

# Investigation of Copper and Manganese Ion Diffusion through Hydrogel Contact Lens Materials Using ESR Technique

Katarzyna Krysztofiak, Andrzej Szczyzewski\*, Zdzisław Kruczyński

Division of Medical Physics, Department of Physics, A. Mickiewicz University in Poznań,  
Umultowska 85, 61-614 Poznań, Poland

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## Abstract

Diffusion of tear film components through a hydrogel contact lens is significantly influenced by its interactions with material. In our study  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions were used to describe transport properties of the membranes which were hydrogel contact lens materials. Ion concentrations were measured by an electron spin resonance (ESR) spectrometer, and differential scanning calorimetry (DSC) was used as a complementary technique. The materials investigated were nelfilcon A and etafilcon A. Diffusion  $D$  and permeation  $P$  coefficients were calculated. In both materials transport dynamics can be described by two stages (except for  $\text{CuSO}_4$  in etafilcon A), where the first is shorter and characterized by higher diffusion  $D$  and permeation  $P$  coefficients than the second one. The results obtained allowed us to make conclusions about the interactions between the ions and polymer chains that may happen inside the hydrogel matrix during diffusion, affecting transport dynamics.

**Keywords:** hydrogel, copper, manganese, diffusion

## Introduction

Hydrogels are materials capable of swelling and retaining water without dissolving. Because of their unique physical properties, resembling body tissues, they have gained many biomedical applications [1, 2]. In optometry and ophthalmology hydrogels are used to produce contact lenses, artificial corneas, and substances replacing vitreous body. In contact lens production weakly cross-linked polymers with hydrophilic properties generally are used. Usually the basic monomer is 2-hydroxyethyl methacrylate (HEMA), with hydrophilic -OH groups. By changing the composition and proportions of monomers, a material of desired physical and chemical properties (e.g. water content, wettability, oxygen permeability, stiffness) can be synthesized.

Hydrogels have also a wide range of other biomedical applications, e.g. drug delivery systems, controlled-release fertilizers, soft-tissue substitutes, cell culture substrates [1, 2]. Sorption and diffusion are very important in heavy metal ion detection or their extraction (waste water purification) and in fresh water desalination [3-5]. Therefore, it was also a reason for this study to answer the question whether hydrogels (such as contact lens polymers) may be useful in protecting the environment. Heavy metal pollution has in recent years become one of the most important environmental problems. They accumulate in the environment, are not biodegradable, and pose a threat to human health. Lately, diffusion of ions through the hydrogel membranes has become a phenomenon often used for measurement methods in environmental chemistry, allowing to determine the diffusion coefficient of individual ion characteristics, e.g. diffusive equilibration in thin films (DET)

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\*e-mail: aszy@amu.edu.pl

and diffusive gradients in thin films (DGT) [6, 7]. Diffusion is also widely examined in terms of the transport of trace metals through permeation liquid membranes [8].

One of the most important properties of hydrogels is its equivalent water content (EWC), defined as the total weight of water over total weight of hydrated material. Water, which is an integral part of hydrogel, influences its mechanical properties as well as transport characteristics [9, 10]. In hydrogel contact lenses the existence of a homogeneous aqueous phase determines the oxygen permeability and affects other parameters of these materials, e.g. pore structure or diameter in different environments.

For characterization of transport phenomena A. Fick has formulated the following equation describing diffusion [11, 12]:

$$J = -D \frac{dc}{dx} \quad (1)$$

...where  $D$  – diffusion coefficient,  $dc/dx$  – gradient of concentration, which stimulates diffusion. The observed flow of dissolved substance leads to concentration compensation, so the diffusion rate decreases. The diffusion coefficient  $D$  depends on the system, i.e. on the type of solvent and dissolved substance, concentration, and temperature.

The special case of transport phenomena is diffusion through the membrane. Consider a vessel with two compartments containing liquids differing in concentrations  $c_1 > c_2$  separated with permeable membrane of thickness  $dx$ . In this case Fick's law can be written as follows:

$$\frac{dn}{dt} = -DS \frac{dc}{dx} = -\frac{D}{dx} S(c_1 - c_2) = -PS(c_1 - c_2) \quad (2)$$

...where  $P$  – permeation coefficient,  $c_1$  and  $c_2$  – concentrations on both sides of membrane.

Since the cornea is almost deprived of blood supply, to maintain normal corneal metabolism it is necessary for contact lens material to be permeable for oxygen. Appropriate water and ion permeability is required to maintain adequate on-eye mobility of the lens and to reduce dehydration [13]. Additionally, for hydrogel contact lenses oxygen transport depends strongly on water content.

