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Additional Information

Oxygen, water and sodium chloride transport in Soft Contact Lenses Materials

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Abstract

Oxygen permeability, diffusion coefficient of the sodium ions and water flux and permeability in different conventional hydrogel (Hy) and silicone-hydrogel (Si-Hy) contact lenses have been measured experimentally. The results showed that oxygen permeability and transmissibility requirements of the lens have been addressed through the use of siloxane containing hydrogels. In general, oxygen and sodium chloride permeability values increased with the water content of the lens but there was a percolation phenomenon from a given value of water uptake mainly in the Si-Hy lenses which appeared to be related with the differences between free water and bound water contents. The increase of ion permeability with water content did not follow a unique trend indicating a possible dependence of the chemical structure of the polymer and character ionic and non-ionic of the lens. Indeed, the salt permeability values for silicone hydrogel contact lenses were one order of magnitude below those of conventional hydrogel contact lenses, which can be explained by a diffusion of sodium ions occurring only through the hydrophilic channels. The increase of the ionic permeability in Si-Hy materials may be due to the confinement of ions in nanoscale water channels involving possible decreased degrees of freedom for diffusion of both water and ions. In general, ionic lenses presented values of ionic permeability and diffusivity higher than most non-ionic lenses. The tortuosity of the ionic lenses was lower than the non-ionic Si-Hy lenses. Frequency 55 and PureVision exhibited the highest water permeability and flux values and, these parameters were greater for ionic Si-Hy lenses than for ionic conventional hydrogel lenses.

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1. Introduction

Raw materials used in the preparation of soft contact lenses should give optically transparent films, with good chemical and thermal stability, suitable mechanical properties and low modulus of elasticity. Moreover, the lenses should be highly permeable to oxygen with enough water content to guarantee the wettability and delivery of ophthalmic drugs for an extended period of time ranging from weeks to months maintaining always the ocular health[1-5]. Hydrogel lenses are oxygen permeable since they contain certain quantities of water. Oxygen dissolves in the tear film within the lens and diffuses from the face of the lens in contact with the atmosphere to the other face in contact with the corneal surface. In this kind of lenses the oxygen permeability increase with the water content of the lens[6]. The incorporation of more hydrophilic monomers in order to increase the water content of the lens gives as result an increment of oxygen permeability but a decline of mechanical properties. In this sense, it is generally accepted that the conventional hydrogel contact lenses are not suitable for extended wear fundamentally due to limited oxygen transmissibility[1,2,7]. To meet these requirements, Silicone hydrogel (Si-Hy) materials have been introduced to design and synthesize new and improved contact lenses alternative to conventional hydrogel lenses (Hy) which can be worn continuously for large time periods even during sleeping [8-11]. Maximising the silicone component makes it possible to obtain lenses with high oxygen supply; however, the surface of the Si-Hy lenses is very hydrophobic generating a poor compatibility with the surface of the cornea and may even disrupt lens movement over the cornea (i.e. non-binding contact lenses)[12].

The transport of water and ions through contact lenses is crucial for the provision of essential nutrients and removal of waste products and debris. The water flow through the lens is also necessary for adequate on-eye lens movement, comfort and

wettability[13-16]. The diffusion of water through hydrogels, such as those constituting contact lenses, is a bidirectional process, where water diffuses from the corneal surface to the anterior contact lens surface where it evaporates into the open air and from the anterior surface to the post-lens space by osmotic pressure or lid stress. While the first process (permeation out) is undesirable, inducing lens dehydration, potential corneal desiccation and lens adherence, the water permeation in through hydrophilic soft contact lenses (SCL) is generally accepted to be a fundamental process needed to ensure an adequate post-lens tear film, lens movement and debris removal[1,12,17]. Changes in contact lens fitting parameters do not always demonstrate effectiveness on increasing post-lens tear mixing. To do so, it would be necessary to increase lens movement beyond a clinically acceptable level, increasing the risk of contact lens discomfort[18]. Accordingly, some authors have proposed the use of micro-channels and fenestrations to improve tear mixing. In fact these strategies have been already used with significant success by Weidemann et al[19] and Miller et al[20], respectively, in the research context, but they have not been clinically implemented yet.

Water or salts can move across a hydrogel lens through two mechanisms called bulk flow and diffusion. Bulk flow consists on the movement of water molecules through pores in the lens when a difference in hydrostatic pressure is present across the contact lens. Conversely, in the diffusion mechanism, water or salt molecules move by diffusive permeability which depends on the solubility of the permeating substance in the bulk of the lens and its diffusion coefficient. This process is governed by thermodynamic activity which depends on the difference in water activity (relative humidity) at both sides of the membrane. Under this condition, the water pervaporates through the lens, and it is the main mechanism responsible for water permeation through silicone rubbers materials. Pervaporation is a phenomenon of high clinical significance in contact lens wear. During pervaporation through contact lenses, the water contained behind the contact lens, permeates and evaporates at the front lens surface where the water activity in the surrounding air is below 100%[21]. In such cases the lens produce adherence to the corneal surface, but this is not the general case for hydrogel lenses based in p-HEMA[22] . In biphasic co-continuous silicone hydrogel materials used for extended-wear contact lenses, the oxygen and fluid permeability are "uncoupled" allowing a much greater level of hydraulic and ionic permeability than that available through a poly-HEMA with an equivalent water content[23,24]. As a result, lenses made

from this material display adequate lens movement while still benefiting from the additional oxygen permeability afforded with a water content of about 24%. In the case of the Balafilcon A material, a water content of 36% provides a hydraulic permeability which actually corresponds with that normally offered by a lens with 40% water content. This suggests that there might also be some degree of phase separation of the material[15,25].

Austin et al.[11] have stated that conventional non-silicone polymers would require a equilibrium water content (EWC) of about 38% to maintain on-eye movement. Nevertheless is still under study to determine just how water and ion permeability affect the ability of a lens to move on the eye. However, there are reports of silicon hydrogel lenses with lower EWC (from 24-38%) for overnight wear, which have shown satisfactory on-eye movement and on-eye performance, only when produced in controlled conditions. In addition, sodium ion permeability coupled with continuous aqueous pathways across the contact lens has been indicated as a prerequisite for on-eye movement (avoid binding)[1, 9, 12, 17].

There are different techniques to measure the salt and water transport through hydrogels membranes. Most of them are based on Fick's law and the solution-diffusion model, where the diffusion coefficient of the solute in a membrane can be determined from the pseudo-steady state permeation rate, time-lag method, and concentration profiles within the membrane in the transient and pseudo-steady states[2,13,26-29].

The present study was conducted to determine the oxygen permeability and diffusion coefficients following the electrochemical technique previously used[10]. The NaCl permeability, diffusivity and partition coefficient was determined using an experimental set-up that involved the use of a cell containing the lens under study separated by two chambers, the donor chamber and the receiving chamber. On the other hand, water flux and permeability, of two different series of commercially available hydrogel contact lenses (seven conventional hydrogel lenses and seven siloxane-hydrogel contact lenses (Si-Hy)). The results have been interpreted by means of the free volume theory, using the equilibrium water content (EWC) to estimate the free volume, as suggested by Yasuda et al.[12,30,31] The second objective of this study was to correlate the water flux with the ionic permeability and EWC to check whether this parameter

meets the levels that potentially promote the formation of a post-lens tear film and maintain lens motion.

2. Experimental

Commercial contact lenses (silicone hydrogel lenses and conventional hydrogel lenses) with the same optical power of 3.00 Diopters, all of them used in the international market, were studied in this work. Their names, material type, equilibrium water content (EWC), dimensions and oxygen mass transport properties are detailed in table 1. As can be seen, the equilibrium water content (EWC) varied from 24 to 48% for silicone hydrogel materials and from 55 to 69% for conventional hydrogel materials.

