

Determination of diffusion coefficient of zinc (II) ions in polymeric membrane by absorption spectroscopy

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The paper presents the new determination method of ions diffusion coefficients in polymer membranes. The investigations were performed in a specially constructed cell. The method is based on membrane absorbance measurement in time function. The membrane included chelating 1-(2-pyridylazo)-2-naphtol (PAN) component which forms colorful complex with Zn(II) ions. On the basis of performed measurements and interpretation of second Fick's law zinc ions diffusion coefficient in investigated membranes was calculated to be $3.28 \cdot 10^{-8} \text{ cm}^2/\text{s}$.

1. INTRODUCTION

The knowledge of diffusion coefficient ions in polymer membranes is essential to explain the electrodes operation mechanism and selectivity row.

So far the following methods of diffusion coefficient determination in polymers methods have been used:

- gravimetric techniques
- techniques relying on concentration changes measurement in solutions separated by membrane:
 - potentiometric methods
 - spectrophotometric methods
- techniques relied on the measurement of polymeric films characteristic, for example, fluorescence

In gravimetric methods, an increase or decrease of a polymeric sample mass during sorption or desorption is measured. The sample may be of irregular shape. Measurements can be conducted in two ways: continuously or

periodically (sample is taken out and weigh in given time periods). In the measurements gravimetric set with sensitivity of 10^{-7} g was used [1].

Diffusion coefficient in polymer membranes can be determined by investigation of substance flow across membrane. This is achieved by analyzing of solutions concentration changes at one or both sides of the membrane. In order to determine diffusion coefficient Schwitzgebel et al.[2] applied two electrodes Ag/AgCl in HCl solutions separated by the membrane and they measured the potentials changes in time. Nomura [3] determined diffusion coefficient of Na^+ ions inside membrane. He measured polymeric membrane resistance changes in time. Nomura applied two platinum electrodes placed in solutions separated by the membrane.

Solution concentration change occurring in time at both sides of membrane can be also measured by spectrometric method. Diffusion vessel is placed outside the spectrophotometer and solutions from the membrane separated chamber are pumped into optical cell placed inside the spectrophotometer [4,5]. Shaposhnik et al.[6-7] applied laser optical interferometry to determine diffusion coefficients in membranes, by measuring concentration changes in time.

Polymer mass change (hence diffusion coefficient) can be also determined by spectrophotometric measurements of polymers fluorescence change while sorption. A microscopic plate covered by polymer film constitutes a sample [9].

Attenuated total reflectance (ATR) method is also used to investigate the diffusion in polymer. In this method a special-shaped crystal is covered by polymer film and the light beam absorbance change is investigated in time. The light beam reflects from the interface crystal ATR / polymer film [10,11].

The aim of our paper was the determination of the diffusion coefficient of Zn(II) ions in polymer membranes, which are used in ionoselective electrodes.

In this paper we presented a brand new, so far not described spectrophotometric method of diffusion coefficient in polymers determination. This method consists of a direct measurement of membrane absorbance in time with fixed wave length.

2. THEORY

To calculate diffusion coefficients in the polymer-solution system, it is necessary to solve the second Fick's law:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (1)$$

where c is component concentration inside polymer after time t in the distance x from the polymer surface and D is diffusion coefficient.

In the case when the polymer sample is a thin foil and sorbent concentration at the surface is constant, from both sides of polymer surface the equation for diffusion is:

$$\frac{M_t}{M_\infty} = 2 \left(\frac{4Dt}{l^2} \right)^{1/2} \left[\frac{1}{\sqrt{\pi}} + 2 \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nl}{2\sqrt{Dt}} \right] \quad (2)$$

where:

M_t - sorbate mass absorbed in sorption process by polymer sample after time t

M_∞ - sorbate mass absorbed to moment of settled down equilibrium state ($t=\infty$)

D - diffusion coefficient,

l - membrane thickness,

t - time

$$\operatorname{erf} = \frac{1}{\sqrt{\pi}} \int_0^x e^{-y^2} dy, \quad \operatorname{erfc}x = 1 - \operatorname{erf}x$$

$$y = \frac{u}{2\sqrt{Dt}} \quad \operatorname{ierfc}x = \frac{1}{\sqrt{\pi}} e^{-x^2} - x \operatorname{erfc}x$$

u - the distance from the du thickness layer in the diffusing substance of constant concentration to the point of sample testing.

