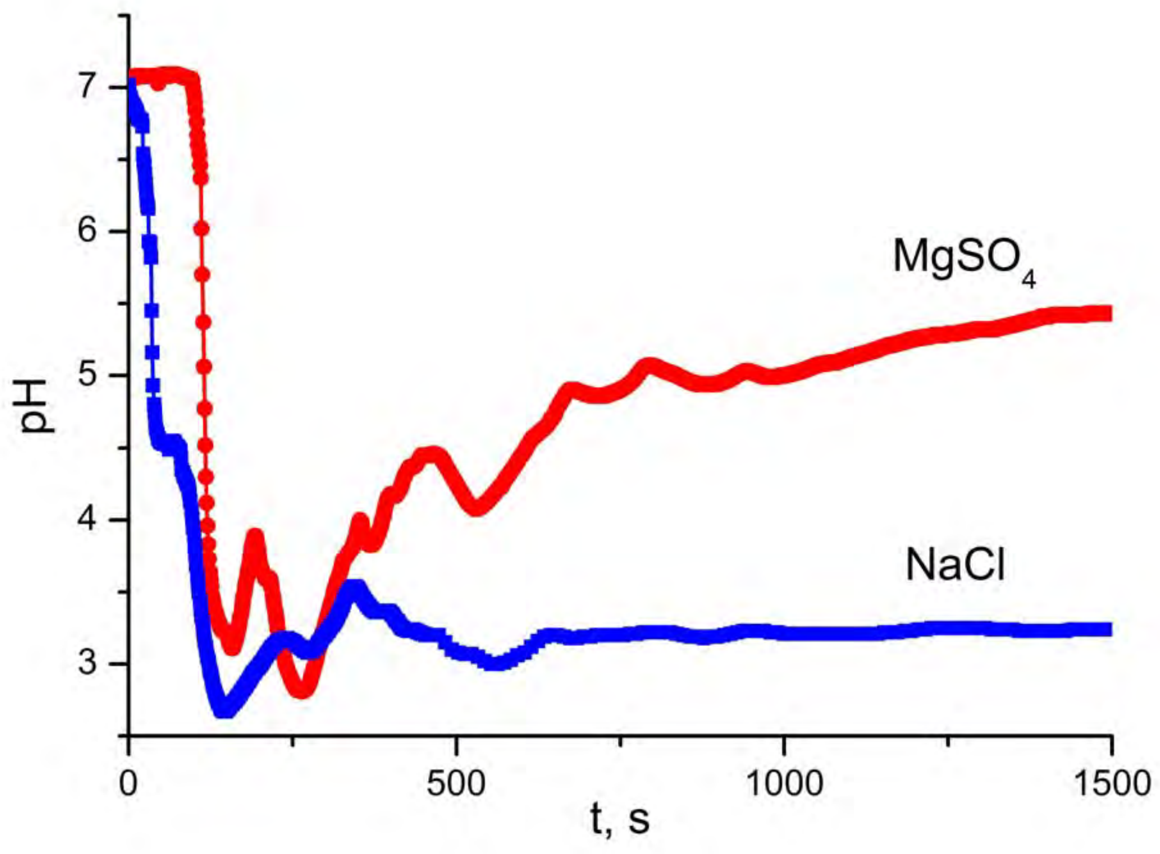


Aluminic diffraction grating, NaCl aqueous solution, C = 10^{-1} M. The range of studied concentrations: 10^{-4} – 1 M.