As some materials experienced dimensional changes when transferred from saline to ultrapure water (particularly significant in ionic materials), lens thickness was measured immediately after extraction from the original containers where they were stored in saline solution (0.9% NaCl) and after removal of the salt. To do this, after removal from the packaging, lenses underwent repeated washing processes to remove solutes from the material by being stored in ultrapure water (conductivity below 1 μS) for 20 minutes each time until the solution where the lens was stored showed a conductivity inferior to 0.01 mS. Three repeated processes were usually enough to fulfil this condition. The thickness of the lenses was measured with a Redher ET10 gauge (Rehder Developments, CA), where the average value of 5 measurements obtained across the central 8 mm of the lens (harmonic central thickness or T_{av}) has been calculated with a precision of $\pm 2\mu m$. The actual harmonic thickness of the lens over the central 8 mm was measured also right after their extraction from the original containers (in saline solution). These data are collected in the two last columns of table 1.

TABLE 1

2.1. Differential Scanning Calorimetry measurements (DSC)

DSC measurements were obtained from -60 to 10ºC at 10K·min^{-1} under a nitrogen atmosphere (Mettler Toledo DSC). Two heating and cooling runs were performed, the first heating and cooling to remove the thermal history of the samples, and the second heating and cooling runs to characterize freezing of sorbed water. In each measurement, the lens was previously equilibrated with a saline solution of 0.9%

during 24 hours. Then, the lens was lightly blotted with filter paper to remove surface water, placed into aluminium containers, quickly weighed, encapsulated and immediately placed in the DSC equipment.

2.2. Oxygen permeability measurements

Oxygen transport in some of the conventional and silicon hydrogel contact lenses selected in this study (Acuvue Oasys, Biofinity, PureVision, Avaira, Proclear, Acuvue2) was analysed previously[10,32-38]. For the other lenses (Air Optix N&D, Air Optix, Acuvue Advance, Focus Daylies, Proclear One-day, Soflens One-day and Frequency 55) the oxygen permeability and diffusion coefficients were obtained following the electrochemical technique described previously by Aiba et al.[31] for polymeric membranes, utilizing a permeometer model 201T (Rherder Development Co.). In brief, the apparent oxygen permeability of the lenses materials is determined from the measurement of the electric current generated at the electrode as consequence of the reduction process of oxygen that has passed through the lens. In the steady state conditions, the apparent permeability (P) can be obtained from equation[36]

$$P = I_\infty \frac{T_{av}}{n \cdot A \cdot F \cdot \Delta p} \qquad (1)$$

Where I_∞ represent the current intensity at the steady state conditions (t→∞), T_{av} is the harmonic thickness of the lens, n is the number of electrons exchanged in the cathodic reaction (n=4), F, the Faraday constant, A, the area of the cathode and Δp is the oxygen partial pressure difference across the lens at sea level (~155 mmHg).

The apparent oxygen diffusion can be obtained as

$$D = \frac{I_\infty \cdot T_{av}^2}{6(I_\infty \cdot t - Q(t))} \qquad (2)$$

Where $Q(t)$ is the total charge transferred to the cathode as consequence of the oxygen reduction process from t=0 until the system reaches the stationary state and t the total elapsed time.

2.3. Ion permeability measurements

The ionic permeability of the lenses has been determined following the experimental procedure described elsewhere[39]. In brief, the lens was fixed to the inferior

end of the lens holder cell and a cover lid locked the lens in position leaving a circular aperture of 8 mm in diameter that was immersed in the receptor chamber containing 60 mL of ultrapure water (milli-Q). The inner part of the lens holder cell acted as donor chamber (A) filled with 16 ml of 1M NaCl solution ($c_{L,0}$). The receiving chamber was situated on a heating plate to maintain the temperature of the system at 35 ± 1 °C. The receiving chamber is also well stirred to distribute homogenously the salt concentration ($c_R(t)$) and the chamber temperature. The conductivity of the solution in the receiving chamber (B) was monitored at regular intervals and until steady state conditions by a Crison CM-35 conductivity-meter with temperature sensor. Previously, a calibration curve was obtained by measuring in successive steps the conductivity of deionised water and solutions of 10^{-5}, 5×10^{-5}, 10^{-4}, 5×10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M NaCl. The conductivity of each solution was measured with the electrode and its values were plotted for each concentration to obtain the calibration curve with a correlation coefficient of 0.9999. A value of 0.00065 mS corresponding to the background conductivity of our Milli-Q water was subtracted from all the conductivity values obtained. From the calibration curve, the concentration of sodium ions in the measurement cell can be obtained and considering that $c_L(t) >> c_R(t)$ and therefore $c_L(t) \approx c_{L,0}$, as it happens in these experiments, apparent permeability of ions,(P_s), can be obtained as[39]

$$P_s = \frac{V_R \cdot T_{av}}{A \cdot c_{L,0}} m \qquad (3)$$

being $c_{L,0}$ the initial concentration of salt in the donor chamber (A) and m the slope of the concentration rate ($\frac{dc_R}{dt}$) in the receiving chamber at steady state. A complete description showing the obtaining of eq. (3) is well developed in reference[39].

2.4. Water vapor permeability (WVP) .test

WVP tests were carried out by exposing the lenses to several humidity gradients with a procedure based on the ISO 2528 standard. 125 mL thermoformed PP/EVOH/PP cups (RPC Envases, Madrid, Spain) with a circular open top of 82 mm and a 6 mm wide thermo sealing annulus were filled with 90 mL of distilled water to maintain a constant 100% RH inside the cup.

The lenses were removed from the original container, water excess drained with filter paper and immediately sandwiched between two self-adhesive aluminum masks (Miarco, Valencia, Spain) with a central 4 mm perforation (12,57 mm^2 permeation area). This mask was then used as cup cover to constitute the permeation cell. Samples were stored at 23ºC and constant humidity in desiccators containing salt solutions: potassium acetate (23 % RH), magnesium nitrate (53 % RH), or sodium chloride (75 % RH). The cups were weighed daily, and the plot of the weight increment vs. time provided the water vapor transmission rate.

3. **Results**

3.1. DSC results

Figures 1 and 2 show second heating and cooling DSC thermograms for four Si-Hy and four conventional hydrogels contact lenses used in this study, respectively. For Si-Hy contact lenses, an endothermic peak centred at about -2ºC that complete the fusion above 1ºC and an exothermic peak centred at about -25ºC corresponding to water freezing were observed, with the exception of: Acuvue Advance lens whose thermogram presented two endothermic features at about -2ºC and -10ºC, whilst the freezing feature is broader; and PureVision lens whose thermogram apparently presented no first-order transition assigned to water freezing at low temperatures, so that the solidification is nearly continuous. This behavior might be associated both, to the presence of pores which are larger than in the other lens and the character ionic of this lens in comparison with the others non-ionic Si-Hy lenses.

FIGURE 1

FIGURE 2

In the case of conventional hydrogel lenses, a single and broad freezing exothermic peak centred at about -22ºC and two peaks from the heating cycle, one sharp peak (peak 1) that complete the fusion above 2ºC and another broad peak (peak 2) at about -10ºC were observed. This behavior might be related to the interaction of the hydrogel polymer with water. According to Tassaka et al.[40], in endothermic DSC curves, the acute peak 1 corresponds to the free water and wide peak 2 corresponds to water molecules with partially restricted movement due to the presence of fixed charges, that is, loosely bound water.