As mentioned above, EWC is very important for transport behavior of hydrogel materials. However, it is the water structure that decides on diffusion through the lenses [10]. According to Pedley and Tighe [14], in the hydrogel matrix there are three types of water: tightly bound, loosely bound, and free (bulk) water. Tightly bound water refers to the water molecules that strongly interact with polymer matrix. Loosely bound are those water molecules that interact with hydrogel polar groups to a much lesser extent. Free water refers to those water molecules that do not interact with the material at all. To distinguish between these three classes one can use the differential scanning calorimetry (DSC) method, where bulk water is represented by all the molecules, which are freezing at the temperature of 0°C, loosely bound water – by those molecules, which are freezable at temperatures lower than 0°C, and tightly bound – by

Table 1. Parameters and of contact lenses studied.

Trade name	1 Day Acuvue Moist	Focus Dailies All Day Comfort
Material	Etafilcon A	Nelfilcon A
EWC	58%	69%
FDA Group	IV	II
Dk/t	25.5	26.5
Central thickness [mm]	0.084	0.1

molecules that do not freeze (or are able to freeze below -100°C) [13]. In the permeation studies the most important information is that since tightly and loosely bound water interact with polymer matrix, it is the amount of free water that decides about the diffusion through the hydrogel membrane.

## Experimental Procedures

### Contact Lens Hydrogels

In our study daily-wear hydrogel contact lenses 1 Day Acuvue Moist (Johnson&Johnson) and Focus Dailies All Day Comfort (CIBA Vision) were investigated. The most important parameters of the lenses used are summarized in Table 1.

Nelfilcon A (Focus Dailies) according to the U.S. Food and Drug Administration (FDA) belongs to group II, which means that it is a high-water content non-ionic material. Because of their high-water content, group II hydrogels have a tendency to adsorb proteins. However, FDA group IV hydrogels, i.e. etafilcon A (Acuvue Moist), because of their high water content and ionic properties, have even higher affinity to Nelfilcon A, which is a mixture of polyvinyl alcohol (PVA) partially acetalized with N-formethyl acrylamide [15]. The high water content of this material comes from the presence of hydroxyl and carbonyl groups, which attract polarized water molecules with their positive charge. Etafilcon A is a copolymer of 2-hydroxyethyl methacrylate (HEMA) and methacrylic acid (MAA) cross-linked with 1,1,1-trimethylol propane trimethacrylate (TMPTMA) and ethylene glycol trimethacrylate (EGDMA) [16]. An ionic way of binding water is due to the presence of MAA dissociating into hydrogen cations and acidic residues anions, which attract polar water molecules.

### Diffusion Procedure

To investigate diffusion through the contact lenses, the following paramagnetic salt solutions were prepared:  $\text{CuCl}_2$ ,  $\text{CuSO}_4$ ,  $\text{MnCl}_2$ ,  $\text{MnSO}_4$  each of 150 mM concentration. The purities of these compounds (Sigma-Aldrich) were as follows:  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot (99.999\%)$ , and  $\text{MnSO}_4 \cdot \text{H}_2\text{O} (\geq 99\%)$ .

To investigate the diffusion kinetics a device related to diffusion cell was invented, allowing the use of a contact lens as a membrane separating two 3.75 cm<sup>3</sup> vials containing liquids with different salt concentrations. Effective area of diffusion was 0.64 cm<sup>2</sup> and was fixed with diffusion cell construction. Experimental procedure was the same for all lenses studied. At first the bottom part of the device was filled with a given salt solution. Then the contact lens was placed onto the bottom vial. It was important to avoid air bubble formation and any leakage that could disturb the transport through the lens. After placing the upper part of the device on the contact lens it was flooded with distilled water (pure solute). The whole setup was left for a certain period of time, fixed with the conditions of investigation. Then the solution from the upper part was placed in a test-tube.

For all salt – material combinations after 30, 60, 120, 180, 360, and 540 minutes ESR spectrum of the solution collected from the upper vial was recorded. The experimental procedure was the same for all measurement points at which 2-5 measurements were made and each lens was used once. The differences in concentrations between the salt solution from the bottom and the samples collected from the upper vial were so small that the difference in concentrations coming from the experiment's duration was neglected.

To compare the diffusion rate for each combination of contact lens and the metal salt, the permeability  $P$  and diffusion  $D$  coefficients were calculated. The overall molar concentration of the solute in both vials together stays the same, thus:

$$c_1 = c_0 - c_2 \quad (3)$$

...where  $c_0$  is the concentration in bottom vial at time  $t = 0$ ,  $c_1$  – concentration in the bottom vial, and  $c_2$  – concentration in the upper vial at time  $t = t_1$ . Using laws of diffusion, ions concentration on both sides of the membrane has been determined.