In the first stage of the sorption the second equation element is not important until the value $M_t/M_\infty=0.55$, so it can be neglected. Then the equation becomes:

$$\frac{M_t}{M_\infty} = \frac{4}{l\sqrt{\pi}} D^{1/2} t^{1/2} \quad (3)$$

When polymer membrane absorbance changes in time, it follows that:

$$\frac{M_t}{M_\infty} = \frac{A_t}{A_\infty} \quad (4)$$

where:

A_t – absorbance of polymer membrane after time t

A_∞ - absorbance of polymer membrane after a moment of settled down equilibrium state ($t=\infty$)

so the equation (3) becomes:

$$\frac{A_t}{A_\infty} = \frac{4}{l\sqrt{\pi}} D^{1/2} t^{1/2} \quad (5)$$

From the plot dependence slope, made in system $A_t/A_\infty = f(t^{1/2})$, the diffusion coefficient can be calculated:

$$\operatorname{tg} \alpha = \frac{4}{l\sqrt{\pi}} D^{1/2} \quad (6)$$

$$D = \left(\frac{\operatorname{tg} \alpha l\sqrt{\pi}}{4} \right)^2 \quad (7)$$

3. EXPERIMENTAL

3.1. Apparatus and chemicals

Reagents

Zinc chloride –Merck, Darmstadt, Germany

Polyvinyl chloride (PVC) (low molecular weight)- Aldrich Chemical Company, Inc., Milwaukee, USA

1-(2-Pyridylazo)-2-naphtol (PAN)– Sigma Chemical CO., St. Louis , USA

Tri(2-etyhylhexyl)phosphte (TEHP) – K&K Laboratories, INC., Cleveland, OH, USA

Tetrahydrofuran (THF) - Merck, Darmstadt, Germany

Apparatus

Spectrophotometric measures were done with spectrophotometer SPEKORD M40 combined with computer.

3.2. Procedures

Membrane preparation procedure consists of the following steps:

1. Preparing of ingredients mixture: 0.12% PAN, 32.88% PVC, 67% TEHP
2. Dissolving of mixture in THF
3. Pouring of solution portion to glass ring and solvent evaporating
4. Membrane cutting and placing in measuring cell

where:

PVC- Polyvinyl chloride

PAN- 1-(2-Pyridylazo)-2-naphthol

TEHP- Tri(2-ethylhexyl)phosphate

THF - Tetrahydrofuran

1.2 mg of PAN, 0.67 g of TEHP and 0.3288 g of suspensional PVC was weighted and precisely mixed. Then 8ml THF was added and mixed again until clear solution was obtained. From this solution membranes were poured to glass ring of 34mm diameters placed on glass plate. While the mixture was dissolving and the membrane was being poured, the vessel with membrane solution was placed in bigger vessel with THF under lid. It prevented evaporating and changing of solution composition. The membranes made in this way were dried for 24 hours at room temperature. After that membranes were dried for 3 hours in 313K. Similarly another membrane was prepared which has the same composition but lacked the complex-creative PAN element. Circles of the diameter equal to the diameter of the measured cell were cut from membranes made in this way.

Membranes were placed in a specially-constructed cell, (Figure 1) which was a teflon cylinder with two chambers, and the way of placing membranes was that it separates those both chambers. $ZnCl_2$ solutions were poured to the chambers through special holes by means of a syringe.

Two identical cells were used in investigations. One was placed on the measuring light beam while the other in the reference beam. Light fell perpendicularly to the membrane surface. Thickness of both the membrane and solutions concentration was equal. The only difference was that membrane in reference cell did not include PAN.

The absorbance dependence in time was measured. The absorbance measurement was conducted using the analytical wave length of complex $Zn(PAN)_2$ – 558.9 nm. Membranes' thickness was 0.013-0.035cm and membranes were immersed in 0.001 M $ZnCl_2$ solution.