From figures 1 and 2, the area of each peak was estimated from the difference between the endotherm curve and the straight baseline drawn in each figure, using the DSC computer program. Assuming that the heat of fusion for pure water is 340.6 J/g (79.72 cal/g), the concentration of water assigned to peaks 1 and 2 have been estimated by mean of the expression[41,42]

$$C = \frac{\Delta H_{tr}}{m} \frac{1}{\Delta H_f} \cdot 10^6 \qquad\qquad (4)$$

Where C is the concentration of water (µg/g), ΔH_{tr} is the heat of transition (mJ), m is the sample weight (mg), ΔH_f is the heat fusion of water (340.6J/g). To determine the heat of transition, we have taking into account that $\Delta H_{tr}= A \cdot B \cdot E \cdot \Delta q_s$; being A the peak area (cm^2), B the time base (min/cm), E is the cell calibration coefficient (mW/mV) and Δq_s the sensitivity in Y-axis (mV/cm). The results calculated from figures 1 and 2 are shown in table 2, where the corresponding values for free and confined water are tabulated.

TABLE 2

From the results shown in table 2, it can be observed that the transition time interval ΔT_m is wider for the Si-Hy lenses than for the conventional hydrogel. This is indicative that the pore size was greater in the Si-Hy than in Hy lenses. As an extreme case, the DSC analysis of PureVision lens appears to reveal that the first-order transition corresponding to water melting/freezing was nearly continuous and this may be explained by the presence of pores larger than those present in other lenses as previously reported by A. Lopez-Alemany et al.[25].

A comparison between conventional hydrogel and silicone hydrogel lenses shows that the water content occluded in the pores is quite similar for all hydrogel lenses. On the contrary, the Si-Hy lenses presented greater diversity of values and the average content is lower than that for the hydrogels. Indeed, we have observed that the percentage of non-bulk water in Acuvue2 lenses is 1.6-fold that of PureVision lenses and 2.4-fold that of Air Optix. One explanation for this phenomenon may be that not all hydrophobic pores contain water, reducing the percentage of confined water. Another possible justification is that water solidifies co-continuously within the hydrophobic pore as free water does, this possibility being more plausible in lenses such as PureVision or Air Optix which contain large pores. This fact is compatible with the theory of gas diffusion

through non-aqueous porous structures that increases the oxygen diffusion performance of these materials compared to conventional hydrogels where oxygen only flows through the aqueous phases[25].

As can be seen from the last column of table 2, the confined water or bound water largely varies between samples, from 10% to 46%. The lenses Proclear1–day, Soflens One-day, Frequency 55 and Acuvue2 (the conventional hydrogel lenses) have higher confined water or bound water percentages than Air Optix N&D, Air Optix and PureVision, between 3 to 4 times higher. This water portion is related to the amount of water which strongly interacts with the polymer and, therefore, it does not presumably participate in the transport of ions, solutes or gases. As can be seen, low-ECW hydrogels have as well low confined water ratios. A comparison between the hydrogel lenses shows that ionic lenses such as Frequency 55 and Acuvue2 have higher free water content than non-ionic hydrogel lenses. However, the opposite happens for the confined water, where the ionic lens has around 10% less than non-ionic lenses.

3.2. Oxygen permeability

The values of both permeability and diffusion coefficients can be readily determined from the time evolution of current intensity monitored in the permeometer by means of equations (1) and (2), respectively. In this study, the diffusion resistance of the solution layer separating the membrane from the electrode has not been considered, for that reason the permeation measurements includes the contribution of the membrane (lens) and this just commented thin solution layer. Since eq. (1) does not take into account the resistance to oxygen transmission of the liquid boundary layers between the lens and the cathode and over the lens, the results obtained for P and D with this experimental device are apparent values. To obtain the true permeability it is necessary to carried out alternative experimental procedures[35,36]. In this study, the uncertainty involved in the diffusive parameters due to the resistance of the layer is negligible compared to the resistance of the lens, and so it is its contribution to mass transport.

Studies carried out on hydrogels used as contact lenses have shown that the absorption-diffusion mechanism is basically controlled by the hydrogel[38]. The results found for the apparent oxygen permeability and diffusion coefficient measured in this study for the Air Optix N&D, Air Optix, Acuvue Advance, Focus dailies, Proclear One-day, Soflens One-day and Frequency 55, are presented in Table 1, together with those previously measured and reported elsewhere[26].

The values obtained for the oxygen permeability of conventional hydrogel and siloxane hydrogel lenses are in good agreement with those claimed by lens manufacturers (within 10% to 20% range) and with those measured by others researchers (within 3% to 15% range) [26,34-38,43]. This accordance with other procedures and experimental setups corroborates the validity of the method used in this work to measure P and D. As expected, the oxygen permeabilities for Hy lenses increased with increasing water content, because the water phase is the main responsible for the oxygen transmissibility. However, this correlation between oxygen permeability and water content was not observed for Si-Hy lenses. For example, a comparison between Biofinity (48% of EWC) and Acuvue Advance (47% of EWC) shows that the permeability of Biofinity is more than double that Acuvue Advance lens. The transmissibilities of Si-Hy lenses were practically five times higher than Hy lenses, with the exception of Avaira and Acuvue Advance where the differences were only 2-3 folds. It is known that the incorporation of bulky polysiloxane containing monomers to replace the poly-dimethyl siloxane (PDMS) macromers has been the strategy to maintain or increase the oxygen permeability and to reduce the crosslinking density[44]. From the values of the apparent permeability and taking into account the thicknesses of lenses, the transmissibilities of the lenses can be estimated. These calculations showed that only Acuvue Oasys (122 ± 6) barrer/cm, Air Optix N&D (116 ± 5) barrer/cm, Air Optix (114 ± 5) barrer/cm, Biofinity (139 ± 6) barrer/cm and PureVision (101 ± 4) barrer/cm have values above the critical value for the oxygen transmissibility (87.0 ± 3.3 barrer/cm) and equivalent oxygen percentage (EOP) of 17.9% established by Holden and Mertz for extended wear contact lenses[45]. The other lenses have lower values than this criterion and, therefore, they cannot be recommended for sleeping overnight because the low oxygen tension at the interface cornea-tears-lens (below 74 mmHg, the minimum pressure necessary to prevent corneal swelling) [46] could cause corneal swelling.

3.3. Ionic conductivity results

Though ionic diffusion in polymeric membranes is not a well understood phenomenon, this process presumably involves: 1) dissociation of the ions from the salt; 2) transference of the anion and cation to the aqueous medium, and finally, 3) diffusion of the ions in the confined water within the polymer matrix. Therefore, ionic mobility

depends on water flux which is a critical parameter together with the water uptake by the lens.

Prior to determine the ionic conductivity of lenses at 35ºC, a calibration curve of conductivity vs. NaCl concentration was prepared. A linear correlation was obtained with a slope of 107.1±0.7 mS. Making use of this calibration, the behaviour of the Na^+ concentration as a function of time was monitored. The results are shown in figures 3 and 4 for conventional hydrogels and Si-Hy lenses, respectively. From the slopes obtained for each lens, the NaCl apparent permeability coefficient values, P_s, were calculated by means of eq. (3) and the results are listed in table 3, where P_s ($P_s=D_mk_m$) represent the product of NaCl diffusivity (D_m) obtained by time-lag method and salt partition coefficient (k_m) of the lens. Both coefficients are also included in table 3 for all studied lenses.