The following expression (4) was used to estimate permeation coefficient  $P$ .

$$\operatorname{tg} \alpha = 2 \frac{SP}{V} \quad (4)$$

...where  $S$  is the effective area of diffusion and  $V$  is the volume of vials.  $\alpha$  is the slope of the diffusion curve (see the Results section). Additionally, using the equation  $P=D/dx$ , diffusion  $D$  coefficients were calculated. We assumed that the hydrogel layer is thin and equal as an approximation. The central thickness of -3.00 dptr lens given by the manufacturer was used as the membrane thickness  $dx$ .

### ESR Method

Concentrations of basic solutions and the solutions from the upper vial were recorded using electron spin resonance (ESR) spectroscopy. The ESR phenomenon involves the resonance absorption of microwaves by paramagnetic substances, i.e. those whose valence shells have at least one unpaired electron (for example free radicals or paramagnetic ions such as Cu<sup>2+</sup> or Mn<sup>2+</sup>).

ESR spectra were recorded at room temperature as the first derivatives of absorption using a Bruker EMX-10 EPR spectrometer operating at X-band (9.4 GHz) microwave frequency using 100 kHz field modulation. The following measurement conditions were used: modulation amplitude of 10 G, modulation frequency 100 kHz and microwave power 20 mW. The magnetic field was controlled by a digital NMR magnetometer.

The changes in ion concentrations were reflected in the changes in the intensity of the first resonance line. Signal intensity is proportional to the concentration of paramagnetic centers, thus for each salt the spectrum had always the same shape and the only difference was in the signal intensity, depending on the time of diffusion, i.e. on the amount of ions, which succeed in passing through the lens to the upper vial of the device.

### DSC Measurement

To establish the proportion of free and loosely bound water in the materials studied, DSC measurements of new lenses were conducted. DSC technique involves measurements of the heat flux between a reference and the sample studied while heating or cooling. The heat is delivered to the sample and the reference in such a way that the temperature of both of them is the same during the measurement. If the sample studied emits (or absorbs) more heat than the reference, a transition will be recorded on the calorimetric curve. The overall thermal effect of the transition observed can be calculated from the peak surface area on the DSC curve.

Before each DSC measurement the lenses were gently dried with blotting paper and cut into small pieces. The measurements were made on a DSC Q2000 (TA Instruments) in WLBS at the Adam Mickiewicz University Faculty of Physics.

### Additional Procedures

Additionally, pH of salt solutions was measured. Unlike the distilled water, all salt solutions were acidic, with pH ranging from 3.01 to 3.94.

Ionic strength  $\mu$  of the salt studied was calculated from the following equation:

$$\mu = \frac{1}{2} \sum c_i (z_i)^2 \quad (5)$$

...where  $c_i$  is the molar concentration of ion and  $z_i$  is the charge of that ion. Ionic strength tells about the activity of the ions in solution: the higher the ionic strength, the lower the activity.

### Results

Graphs showing  $\ln[c_0/(c_0-c_2)]$  as a function of time were drawn (Figs. 1-4; note that for a better illustration of diffusion kinetics, the curves are drawn in different scales) and

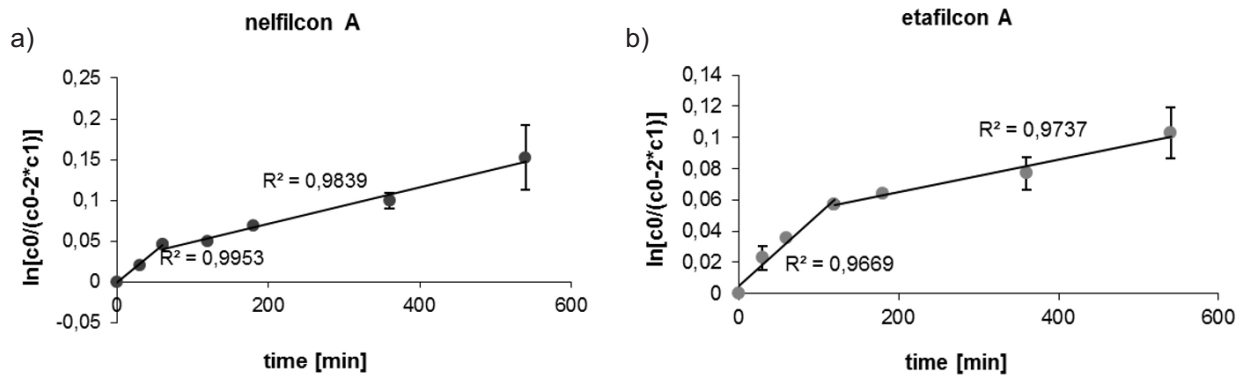


Fig. 1. Manganese cation diffusion through nelfilcon A (a) and etafilcon A (b) for  $MnCl_2$ .