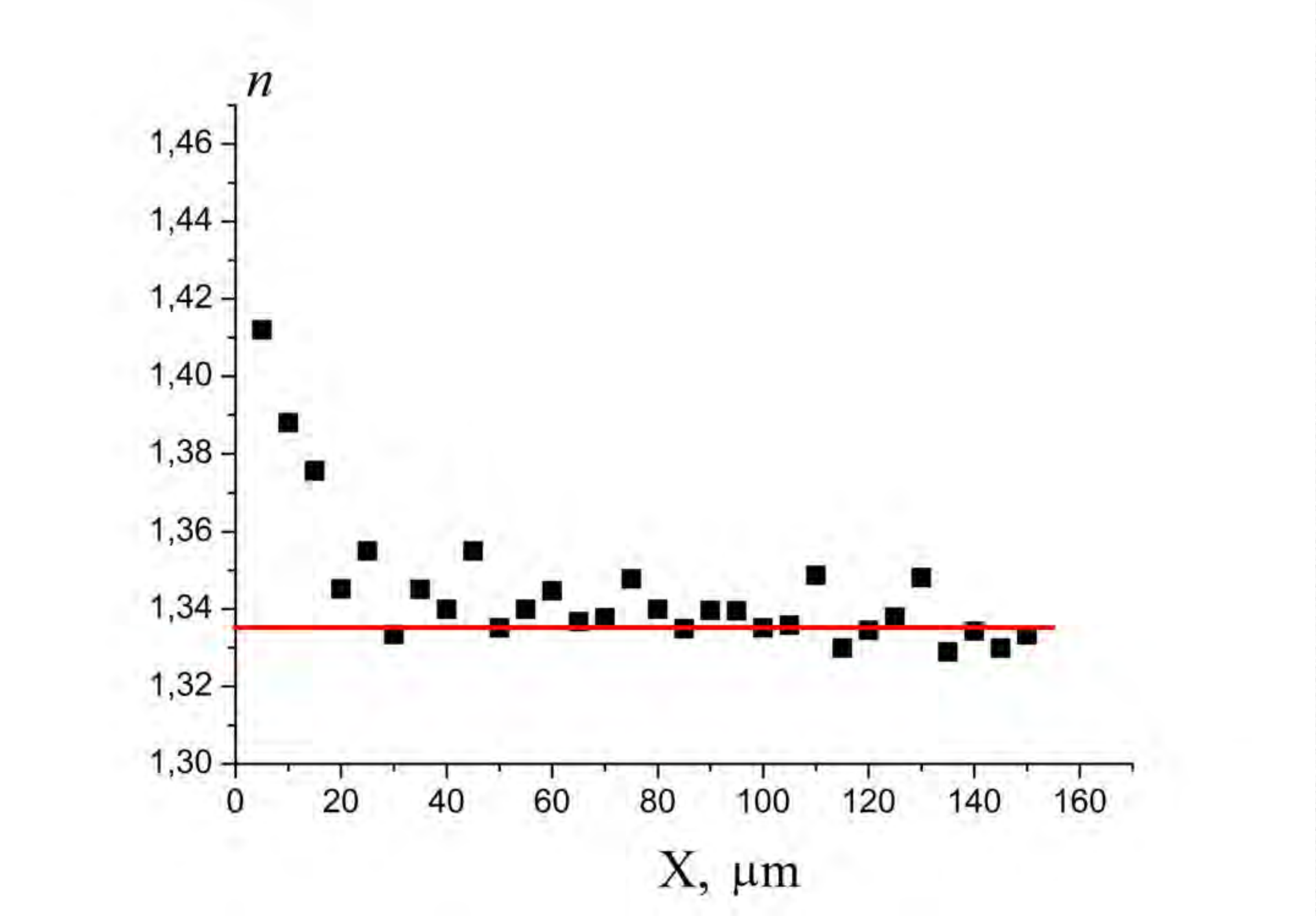
ТРАВЛЕНИЕ ПОДЛОЖКИ; NaCl (2)