FIGURE 3

FIGURE 4

TABLE 3

The values shown in table 3 for conventional hydrogel lenses, are in reasonable agreement with previously reported data on methacrylate hydrogels by Yasuda et al.[30,31] and with the values obtained by Hao Ju et al. for poly(ethylene oxide) hydrogels[12]. A close inspection of table 3 shows that the salt apparent permeability varies almost one order of magnitude among conventional hydrogel contact lenses and Si-Hy lenses. Considering the value of Na^+ self-diffusion coefficient in pure water[47] (ca. $2.089x10^{-5}$ cm^2/s), the tortuosity of the material composing the lens can be estimated according to the relation[6]

$$\tau = \sqrt{\frac{D_0}{D}} \qquad\qquad (5)$$

The estimated τ-values are collected in table 3. In general, the expected tortuosity decrease with increasing water content was observed for conventional hydrogels. These values are indicative that Acuvue Oasys, Air Optix N&D and Air Optix lenses have greater tortuosity in their channels than the other lenses, Acuvue Advance and

Purevision lenses presenting the lowest values. In studies of ion permeability for different contact lenses as a function of Vitamin E concentration, Cheng-Chun Peng et al.[48] found a similar behaviour. Indeed, the decrease in ion permeability was related to the increase of the loading of Vitamin E in all the lenses. The present study shows that the tortuosity is much greater for Acuvue Oasys than for other lenses such as Air Optix and Optix Night&Day and, therefore, the decrease in ion permeability by the addition of Vitamin E would be even more significant. Hence, our hypothesis is that lenses such as Acuvue Advance and PureVision that provide also the highest values of Vitamin E and ion permeability than the other lenses because of their lesser tortuosity. Therefore these lenses would satisfy the critical parameter for the lens motion on the eye (according to Domscheke et al.[16] criterium) better than the others silicon hydrogel lenses. On the other hand, conventional hydrogel lenses would present similar response to the behaviour of the ion permeability of Vitamin E loaded in the lenses[48].

3.4.   Water permeability results

Water permeability has been analyzed to check for the correlation between water flux and water content and its relationship with the ionic transport through the lens, and this with the mobility of the lens on the cornea. The typical weight-loss evolution registered for the eight selected lenses at 23, 53 and 75% RH are shown in figures 5, 6 and 7. As can be seen from figures 5, 6 and 7, the mass loss and flow rate data presented linear corralations at the three RH tested. From their slopes, the steady state water flux (Flux), $Flux = \dfrac{dm}{A \cdot dt}$ were estimated, being *dm/dt* the slope of the plot of sample mass vs. time of storage and *A,* the surface area of the lens exposed to the permeation experiment.

FIGURE 5

FIGURE 6

FIGURE7

13

On the other hand, water permeability values were estimated for all the lenses and relative humidity gradients by dividing the Flux values by the experimental water pressure difference of the experiment, following the expression

$$P = \frac{Flux \cdot T_{av}}{p_w^0 (\frac{RH_i - RH_0}{100})} \tag{6}$$

where, p_w^o is the water pressure at saturation at the temperature of the experiment, and (RH_i-RH_o) is the difference in relative humidity between the internal and external atmospheres. The obtained values for the water Permeability and Flux are gathered in table 4. On the other hand, in figures 8 and 9, the water permeability values (P) and the experimental steady state water flux (Flux) are plotted for all samples and relative humidity gradients from 100% RH to 23, 53 and 75 %RH, respectively.

FIGURE 8

FIGURE 9

TABLE 4

A close inspection of figure 8 shows the same permeability patterns for all studied lenses. The permeability decreases as the RH of the test decreases. The plot of water flux values (Figure 9) shows the oposite profile, that is, the flow increases as the RH of the test decreases (and the humidity gradient decreases). This trend could be expected considering that the lower the RH at which the sample is exposed, the greater the humidity gradient across the lens which, at the end, is the driving force of the water transmission. From these two figures, it can be observed that Air Optix and PureVision presented the highest values of water flux and transmissibility despite these two lenses contained the lowest amounts of equilibrium water content of the Si-Hy lenses. On the other hand, water flux and permeability values of conventional hydrogel lenses are strongly correlated with water uptakes. These trends are reasonable since the materials of those lenses with high equilibrium water contents and high fluxes can have lower crosslinking densities, possibly due to longer chains of hydrophylic comonomers constituing the lenses.

4. **Discussion**

Table 3 shows the results of salt apparent permeability, diffusion coefficient, partition coefficient (i.e. solubility coefficient) and tortuosity for some of the lenses considered in this study, together with the equilibrium water content to better show parameters trends. As it can be seen, the apparent permeability and diffusion coefficient values for conventional hydrogel lenses are in general about one order of magnitude higher than those for Si-Hy lenses. Also, the diffusion coefficient values increased significantly with increasing lenses equilibrium water content (EWC). Sodium-chloride diffusive permeability is well above $2x10^{-7}$ cm^2/s for all lenses, value representing the critical limit to prevent lens adhesion to the epithelium and to enable lens movement during blinking[14]. These high values may be due to the confinement of water and ions in nano-scale channels involving decreased degrees of freedom for diffusion in comparison with Si-Hy lenses. The presence of this type of water molecules has also been observed from DSC studies, which results has been plotted in figures 1 and 2 and the values of free and confined water collected in table 2. On the other hand, the pores in the hydrophobic phase present tortuosity values between 3-5 times higher than in hydrogel conventional lenses. Similar behaviour was observed for water confined in narrow cylindrical pores in carbon nanotubes (2-10 nm diameter), where a one-dimensionally ordered water layer is somewhat self-aligned to give an almost all-transzigzag arrangement[49]. Under this highly constricted condition, and taking into account that the water confined does not interact, or interact quite weakly with the surface, water diffusion is slower in hydrophobic channels than in bulk water, at least when lens is exposed to low HR% environments. This might be relevant in the behaviour of hydrogel and silicone hydrogel contact lenses as they are subjected to dehydration at the ocular surface[50-53], and particularly when the environmental conditions change[54,55].

A recent work published by Martín-Montañez et al[54] showed that among diverse conventional hydrogel and silicone hydrogel lenses, Comfilcon A was the lens with faster evaporation rates after exposure to extreme environmental conditions of low RH and high temperature. However, a comparison between Si-Hy lenses demonstrates that water flux and transmissibility values decrease when the EWC decreases. On the other hand, water confined within hydrophilic channels becomes more restricted than in hydrophobic ones due to stronger interactions between water molecules and pore walls, and thus, water diffusion decreases compared to its transport as bulk water. Therefore,

the nature and dimensions of the pores are important parameters for water and ion diffusion[49]. In this sense, water permeability values are lower for Si-Hy lenses than for Hy lenses, probably due to the tortuosity factor which is higher in the Si-Hy lenses than in conventional hydrogel lenses.

Pozuelo et al.[26] reported that, in general, the diffusion coefficients of water, Na^+ and Cl^- ions in conventional hydrogels were higher than in Si-Hy lenses and when the water content was above 25% and particularly above 35% where a percolation phenomenon was observed, presumably because of the critical balance of the hydrophilic and hydrophobic phases. In this way, when the diffusion of water through the lens is high, the diffusion of ions will also be high and therefore, a better physiological behaviour of the lens should be expected, in agreement with the present results.

Therefore, the ion diffusion has been shown to be critical for the metabolism of the cornea but also to warrant the on-eye movement of the lens and to improve the comfort. Besides greater comfort, it is expected that Si-Hy lenses with such content of water, as occurs with conventional hydrogels with these water contents (25-35%), may move in the eye and avoid the adherence to the cornea that had this type of lenses. In a clinical paper comparing the movement of five different soft contact lenses including two silicone hydrogel materials (Balafilcon A and Galyfilcon A) and three conventional hydrogels (Etafilcon A, Nelfilcon A and Hilafilcon B), Wolffsohn et al. showed that their ability to move on the eye with blinking was very similar irrespective of their different water content and the observed asymmetries in ion and water transmissibility obtained in our work[56]. This finding is in agreement with the fact that over a percolation point that is met by all the lenses evaluated, the lenses will allow the formation of a hydrodynamic post-lens tear film over which the lens can move pushed by the external forces of the eye such as blinking. Furthermore, this value needs to be maintained after the lenses are worn for several hours, days or months. This seems to be the case as shown in a recent paper published by our group that predicts a 30% reduction in the ionic permeability after one month of daily lens wear[39].