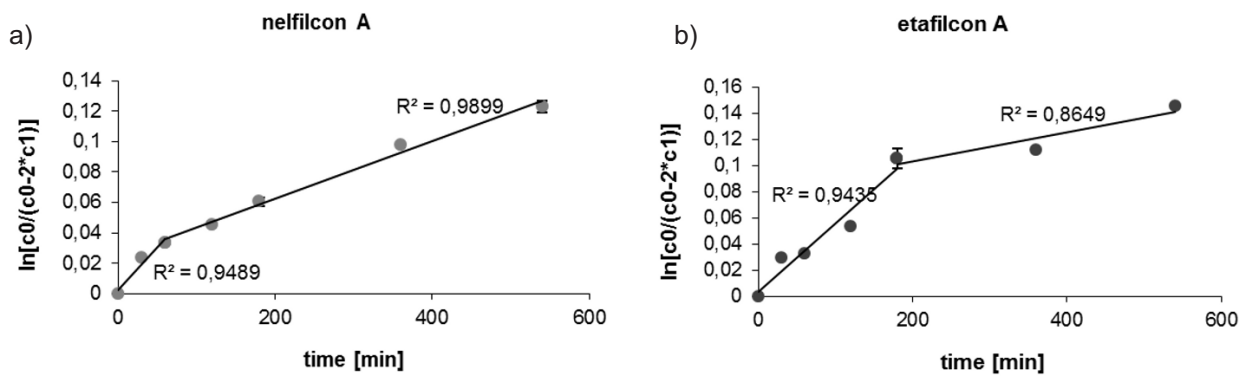


Fig. 2. Manganese cation diffusion through nelfilcon A (a) and etafilcon A (b) for  $MnSO_4$ .

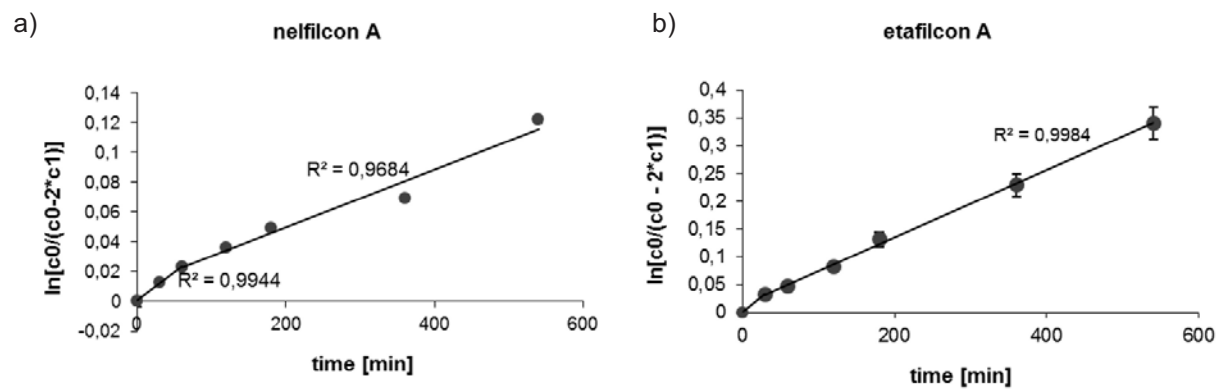


Fig. 3. Copper cation diffusion through nelfilcon A (a) and etafilcon A (b) for  $CuCl_2$ .

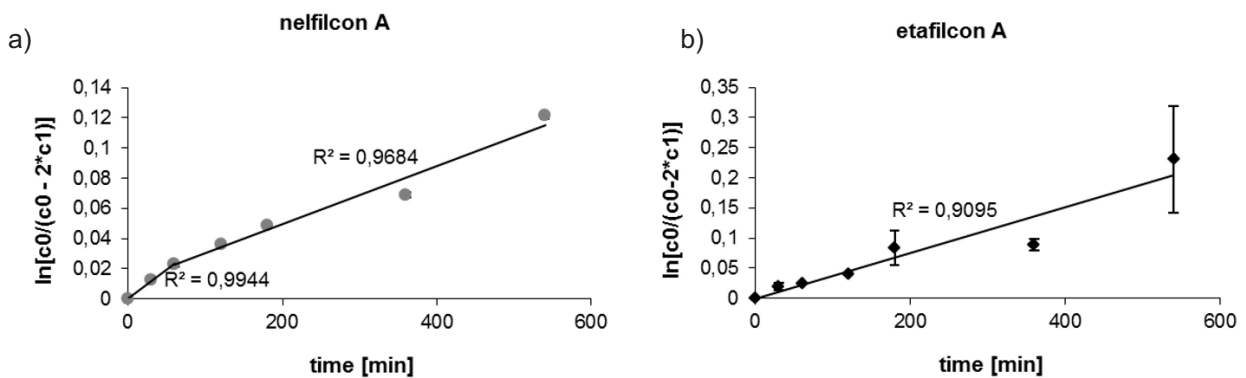


Fig. 4. Copper cation diffusion through nelfilcon A (a) and etafilcon A (b) for  $CuSO_4$ .