Golden diffraction grating, NaCl aqueous solution, C = 10^{-1} M

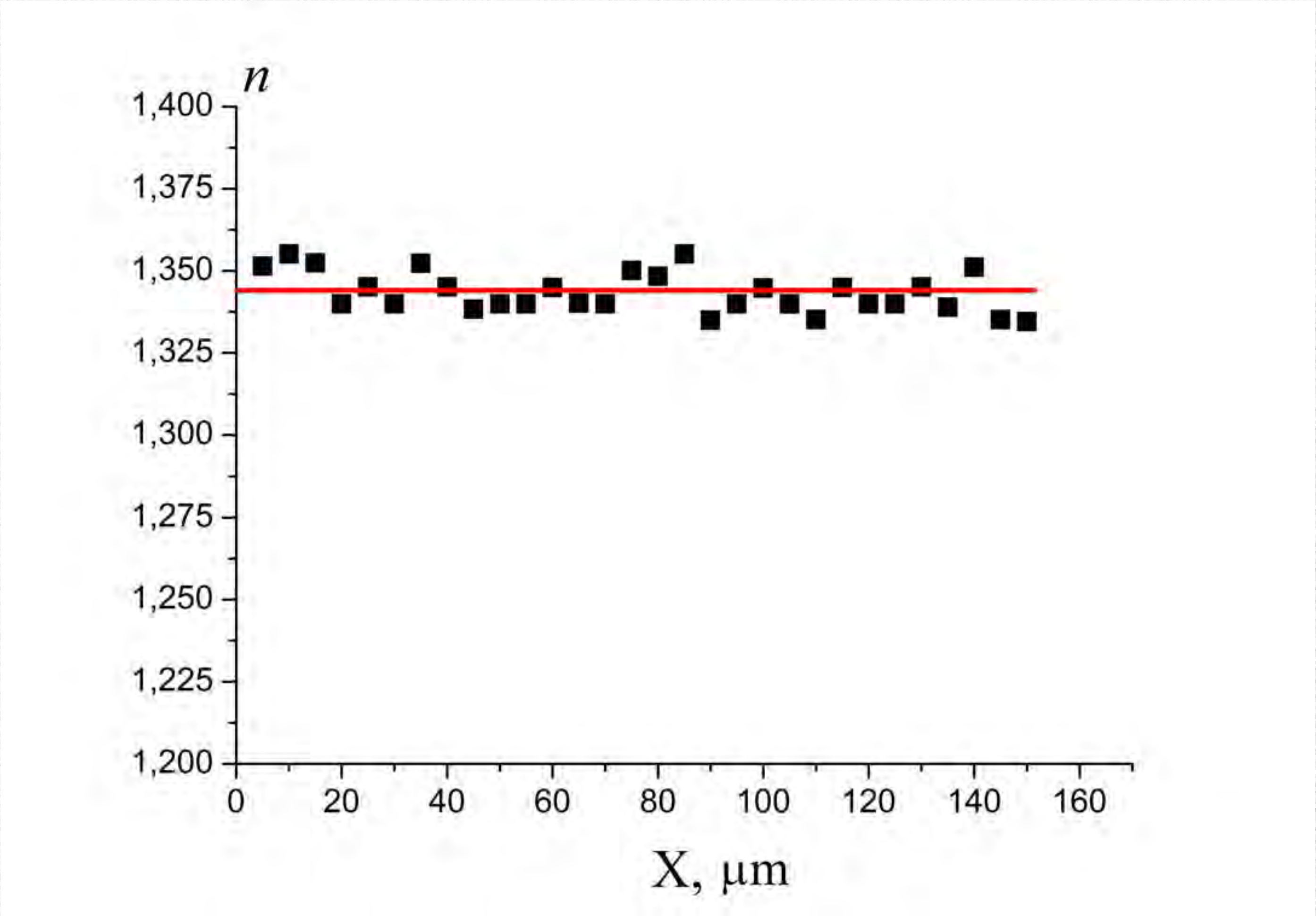
Динамика pH для растворов $Mg(SO_4)$ и NaCl (10^{-1} M) вблизи границы с Нафионом