In principle, the salt permeability data should be correlated with water uptake measured in the presence of the same concentration of salt (0.1M). In figure 10 we plot the variation of the apparent permeability of NaCl as a function of the reciprocal of hydration (1/H), (H=(EWC)/100). However, in most of the samples, the equilibrium uptake was not affected by the presence of salt, as observed in table 1. Only Frequency

55 (Methafilcon) and Acuvue 2 (Ethafilcon A) lenses significantly modified their thicknesses with 114.8 and 116.6 μm in the presence of water whereas these values were about 106 and 104μm, respectively, in the presence of salt solution. These results can be related with the character ionic of Frequency 55 and Acuvue2 lenses in comparison with non-ionic hydrogel lenses.

FIGURE 10

As figure 10 shows, salt diffusivity (i.e. the Na^+ conductivity) increases with equilibrium water content of the polymer but this behavior is not linear or exponential. There are certain phenomena of percolation around 55% hydration with remarkable increase of conductivity with a hydration increase of only 5-10%. Finally, we can observe in figure 10, the asymptotic tendency from the 60% water in the sodium diffusivity, where the apparent diffusivity of the sodium ions was in the $40-66\times10^{-7}$ cm^2/s range. This is the case of the lenses Focus Dailies (Nelfilcon A) and Proclear One-day (Omafilcon A), Soflens One-day and Proclear, respectively. These values may possibly be related with the solubility of sodium in the polymer matrix of the lenses. Apparently, from a EWC of 70%, the value of the diffusivity tends to a constant value that may be related to the solubility of the salt in the polymer. Also this trend is pointing out that most of the hydrogel lenses show some selectivity for water over salt. Similar results has been presented by Sagle et al.[57] in their study of hydrogels copolymer synthesized using co-monomers of poly(ethylene glycol) diacrylate (PEGDA) as crosslinker and acrylic acid (AA), 2-hydroxyethyl acrylate (HEA) and poly(ethylene glycol) acrylate (PEGA).

Yasuda et al. [30,31] using the concept on the free volume theory, have proposed that water and salt diffusion coefficients through hydrogels can be interpreted as an exponential function of the reciprocal free volume function. Assuming that the free volume in hydrogels materials is proportional to their equilibrium water content (i.e. EWC), that water or salt diffusion is hindered by its polymeric network, and that the water molecules "bound" to it do not efficiently participate in diffusion, they reported that the salt apparent diffusion coefficient may be expressed as

$$\ln D_m = \ln D_0 - K(\frac{1}{H} - 1) \qquad (7)$$

where D_0 is the salt diffusion coefficient outside the membrane (i.e. in bulk solution). In this equation the salt is considered to be completely dissociated so that the salt apparent permeability P_s, is constant and independent of NaCl concentration. It is accepted that Na^+ and Cl^- ions diffuse with identical diffusion coefficient ($D_+=D_-=D_m$), where D_m represent the binary salt diffusivity, H is the hydration of the hydrogel which represents the volume fraction of water absorbed by the contact lens at equilibrium and K is a proportionality constant related to the characteristic volume required (v_f) for a molecule diffusing though the lens.

In conventional hydrogels we can express that $v_f = Hv_{f,water,}$, but in Si-Hy since the siloxane phase is very porous the relation should be function of the available volume in the Si-Hy phase. Then, the average free volume available in the polymer will be $v_f=Hv_{f,water}+(1-H)v_{f,polym,}$.

As can be seen in figure 10, the plotted results present significant deviations from the theory of Yasuda et al. [30,31]. The results do not show a clear linear relationship between the apparent diffusion coefficient and the reciprocal of the hydration. In solid line, the extrapolation for hydrogels membranes (HEMA 32.6%) and pure water have also been plotted. The intercept represents the diffusion coefficient of NaCl in pure water, about $D_0=2.089 \cdot 10^{-5}$ cm²/s at 35ºC[47]. This result confirms that salt diffusion occurs through the water phase of the lens. However, in the case of Si-Hy lenses, the transport through the free volume available in the polymer matrix (siloxane phase) can be relevant due to the chemical structure of the lens, as it is observed for the Acuvue Advance, PureVision and Biofinity lenses in which the diffusivity is 4 or 5 times higher than in Acuvue Oasys, Air Optix N&D, Air Optix and Avaira.

In the solution-diffusion model, the salt apparent permeability coefficient, P_{app}, depends on the product of the solubility of a penetrant in a polymer, k_m, times the effective diffusivity, D_m, of that penetrant through the polymer. Then, the eq(6) can be written as

$$\ln P_{app} = \ln k_m + \ln D_0 - K(\frac{1}{H}-1) \qquad (8)$$

The experimental natural logarithm of sodium chloride permeability data for these contact lenses is presented in figure 11 as a function of [(1-H)/H] where H is the equilibrium water content. A close inspection of this figure shows that the apparent permeability coefficient of Hydrogels and Si-Hy contact lenses is function not only of water content but also of the polymer chemical structure, because the free volume cavity

size determines the diffusion coefficient of penetrates, and controls the diffusion selectivity of one penetrant over another. Similar results have been obtained by other researchers[46]. From our experimental results, the value of apparent permeability in pure water from the extrapolation of permeabilities for all the lenses ($P_0 = D_0 k_m$) is 5.1×10^{-6} cm^2/s, and the value of parameter K of eq(7) is $K = 1.4 \pm 0.3$. This parameter is sensitive to the characteristic volume required for water or salt molecules to diffuse through the lens. From our studies we can conclude that Si-Hy lenses (which equilibrium water content was smaller than conventional Hydrogels) can present diffusion possibly due to water confined into the porous of the polymer matrix.

FIGURE 11

Salt partition coefficient, k_m, was also determined from experiments of permeation and time-lag method by mean of the relation ($P_s = D_m k_m$). Figure 12 plots the equilibrium partition coefficients versus the equilibrium water content at 35ºC for all the studied lenses. In general, the partition coefficients measured for conventional Hy and Si-Hy lenses were below the ideal partitioning line. Only, the Soflens One-day, Acuvue Oasys, PureVision and Avaira lenses have values of partition coefficient above this line or just in the line. This result is in good agreement with the data obtained through different experimental techniques by others researchers in similar contact lenses materials[5,9]. In general, Hydrogel contact lenses exhibited higher k_m values than Si-Hy contact lenses in accordance with their higher water content. This result is reasonable since the amount of salt sorbed by the material polymer network configuring the lens can, in some cases, be proportional to the equilibrium water content (EWC). If neither salt ions nor water interact with the polymer matrix, the partition coefficient tends to the value of the equilibrium water content, i.e. the saturated-water volume fraction in the lens[47]. In such situation, the parameter k_m and ECW present the same values, (k_m= EWC%). Figure 12 shows that Air Optix N&D, PureVision, Avaira and Focus Dailies lenses, have k_m values practically identical to their EWC values, and are situated practically in the ideal line.

FIGURE 12

Exceptionally, Acuvue Oasys and Biofinity lenses showed k_m values closed to those for hydrogels lenses. On the other hand, the Soflens One-day lens presented a much higher k_m value (0.78) than the others conventional hydrogel lenses (in the 0.52-0.55 range). The Frequency 55 lens showed the opposite behaviour, with a low k_m value of 0.44. Surprisingly, the behaviour exhibited by Frequency 55 could be related with the character ionic of this lens. This observation suggests that soft contact lenses with polymeric chemicals structures accompanied of ionic substituents should have lower k_m values, such as Guan et al.[5] confirmed applying Flory-Rehner-Donnan (FRD) theory.