Table 2. P and D coefficients of  $\text{Cu}^{2+}$  calculated for  $\text{CuCl}_2$  salt (with division into stages).

	Time [min]	P [ $10^{-4}$ cm/s]	D [ $10^{-6}$ cm/s]
Nelfilcon A	0-60	10.08	10.08
	$\geq 60$	5.66	5.66
	mean	5.98	5.98
Etafilcon A	0-30	32.76	27.52
	$\geq 30$	17.73	14.89
	mean	18.05	15.10

Table 3. P and D coefficients of  $\text{Cu}^{2+}$  calculated for  $\text{CuSO}_4$  salt (with division into stages).

	Time [min]	P [ $10^{-4}$ cm/s]	D [ $10^{-6}$ cm/s]
Nelfilcon A	0-120	6.68	6.68
	$\geq 120$	2.78	2.78
	mean	3.53	3.53
Etafilcon A	mean	11.05	9.28

Table 4. P and D coefficients of  $\text{Mn}^{2+}$  calculated for  $\text{MnCl}_2$  salt (with division into stages).

	Time [min]	P [ $10^{-4}$ cm/s]	D [ $10^{-6}$ cm/s]
Nelfilcon A	0-60	22.28	22.28
	$\geq 60$	6.53	6.53
	mean	7.42	7.42
Etafilcon A	0-120	13.51	11.35
	$\geq 120$	3.06	2.79
	mean	4.77	4.01

for each one  $R^2$  and slope were calculated. The results obtained allow us to distinguish two ranges of time differing in diffusion rates (see Discussion). Knowing the setup geometry and the slope, it is possible from equation (4) to calculate permeability and diffusion coefficients (Tables 2-5). In Fig. 5 one can compare the diffusion rate of all samples studied. As seen, there are important differences among the materials and metal salts studied.

DSC thermograms are shown in Fig. 6. In DSC technique we can determine the amount of free and loosely bound water comparing the peak areas corresponding to the phase transition temperatures. The peak around  $0^\circ\text{C}$  refers to free water, and the second one corresponds to loosely bound water, engaged in weak interactions with a polymer that freezes at  $-5^\circ\text{C}$ . The main difference between the two hydrogels studied is the opposite proportion loosely bound to bulk water. Since both materials have high

Table 5. P and D coefficients of  $\text{Mn}^{2+}$  calculated for  $\text{MnSO}_4$  salt (with division into stages).

	Time [min]	P [ $10^{-4}$ cm/s]	D [ $10^{-6}$ cm/s]
Nelfilcon A	0-60	16.36	16.36
	$\geq 60$	5.55	5.55
	mean	6.23	6.23
Etafilcon A	0-180	15.43	12.96
	$\geq 180$	3.25	2.73
	mean	7.43	6.17

water content, the difference observed is probably due to the composition of these polymers (this issue will be discussed below).

## Discussion

### Diffusion Kinetics

The ESR method in studies of transport processes in contact lenses has been used previously by Özgür et al. [17, 18]. In the studies of diffusion of liquids [17] they have prepared contact lenses marked with spin label TEMPO and placed them in a multipurpose solution (used for cleaning and disinfection of contact lenses), which resulted in a gradual washout of labels from the hydrogel matrix. However, although they have used the term of diffusion, in fact the sorption and desorption processes were investigated. Preliminary results concerning the copper diffusion through contact lenses have been published previously in [19].

In the experimentally determined time dependence of  $\ln[c_0/(c_0-2\cdot c_2)]$ , three ranges of time corresponding to different diffusion rates were distinguished [17]. The first one (first 10-15 minutes) was characterized by a high diffusion coefficient, because the molecules could easily penetrate the material. In the second one (15-200 min.) a slowdown in diffusion was observed. For  $t > 200$  min, the diffusion rate increased.