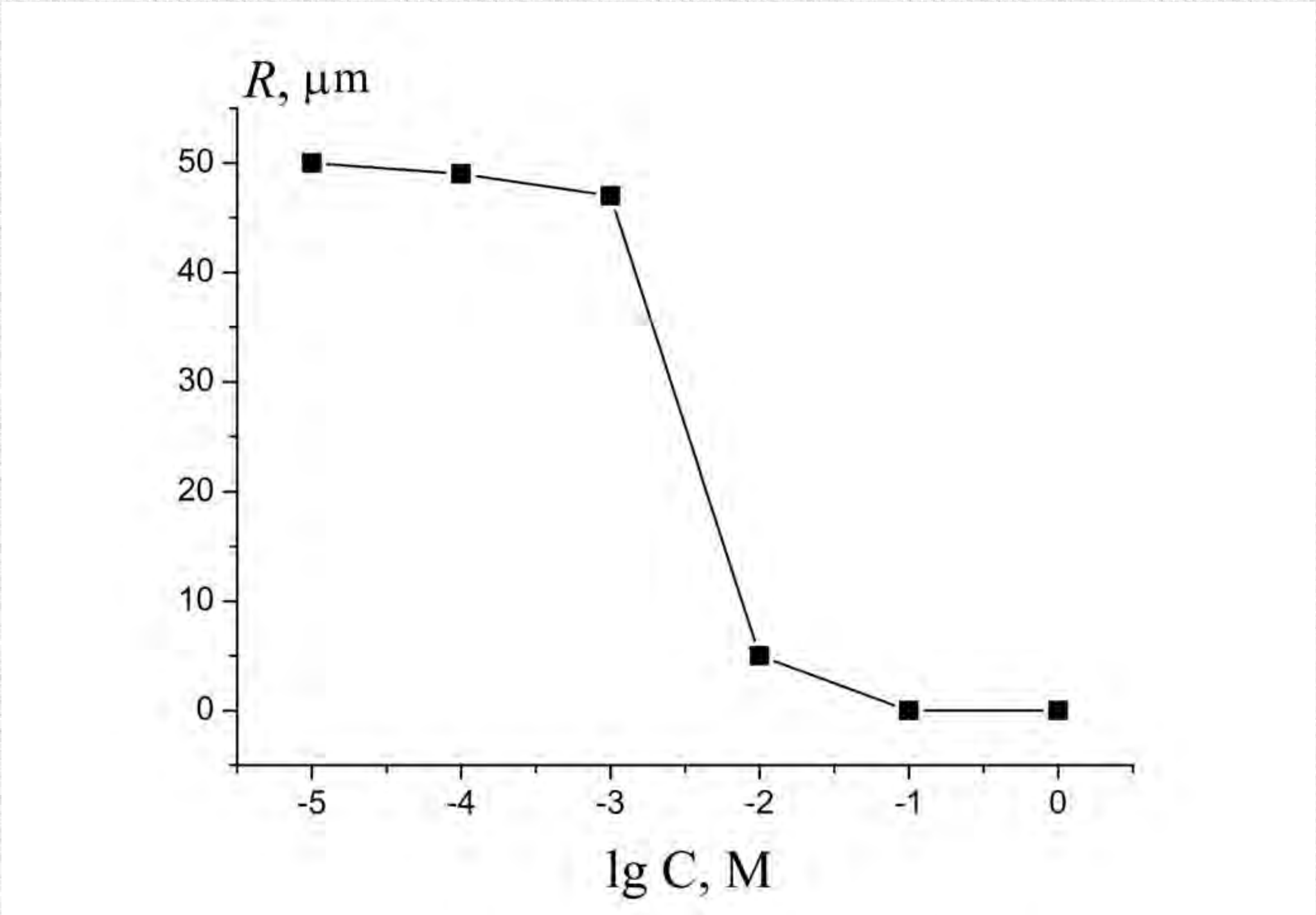
КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ РАСТВОРА $Mg(SO_4)$ (10^{-4} М)



КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ РАСТВОРА $Mg(SO_4)$ (0.1 M)