Water transport through the lenses was measured at three humidity gradients considering that in the eye contact surface the humidity is near 100% and the external surface might be in contact with a humid (75%), an intermediate (53%) or a dry atmospheric environment (23% RH). The results collected in table 4 and plotted in figures 8 and 9 showed that the water transport was affected by humidity and by the lens tested. As figure 8 shows, the water flux through the lenses increases with the humidity gradient established across lens thickness, effect expected from the observation of Fick's first law at stationary state. These flux increased about 10% when air humidity decreases from 75 to 53%, and another 10% from 53 to 23%. Nevertheless, when mass transport was compared considering the humidity gradient, this is, when the parameter inspected is the water permeability (instead of the water flux) as it is plotted in Figure 9, the data profile changes dramatically. The water permeability values of all lenses measured with a 75%-100% gradient are much higher than those with a 53-100% gradient and these than the ones obtained with a 23-100% RH gradient. This observation has been often reported for hydrophilic polymer membranes and is a consequence of water swelling and polymer plasticization. The higher the humidity at which a hydrophilic polymer is exposed the higher the water sorbed in the polymeric matrix. This water swells polymer chains increasing the void volume through which water diffusion takes place and reducing the polymer intersegment interactions providing higher flexibility to polymer chains. When lenses are compared, the water permeability values are higher for conventional hydrogel lenses than for Si-hy ones at the three humidity gradients studied. However, water fluxes are within the same range due to differences in lens thickness which tend to compensate for differences in permeability. Considering the applicability of the solution-diffusion model, the water solubility values in the conventional lenses were higher (nearly double according to the EWC) than in silicone lenses. Since their water permeabilities did not double those of

silicone lenses, the water diffusivities in conventional lenses should be slower. This characteristic could be explained by the already mentioned stronger interaction of water molecules with the polymeric matrix on the conventional hydrogel lenses.

Finally, a close inspection of Table 3 shows that ionic hydrogels lenses such as Frequency 55 and Acuvue2, exhibited lower ionic permeability, diffusivity and k_m values than non-ionic conventional hydrogel lenses. If the values of P_s and D_m of Si-Hy lenses are compared, ionic lenses such as PureVision displayed higher values of permeability and diffusivity than most non-ionic lenses. Also, the tortuosity is lower than in non-ionic Si-Hy lenses, which could be related with the ionic character of the lens material. Similar results were observed when water flux and water permeability values are compared for all the humidity gradients (see table 4). Indeed, ionic lenses such as Frequency 55 and PureVision showed higher values of water permeability and flux than the others lenses and values were generally higher for ionic Si-Hy lenses than for ionic conventional hydrogel lenses. Therefore, it can be concluded that, in general, the ionic character of the lens material enhance the properties of salt permeability and diffusivity, as well as water permeability and flux through hydrogels materials. Moreover, the ionic lenses may provide higher stability, as measured by salt and water transport, producing an ideal balance ratio that could be especially relevant in eyes exposed to dry environmental conditions.

Conclusions

Conventional hydrogel and Si-Hy contact lenses were studied respect to oxygen, NaCl and water transport with the aim of analyzing the influence of water content and chemical structure of polymer on the apparent permeability of salt and water flux. From the observed results we can conclude that the ionic permeability, diffusivity and partition coefficient increases with the water content.

The increase of ion permeability with water content does not follow a clear trend indicating a possible dependence of the chemical structure of the polymer. This may be related to the diffusion of sodium ions occurs, not only through the hydrophilic channels, but also through hydrophobic channels where a ionic diffusivity is observed even in case of equilibrium water content below 5%. There seems to be that from a

EWC of 70% the value of the permeability tends to a constant value that may be related to the solubility of the salt in the polymer.

The partition coefficients are smaller in Si-Hy than conventional hydrogel lenses and only in Acuvue Oasys and Soflens One-day are higher than equilibrium water content that could be related with the tortuosity the highest in case that Acuvue Oasys lens and the smallest for Soflens One-day.

The water permeability of Si-Hy lenses is lower than Hy lenses probably because of higher water content of the conventional lenses. However, since a large portion of the sorbed water has a restricted mobility because of interaction with the polymeric matrix, the final permeability of all lenses is fairly similar. Moreover, the final water flux values are within the same range thanks to differences in lens thickness and tortuosity. Also, it has been shown that the water flux in all lenses increase with the water gradient across the lens thickness, although the exposure to drier conditions reduces the permeability of the lenses.

Our results showed that the ionic character of the lens material enhance the properties of salt and water permeability, diffusivity, and flux through soft contact lenses.

References

1. Nicolson PC, Vogt J. Soft contact lens polymers: an evolution. Biomaterials 2001;22(24):3273-3283.
2. Nicolson PC, Baron RC; Extended wear ophthalmic lens patent EP0819258 (A1). 2001.
3. Willis SL, Court JL, Redman RP, Wang JH, Leppard SW, O'Byrne VJ, Small SA, Lewis AL, Jones SA, Stratford PW. A novel phosphorylcholine-coated contact lens for extended wear use. Biomaterials 2001;22(24):3261-3272.
4. Tighe B. Silicone Hydrogels: structure, properties and behaviour. In: Sweeney DF, editor. Silicone Hydrogels: Continuous Wear Contact Lenses. Oxford: Butterworth-Heinemann; 2004.
5. Guan L, Jimenez MEG, Walowski C, Boushehri A, Prausnitz JM, Radke CJ. Permeability and Partition Coefficient of Aqueous Sodium Chloride in Soft Contact Lenses. Journal of Applied Polymer Science 2011;122(3):1457-1471.

6. Refojo MF. Mechanism of gas-transport through contact-lenses. Journal of the American Optometric Association 1979;50(3):285-287.

7. Grobe GL, Künzler JF, Seelye D, Salamone JC. Silicone hydrogels for contact lens applications. Polym. Mater. Sci. Eng. 1999;80:108-109.

8. Kunzler JF. Silicone hydrogels for contact lens application. Trends in Polymer Science 1996;4(2):52-59.

9. Kim J, Conway A, Chauhan A. Extended delivery of ophthalmic drugs by silicone hydrogel contact lenses. Biomaterials 2008;29(14):2259-2269.

10. Compan V, Guzman J, Riande E. A potentiostatic study of oxygen transmissibility and permeability through hydrogel membranes. Biomaterials 1998;19(23):2139-2145.

11. Austin D, Kumar RV. Ionic conductivity in hydrogels for contact lens applications. Ionics 2005;11(3-4):262-268.

12. Ju H, Sagle AC, Freeman BD, Mardel JI, Hill AJ. Characterization of sodium chloride and water transport in crosslinked poly(ethylene oxide) hydrogels. Journal of Membrane Science 2010;358(1-2):131-141.

13. Holly FJ. Wettability of hydrogels .1. Poly(2-hydroxyethyl methacrylate). Journal of Biomedical Materials Research 1975;9(3):315-326.

14. Nicolson PC, Baron RC, Chabrecek P, Court J, Domschke A, Griesser HJ, Ho A, Hoepken J, Laycock BG, Liu Q and others; CIBA GEIGY AG (CIBA-C) assignee. Extended wear ophthalmic lens patent US 5965631. 1999.

15. Refojo MF, Leong FL. Contact and Intraocular Lens. Medical Journal 1981;7:226-233.

16. Domschke A, Winterton L, Lohmann D. Morphology requirements for on-eye mobility of soft oxygen permeable contact lenses. Abstracts of Papers of the American Chemical Society 1997;213:26-PMSE.

17. Muntz A, Subbaraman LN, Sorbara L, Jones L. Tear exchange and contact lenses: a review. Journal of optometry 2015;8(1):2-11.

18. Graham AD, Truong TN, Lin MC. Conjunctival Epithelial Flap in Continuous Contact Lens Wear. Optometry and Vision Science 2009;86(4):324-331.

19. Weidemann KE, Lakkis C. Clinical performance of microchannel contact lenses. Optometry and Vision Science 2005;82(6):498-504.

20. Miller KL, Polse KA, Radke CJ. Fenestrations enhance tear mixing under silicone-hydrogel contact lenses. Investigative Ophthalmology & Visual Science 2003;44(1):60-67.

21. Doi M, Refojo MF. Histopathology of rabbit eyes with intravitreous silicone fluorosilicone copolymer oil. Experimental Eye Research 1994;59(6):737-746.