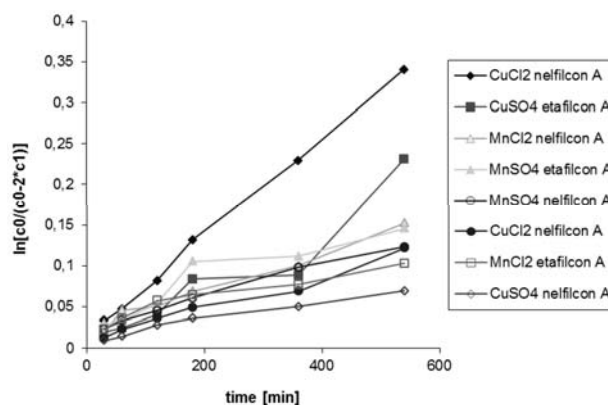


Fig. 5.  $\ln[c_0/(c_0-2\cdot c_2)]$  vs. time plotted for all combinations of salts and lenses studied.

Table 6. The calculated values of radius  $r$ , width of hydration shell  $\Delta r$ , and number of water molecules in this shell  $n$  [18].

Ion	$r$ [nm]	$\Delta r$ [nm]	$N$
$\text{Cu}^{2+}$	0.073	0.224	9.9
$\text{Mn}^{2+}$	0.083	0.203	8.7
$\text{SO}_4^{2-}$	0.230	0.043	3.1
$\text{Cl}^-$	0.181	0.043	2.0

In our study the main aim was to measure ion diffusion through the membranes, which were daily-wear hydrogel contact lenses. The results obtained allow us to distinguish two ranges of time differing in diffusion rates (Tables 2-5). Considering transport coefficients for each stage separately, one can see that in the first stage the diffusion rate is 2-3 times higher than that in the second stage (except for  $\text{MnSO}_4$  and etafilcon A, for which the difference is higher). In comparison with the duration of the first stage established in [17], the first stage in our experiment lasted much longer (30-180 minutes). This extension of the first stage duration is probably related to the fact that ions are much smaller (Table 6) than the spin labels (4-7Å). For this reason, as a result of the interactions between ions and the material, it was much later when the restricting diffusion buffer layer was formed. It seems to us that it was much easier for the ions to penetrate the hydrogel pores, even if some of them were stopped in the material. Thus, early time data reflects the time of achieving the steady state.

Forming a buffer layer on the hydrogel surface, which may restrict diffusion, was evidenced by the results obtained for metal cations ( $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ ) in the adsorption studies performed by Morandi et al. [20]. Moreover, as reported [5, 21] the process goes with the highest efficiency for the first 30-60 minutes from the starting point, then it slows down and stabilizes, similarly as it follows from our results for diffusion through lens materials.

Nevertheless, it is important to remember that in fact this model may be oversimplified. Another explanation of our results may be the non-linearity of the process of diffusion.

## Interactions between Ions and Hydrogel

Tables 2-5 show mean P and D data obtained from this experiment. Our results are in good accordance with the values in literature. Diffusion coefficients may be different in different media, e.g. in polyacrylamide  $4.53 \cdot 10^{-6}$  and  $4.26 \cdot 10^{-6}$  for copper and manganese ions, respectively [3]. In DGT gels it is  $6.25-6.6 \cdot 10^{-6}$  and  $5.1-6.4 \cdot 10^{-6}$  [4].

Table 6 shows the calculated values of ionic radius  $r$ , width of hydration shell  $\Delta r$  and number of water molecules in this shell  $n$  [22]. As seen, copper cation  $\text{Cu}^{2+}$  coordinates more water molecules and creates a thicker hydration layer than manganese cation  $\text{Mn}^{2+}$ , hence the former has a lower ability to form complexes with other substances. With the smaller charge chloride anions are also smaller than sulphate anions  $\text{SO}_4^{2-}$  and coordinate fewer water molecules. This may facilitate material penetration.

As is well known, to bind metal cations hydrogels must contain atoms that are electron donors (e.g. O or N). Among the monomers that can adsorb metals are acrylic acid, acrylate, sodium acrylate and others containing carboxylic acid (-COOH) groups. Thus, it is obvious that the interactions between cations and hydrogels are closely related to their chemical composition.

In the UV-VIS and IR absorption spectra studies [23] it was shown that metal cations form unstable complexes with PVP (polyvinyl pyrrolidone) as a result of the interaction between the oxygen of the carbonyl group and the metal cations. As mentioned earlier, hydroxyl and carbonyl groups determine the way in which water molecules could be bound to nelfilcon A. Complex formation of metal cations with these groups can cause with time a progressive decrease of diffusion. However, the hydroxyl and carbonyl groups allow the formation of weak metal complexes, while the interaction with carboxyl groups would be stronger. It is possible that this is the reason why the permeability and diffusion coefficients are generally lower for etafilcon A. This behaviour may be also explained in terms of different affinities of the lens material to various metal cations [24].