КОЭФФИЦИЕНТ ПРЕЛОМЛЕНИЯ РАСТВОРА Mg(SO_4) ВБЛИЗИ ГРАНИЦЫ С НАФИОНОМ



The dependence of Nafion influence radius versus the content of salt

ВОЗМОЖНОЕ ОБЪЯСНЕНИЕ НАБЛЮДАЕМОГО ЭФФЕКТА – РОСТ ПОЛЯРИЗУЕМОСТИ

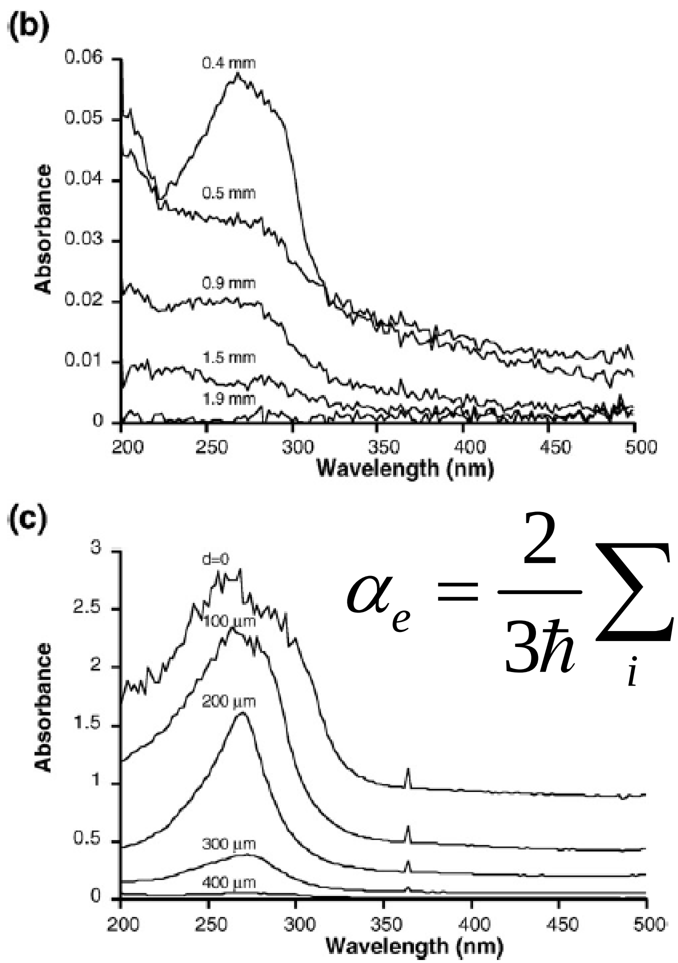
J.Zheng, W.Chin, E.Khijniak

,

E. Khijniak Jr., G.H.Pollack,

Surfaces and interfacial water: Evidence that hydrophilic

surfaces have long-range impact, Advances in Colloid and Interface Science **127** (2006) 19–27



$$\alpha_e = \frac{2}{3\hbar}\sum_i \frac{\omega_{i0}}{\omega_{i0}^2 - \omega^2}\left|\mathbf{P}_{i0}\right|^2$$

Fig. 4. a. Optical system used to measure UV–Vis spectrum as a function of distance from Nafion surface. b. Spectra measured at varying distances from the Nafion surface. c. Same as b, but closer to Nafion surface. Note difference in scale.

TO BE CONTINUED

INTERMEDIATE RESULTS

- The refractive index of water essentially (by a factor of 1.1) grows close to the “water - Nafion” interface. The radius of Nafion influence is $\geq$ 50 μm.
- The Nafion attracts water molecules from aqueous mixtures. The radius of Nafion influence is dependent upon the content of water in the mixture. At the same time, the Nafion does not attract glycerol molecules despite the dipole properties of these molecules.
- The Nafion is very strong catalyst; the presence of Nafion leads to unexpected chemical reactions.