22. Chauhan A, Radke CJ. Settling and deformation of a thin elastic shell on a thin fluid layer lying on a solid surface. Journal of Colloid and Interface Science 2002;245(1):187-197.

23. Tighe B. Silicone Hydrogels Materials-how they work? In: Sweeney D, editor. Silicone Hydrogels: The Rebirth of Continuous Wear Contact Lenses: Butterworth Heinemann; 2000. p 1-21.

24. Monticelli MV, Chauhan A, Radke CJ. The effect of water hydraulic permeability on the settling of a soft contact lens on the eye. Current Eye Research 2005;30(5):329-336.

25. Lopez-Alemany A, Compan V, Refojo MF. Porous structure of Purevision (TM) versus Focus (R) night & day (TM) and conventional hydrogel contact lenses. Journal of Biomedical Materials Research 2002;63(3):319-325.

26. Pozuelo J, Compan V, Gonzalez-Meijome JM, Gonzalez M, Molla S. Oxygen and ionic transport in hydrogel and silicone-hydrogel contact lens materials: An experimental and theoretical study. Journal of Membrane Science 2014;452:62-72.
27. Cussler EL. Diffusion: Cambridge University Press; 1997.
28. Crank J. The Mathematics of Diffusion: Clarendon Press; 1956.
29. Cheng ML, Sun YM. Observation of the solute transport in the permeation through hydrogel membranes by using FTIR-microscopy. Journal of Membrane Science 2005;253(1-2):191-198.
30. Yasuda H, Lamaze CE, Ikenberr.Ld. Permeability of solutes through hydrated polymer membranes .i. Diffusion of sodium chloride. Makromolekulare Chemie-Macromolecular Chemistry and Physics 1968;118(NOV):19-&.
31. Yasuda H, Lamaze CE, Peterlin A. Diffusive and hydraulic permeabilities of water in water-swollen polymer membranes. Journal of Polymer Science Part a-2-Polymer Physics 1971;9(6):1117-&.
32. Aiba S, Ohashi M, Huang SY. Rapid determination of oxygen permeability of polymer membranes. Industrial & Engineering Chemistry Fundamentals 1968;7(3):497-&.
33. Fatt I, Helen RS. Oxygen tension under an oxygen permeable contact lens. . American Journal of Optometry and Physiological Optics 1971;48:545-548.
34. Compan V, Garrido J, Manzanares JA, Andres J, Esteve JS, Lopez ML. True and apparent oxygen permeabilities of contact-lenses. Optometry and Vision Science 1992;69(9):685-690.
35. Compan V, Lopez ML, Andrio A, Lopez-Alemany A, Refojo MF. Determination of the oxygen transmissibility and permeability of hydrogel contact lenses. Journal of Applied Polymer Science 1999;72(3):321-327.
36. Compan V, Andrio A, Lopez-Alemany A, Riande E. New method to determine the true transmissibilities and permeabilities of oxygen in hydrogel membranes. Polymer 1999;40(5):1153-1158.
37. Compan V, Andrio A, Lopez-Alemany A, Riande E, Refojo MF. Oxygen permeability of hydrogel contact lenses with organosilicon moieties. Biomaterials 2002;23(13):2767-2772.
38. Compan V, Tiemblo P, Garcia F, Garcia JM, Guzman J, Riande E. A potentiostatic study of oxygen transport through poly (2-ethoxyethyl methacrylate-co-2,3-dihydroxypropylmethacrylate) hydrogel membranes. Biomaterials 2005;26(18):3783-3791.
39. Ferreira da Silva AR, Compañ V, González-Méijome JM. Reduction in ionic permeability of a silicone hydrogel contact lenses after one month of daily wear. Materials Research Express 2015;2(6).
40. Tasaka M, Suzuki S, Ogawa Y, Kamaya M. Freezing and nonfreezing water in charged membranes. Journal of Membrane Science 1988;38(2):175-183.
41. Mirejovsky D, Patel AS, Young G. Water properties of hydrogel contact lens materials: a possible predictive model for corneal desiccation staining. Biomaterials 1993;14(14): 1080-1088.
42. Tranoudis I, Efron N. Water properties of soft contact lens materials. Contact Lerns&Anterior Eye. 2004; 27: 193-208
43. Gonzalez-Meijome JM, Compan-Moreno V, Riande E. Determination of oxygen permeability in soft contact lenses using a polarographic method: Estimation of relevant physiological parameters. Industrial & Engineering Chemistry Research 2008;47(10):3619-3629.

44. Lai YC. The role of bulky polysiloxanylalkyl methacrylates in polyurethane-polysiloxane hydrogels. Journal of Applied Polymer Science 1996;60(8):1193-1199.

45. Holden BA, Mertz GW. Critical oxygen levels to avoid corneal edema for daily and extended wear contact lenses. Invest Ophthalmol Vis Sci. 1984; 25: 1161-1167.

46. Compan V, Oliveira C, Aguilella-Arzo M, Molla S, Peixoto-de-Matos SC, Gonzalez-Meijome JM. Oxygen Diffusion and Edema With Modern Scleral Rigid Gas Permeable Contact Lenses. Investigative Ophthalmology & Visual Science 2014;55(10):6421-6429.

47. Assev, GG. Electrolytes, Transport Phenomena: Methods for Calculation of Multicomponent Solutions and Experimental Data on Viscosities and Diffusion Coefficients; Begell House: Moscow, 1998, p532.

48. Peng C-C, Kim J, Chauhan A. Extended delivery of hydrophilic drugs from silicone-hydrogel contact lenses containing Vitamin E diffusion barriers. Biomaterials 2010;31(14):4032-4047.

49. Vaitheeswaran S, Rasaiah JC, Hummer G. Electric field and temperature effects on water in the narrow nonpolar pores of carbon nanotubes. Journal of Chemical Physics 2004;121(16):7955-7965.

50. Gonzalez-Meijome JM, Lopez-Alemany A, Almeida JB, Parafita MA, Refojo MF. Qualitative and quantitative characterization of the In Vitro dehydration process of hydrogel contact lenses. Journal of Biomedical Materials Research Part B-Applied Biomaterials 2007;83B(2):512-526.

51. Gonzalez-Meijome JM, Lopez-Alemany A, Lira M, Almeida JB, Oliveira MECDR, Parafita MA. Equivalences between refractive index and equilibrium water content of conventional and silicone hydrogel soft contact lenses from automated and manual refractometry. Journal of Biomedical Materials Research Part B-Applied Biomaterials 2007;80B(1):184-191.

52. Gonzalez-Meijome JM, Lopez-Alemany A, Almeida JB, Parafita MA. Dynamic In Vitro Dehydration Patterns of Unworn and Worn Silicone Hydrogel Contact Lenses. Journal of Biomedical Materials Research Part B-Applied Biomaterials 2009;90B(1):250-258.

53. Gonzalez-Meijome JM, da Silva AC, Neves H, Lopes-Ferreira D, Queiros A, Jorge J. Clinical performance and "ex vivo" dehydration of silicone hydrogel contact lenses with two new multipurpose solutions. Contact Lens & Anterior Eye 2013;36(2):86-92.

54. Martin-Montanez V, Lopez-Miguel A, Arroyo C, Mateo ME, Gonzalez-Meijome JM, Calonge M, Gonzalez-Garcia MJ. Influence of environmental factors in the in vitro dehydration of hydrogel and silicone hydrogel contact lenses. Journal of Biomedical Materials Research Part B-Applied Biomaterials 2014;102(4):764-771.

55. Teson M, Lopez-Miguel A, Neves H, Calonge M, Gonzalez-Garcia MJ, Gonzalez-Meijome JM. Influence of Climate on Clinical Diagnostic Dry Eye Tests: Pilot Study. Optometry and Vision Science 2015;92(9):E284-E289.

56. Wolffsohn JS, Hunt OA, Basra AK. Simplified recording of soft contact lens fit. Contact Lens & Anterior Eye 2009;32(1):37-42.