In the Rodriguez and Katima hydrogel swelling studies [25] it was suggested that the complexation of -COO-

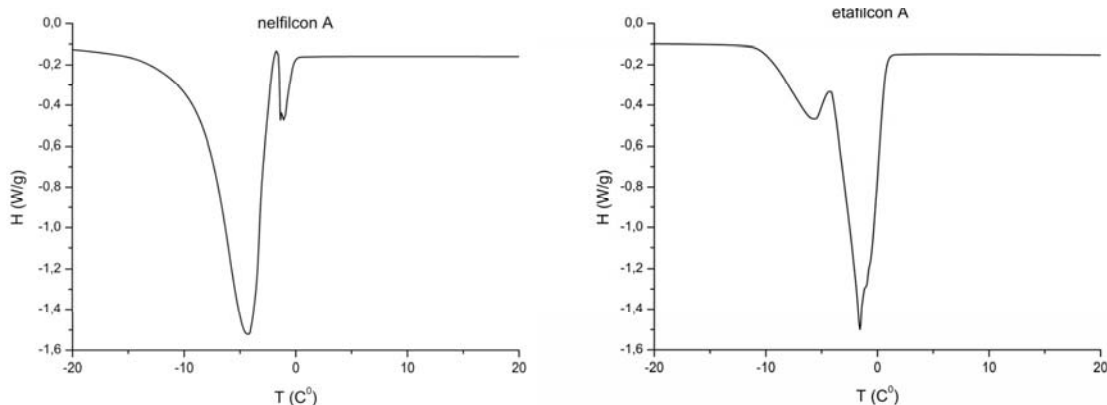


Fig. 6. DSC measurement of nelfilcon A (a) and etafilcon A (b) lenses – peak around  $0^\circ$  corresponds to free water, and the peak around  $-5^\circ$  is assigned to water loosely associated with the material.

groups with metal cations occurs. This may result in the formation of neutral  $-\text{COOMCOO}$  group, where M is a divalent metal cation. They have also found that hydrogel swelling was closely related to  $-\text{COO}-$  group selectivity for certain cations. This selectivity could explain the behaviour of etafilcon A, which is characterized by surprisingly low transport coefficients in combination with manganese cations.

El-Haag et al. [5] investigated PVP and AAc (acrylic acid) copolymers. As they claim, in the first hour of the experiment, metal ion chelation took place rapidly, then it slowed down and after eight hours the process stabilized. In other chelating polymer studies [26] the sorption was the highest in the first 20-30 minutes. It seems to us that the attachment of ions to the polymer chains can cause stiffening of the structure and a decrease in pore volume, reducing the diffusion rate. Hence two-step diffusion kinetics we observed might be a result of the process of chelation, which seems to have similar dynamics. Moreover, the chelates formed may reduce the amount of free water content in the material, further decreasing the diffusion rate. It has also been shown [21] that divalent cations such as  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$  can interact with MAA and form metal-polyacid complexes, involving two carboxylic acid groups on each ion over a wide pH range. On the basis of our results it appears that for etafilcon A, containing a certain amount of MAA, chelation may be stronger for  $\text{Mn}^{2+}$  than for  $\text{Cu}^{2+}$  ions, which probably stems from the fact that the hydration shell around the copper cations decreases their interaction with the lens material. The observed two stages of diffusion may be due to the chelation process, which seems to have similar, multi-step dynamics.

### Cation Effect

In their study on PVP and AAc copolymers, El-Haag and Shawky [5] have shown that the ability of adsorption decreased in the order:  $\text{Fe(III)} > \text{Cu(II)} > \text{Mn(II)}$ , which was in agreement with the relative size and crystal field radii of these ions. In the literature [20, 27] there is much evidence that cations with the smaller radii can diffuse more easily through hydrogel polymers. Indeed, we could observe a similar effect in non-ionic nelfilcon A, but for case of ionic etafilcon A it seemed to be reversed (see diffusion coefficients in Tables 2-5). This could be explained by the fact that copper cations have a higher affinity to coordinate water molecules leading to the formation of hydrated ions  $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ . It may facilitate diffusion, because the interaction between cation and polymer residues would be diminished by the hydration layer. On the other hand, it will significantly increase the ionic radius, impeding transport through tortuous pores of the hydrogel.

### Anion Effect

The study on a hydrogel based on ESA (etherificated sodium alginate), PVA, and NaAA (acrylic acid sodium) [24] has shown that the swelling ratio was higher if the solution contained sulphate anions  $\text{SO}_4^{2-}$  than for the  $\text{Cl}^-$

anions. An increase in swelling is equivalent to a decrease in diffusion, because it is related to the fact that ions, instead of passing through the material, stay inside the polymer matrix.