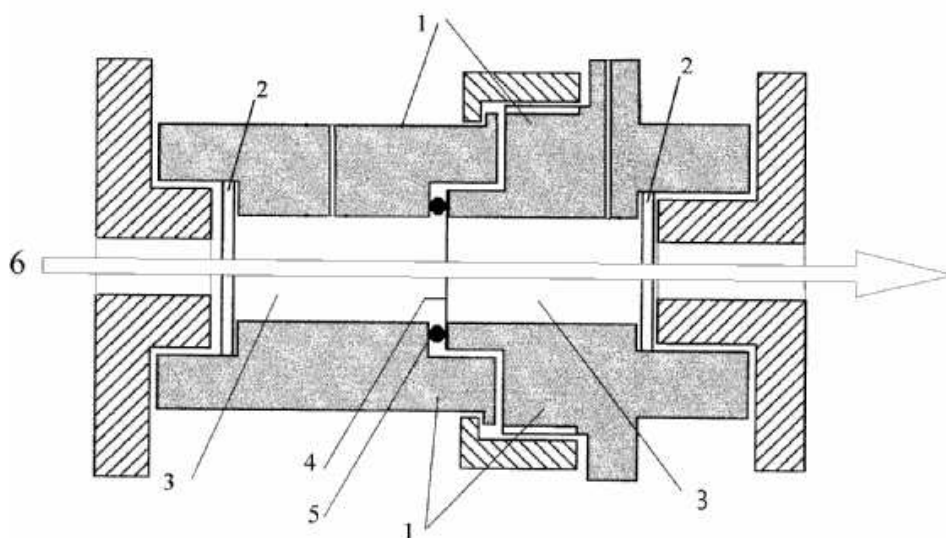


Fig.1. Measurement cell scheme:

- 1 – teflon housing,
- 2 – polyacryl window,
- 3 – chamber,
- 4 – membrane,
- 5 – o-ring,
- 6 – light beam

4. RESULTS

Figure 2 illustrates absorbance changes in time for membranes of different thickness. From curves course it is seen that at the initial stage of ions $Zn(II)$ diffusion process inside the membrane is identical for different thickness membranes. Equilibrium state is achieved more quickly in the smallest thickness membrane (curve 1).

However, in the membranes of the biggest thickness the equilibrium state was not achieved. The absorbance value in equilibrium state for this membrane was calculated on the basis of membrane absorbance value before measurement with the wave length fulfilling maximum PAN absorption.

Figure 3 presents data from Figure 2 converted in relationship to absorbance after achieving a settled equilibrium state. Straight lines are marked which, in accordance with theory, agree with course of absorbance changes in the first

stage of sorption. Zn(II) ions diffusion coefficient was calculated from the slope of those lines and equations (4) and (5). The obtained results are presented in the table 1.

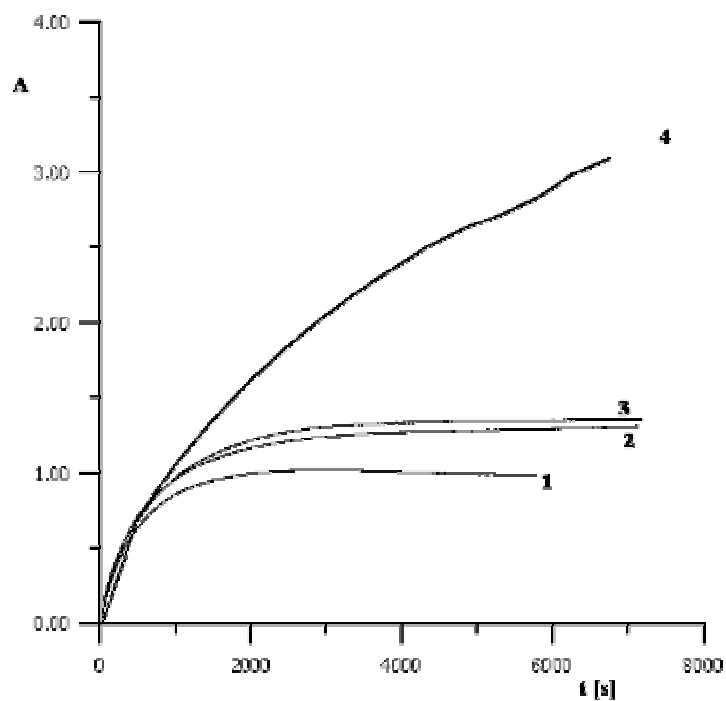


Fig 2. Absorbance changes in time for membranes of different thickness:

1. – 0.013 cm
2. – 0.015 cm
3. – 0.016 cm
4. – 0.035 cm

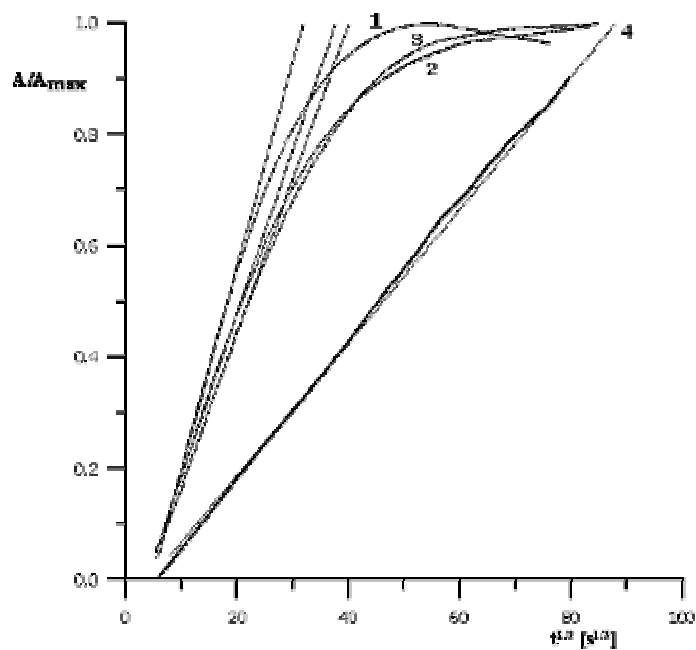


Fig. 3. Absorbance changes in relation to absorbance in the equilibrium state in time function for membranes in Figure 2.

Tab. 1. Ions Zn(II) diffusion coefficients in different thickness polymer membranes.

Membrane Number	Membrane thickness [cm]	$\text{tg}\alpha$	Diffusion coefficient D [$\text{cm}^2/\text{s}^{-1}$]
1	0.013	0.03210	3.41×10^{-8}
2	0.015	0.02685	3.18×10^{-8}
3	0.016	0.02586	3.36×10^{-8}
4	0.035	0.01151	3.18×10^{-8}

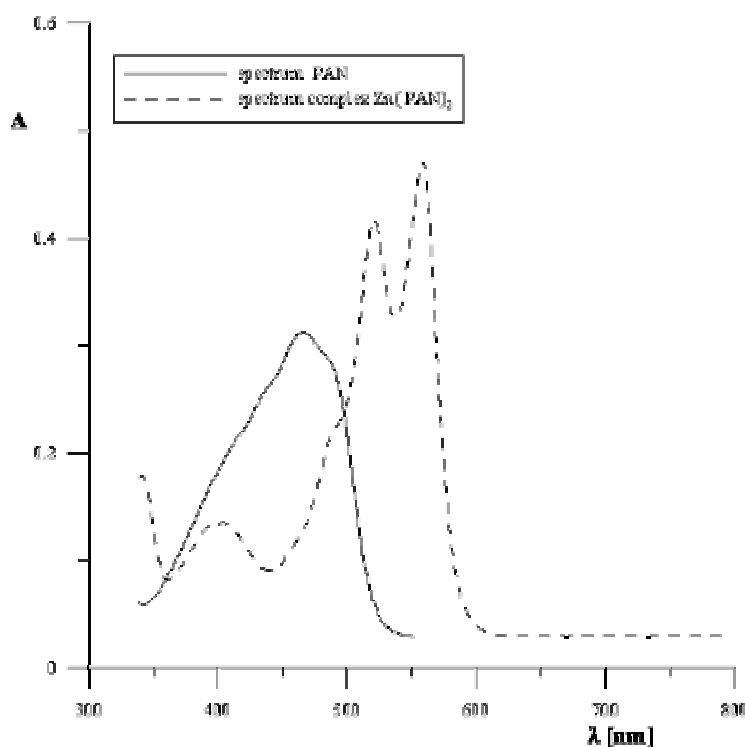


Fig. 4. Absorption spectrum of PAN and of its complex with zinc.

5. CONCLUSION

Results of investigations:

- Zinc ions diffusion coefficient was determined in polymer membrane with composition of 0.12% complex-forming agent, 32.88% PVC and 67% TEHP
- By using PAN as complex-creative active ingredient which forms colorful chelate complex with Zn(II), spectrophotometric measurements of zinc ions changes in membrane were possible
- Membranes of different thickness (0.013-0.035 cm) were investigated and the obtained results were similar
- The medium zinc ions diffusion coefficient in PVC membrane with TEHP was calculated to be $3.28 \times 10^{-8} \text{ cm}^2/\text{s}^{-1}$
- In different polymer membranes diffusion coefficients of cations are 10^{-6} - $10^{-10} \text{ cm}^2/\text{s}^{-1}$ [12-14].

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