A similar effect was observed when comparing both copper salts investigated, where  $\text{Cu}^{2+}$  transport coefficients were higher in a solution containing smaller  $\text{Cl}^-$  ions than in that with sulphate ions. However, for manganese salts this effect was the opposite.

In another study [28] it was shown that in swelling of pHEMA the most important role, especially at low salt concentrations, is played by anions. They are adsorbed by polymer residues, there is repulsion between like-like charges resulting in chain expansion and increase in water sorption. This leads to diminishment in the hydrophobicity of polymer chains and then to electrostatic attraction of cations and their hydration layers. This kind of interaction may explain the behaviour of ionic etafilcon A. Smaller  $\text{Cl}^-$  anions surround themselves with fewer water molecules, similarly to  $\text{Mn}^{2+}$  cations, so for the  $\text{MnCl}_2$  salt the interaction between ions and polymer sites may be stronger. Thus, for this material transport coefficients are the lowest.

### Water Content

Materials studied belong to different FDA groups and the difference in water content between them is 9% (Table 1). According to the literature [13, 29, 30], the character of diffusion is determined not by the water content itself but by the amount of free (bulk) and loosely bound water. Our DSC measurements of new lenses showed that etafilcon A contains significantly more free water than nelfilcon A (Fig. 6). It is possible that this is the reason why the transport coefficients of the salts studied are generally lower for nelfilcon A (except for  $\text{MnCl}_2$ , where diffusion rate seems to be higher – see above).

Nonionic hydrogel nelfilcon A contains a certain amount of uncrosslinked PVA, whose gradual release from the lens during wearing has a positive effect on patient comfort [31]. The presence of hydrophilic PVA not associated with the polymer matrix of the lens seems to explain a higher content of loosely bound water. This in turn may contribute to the reduction of diffusion in comparison to etafilcon A in which the free to loosely bound water ratio is the opposite [13, 30].

### Ionic Strength

The ionic strength values of salt solutions examined have been calculated from eq. (5). The values obtained for copper sulphate and manganese sulphate are both 0.6 and are higher than for copper chloride and manganese chloride, both 0.45. Larner and Seen [32] have shown that in solutions with low ionic strength (relatively high activity) the diffusion increases. A similar effect is found in our experiment. Permeation and diffusion coefficients are generally higher for copper chloride and manganese chloride when compared to those for copper sulphate and manganese sulphate solutions.

## Conclusions

Our study has demonstrated the usefulness of ESR in combination with DSC methods in diffusion studies. These are complementary techniques that bring the information on the interactions that may take place inside the materials studied.

As follows from our results, cation transport through the hydrogel membrane has a two-step kinetics and in the first step the diffusion is 2-4 times faster than in the second one. The duration of the first stage may vary depending on the material composition and type of ions contained in the solution.

In general, the values of permeation and diffusion coefficients may be used to describe the strength of the interactions between ions and the polymer sites of the materials studied. As expected, the interactions between hydrogel and metal cations seem to be stronger for the ionic material etafilcon A. For the nonionic nelfilcon A, the diffusion is higher for smaller  $Mn^{2+}$  cations. A similar effect was observed when comparing anion radius and charge of both copper salts investigated.  $Cu^{2+}$  transport coefficients were higher in solution containing smaller  $Cl^-$  ions than for the sulphate solutions. As a result, the transport coefficients grow in the following order  $CuSO_4 < CuCl_2 < MnSO_4 < MnCl_2$ . For the ionic etafilcon A there is no such relation, probably due to the specific interactions of solution components with this material.

It is well known that bulk water content decides on the transport properties of hydrogel. This effect is especially visible for copper diffusion through the materials studied. As DSC measurements provided, in nelfilcon A there is much less free water than in etafilcon A. As has been shown with copper cations, this may result in a decrease in diffusion of e.g. some tear film components through the lens, affecting its on-eye performance. However, for smaller  $Mn^{2+}$  cations this effect is the opposite and less visible.

From the results obtained it appears that there are many factors affecting the diffusion behaviour in hydrogel contact lens materials. Among them are cation and anion effect, water content of the material, and its composition, and it is the composition that seems to have the strongest influence on transport properties. As follows, the use of hydrogel materials both for measuring ion concentrations (DGT, DET methods) and their removal from polluted waters should take into account previously analyzed composition of cations and anions. Especially the presence of the latter seems to have significant effect on the rate of diffusion of metal cations. It was demonstrated that in the study of metal ion diffusion (in particular  $Cu^{2+}$ ) the type of anions present must be taken into consideration, as they can have a significant effect on the rate of diffusion.

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