57. Sagle AC, Ju H, Freeman BD, Sharma MM. PEG-based hydrogel membrane coatings. Polymer 2009;50(3):756-766.

Table 1. Technical parameters of the lenses used in this study. Values of oxygen permeability, diffusion coefficient and thicknesses measured in water and saline solution. The values with asterisk has been obtained from a previous reference[30].

Lens	Material USAN	EWC (%)	Base curve	Diameter	P Barrer	$Dx10^6$ cm^2/s	T_{av} (water)	T_{av} (saline)
Silicone hydrogel								
Acuvue Oasys	Senofilcon A	38	8,4	14	102,6*	13,5*	90,3	89
Air Optix N&D	Lotrafilcon A	24	8,6	13,8	109,2	15,1	94,4	93,8
Air Optix	Lotrafilcon B	33	8,6	14,2	106,8	14,7	97.0	95,2
Acuvue Advance	Galyfilcon A	47	8,3	14	58,5	7,8	99,6	99,1
Biofinity	Confilcon A	48	8,6	14	138,6*	17,8*	99.0	100,1
PureVision	Balafilcon A	36	8,6	14	100,5*	15,2*	94,0	93,6
Avaira	Enfilcon A	46	8,5	14,2	54,5*	10,1*	119,6	119,7
Conventional hydrogel								
Focus Dailies	Nelfilcon A	69	8,7	14	24,5	2,5	122,3	118,8
Proclear One-day	Omafilcon A	60	8,7	14,2	23,2	1,8	129,3	127,1
Soflens One-day	Hilafilcon A	59	8,6	14,2	25,3	2,0	116,5	119
Proclear	Omafilcon A	62	8,6	14,2	13,8*	1,1*	93,2	92,3
Frequency 55	Methafilcon	55	8,7	14,4	18,9	1,4	114,8	105,8
Acuvue 2	Ethafilcon A	58	8,7	14	22,3*	0,9*	116,6	103,5

Table 2. Properties of several lenses measured by DSC: T_f (freezing point of the water confined in the pores), T_{m1} (initial melting temperature), T_{m2} (final melting temperature), ΔT_m (T_{m2} - T_{m1}), and percentage of confined water (water in pores/total water). The values and the uncertainties in the column of free water represent the mean values and SD of three lenses measured by DSC.

Lens comercial name	EWC (%)	T_f (ºC)	T_{m1} (ºC)	T_{m2} (ºC)	ΔT_m (ºC)	Free WC (%)	Confined water (%)
Air Optix N&D	24	-22.0	-26.8	1.2	28.0	13.1±0.6	10.9±0,6
Air Optix	33	-21.0	-28.0	1.2	29.2	22.2±2.1	10.8±0,4
Acuvue Advance	47	-21.4	-27.8	1.2	29.0	13.0±0.5	34.0±1,1
PureVision	36	-27.7	-42.5	0.2	42.7	19.4±1.8	16.6±1,6
Proclear One-day	60	-18.2	-17.5	2.5	20.0	13.7±0.6	46.3±1,7
Soflens One-day	59	-13.6	-18.5	2.0	20.5	12.3±0.8	46.7±1,8
Frequency 55	58	-20.6	-13.8	3.0	16.8	16.1±0.7	41.9±1,5
Acuvue2	58	-21.0	-15.5	2.9	18.4	16.0±0.8	42.0±1,2

Table 3. Values obtained for the ionic apparent coefficient permeability, P_s, determined from the conductivity measurements. The errors shown in the columns of apparent

permeability and diffusion coefficients have been calculated from the parameters of the straight line that fits the experimental values taking into account that each measurement was repeated three times. The character ionic(I) or non-ionic(NI) of the lens are indicated together with the material name in column material USAN.

Lens commercial name	Material USAN	EWC (%)	P_sx10^{-7} (cm^2/s)	D_mx10^{-7} (cm^2/s)	k_m	τ
Acuvue Oasys	Senofilcon A/NI	38	0,97±0,12	2.3±0,5	0.42	9.5
Air Optix N&D	Lotrafilcon A/NI	24	1,3±0,15	4.1±0,5	0.23	7.1
Air Optix	Lotrafilcon B/NI	33	3,4±0,3	3.9±0,8	0.29	7.3
Acuvue Advance	Galyfilcon A/NI	47	8.2±0,5	23.4±1,4	0.35	3.0
Biofinity	Confilcon A/NI	48	10.5±0,4	14.0±1,7	0.42	3.9
PureVision	Balafilcon A/I	36	6.7±0,3	18.0±1,5	0.37	3.4
Avaira	Enfilcon A/NI	46	6.0±0,5	7.2±1,0	0.35	5.4
Freshlook	Phemfilcon A/I	55	5.5±0,18	8.3±1,2	0.52	5.0
Focus Dailies	Nelfilcon A/NI	69	44,1±0,5	66±2	0.53	1,8
Proclear One-day	Omafilcon A/NI	60	37,7±0,6	60±2	0.55	1.7
Soflens One-day	Hilafilcon A/NI	59	31,1±0, 5	42±3	0.78	1.4
Proclear	Omafilcon A/NI	62	32.8±0,8	60±4	0,55	1.9
Frequency 55	Methafilcon /I	55	18.5±0,5	41±5	0.44	2.2
Acuvue 2	Ethafilcon A/I	58	28.9±0,7	55±5	0.53	1.9

Table 4. Water flux (in g/[h·m^2]) and permeability (P in g·m/[m^2·dia·atm]) values of soft contact lenses. The SD shown in the columns of permeability and flux have been calculated from the parameters of the straight line that fits the experimental data of weight-loss taking into account that each measurement was repeated three times.

Humidity gradient		75%-100%		53%-100%		23%-100%	
		P	Flux	P	Flux	P	Flux
Lens commercial name	Material USAN						
Acuvue Oasys	Senofilcon A	1.38±0.05	106±4	0.80±0.04	115±5	0.60±0.02	141±5
Air Optix	Lotrafilcon B	1.40±0.06	99±4	0.93±0.04	125±5	0.63±0.02	140±4
Acuvue Advance	Galyfilcon A	1.76±0.07	122±5	1.04±0.04	136±5	0.62±0.02	134±5
Biofinity	Confilcon A	1.46±0.06	101±4	0.99±0.04	131±5	0.69±0.03	150±6
PureVision	Balafilcon A	2.32±0.10	161±7	1.14±0.05	149±7	0.75±0.03	162±6
Avaira	Enfilcon A	2.07±0.10	120±6	1.28±0.04	139±4	0.82±0.03	146±5
Soflens One-day	Hilafilcon A	1.72±0.14	102±8	1.03±0.02	116±3	0.67±0.02	123±4
Frequency 55	Methafilcon	2.19±0.09	132±6	1.25±0.03	142±4	0.86±0.03	161±6

FIGURE CAPTIONS

Figure 1. DSC curves for different silicone-hydrogel (Si-Hy) contact lenses.

Figure 2. DSC curves for different conventional hydrogel contact lenses.

Figure 3. Sodium ion concentration versus time for each of one of the Si-Hy contact lenses used in this study.

Figure 4. Sodium ion concentration versus time for each of one of the conventional hydrogel contact lenses used in this study.

Figure 5. Weight loss of the lenses as a function of time observed in the evaporation cell for 75%HR and 23ºC in conditions of saturated saline solution.

Figure 6. Weight loss of the lenses as a function of time observed in the evaporation cell for 53%HR and 23ºC in conditions of saturated saline solution.

Figure 7. Weight loss of the lenses as a function of time observed in the evaporation cell for 23%HR and 23ºC in conditions of saturated saline solution.

Figure 8. Experimental values calculated for the steady state water flux obtained from the water-transport rates for different Hy and Si-Hy contact lenses.

Figure 9. Experimental values of water permeability calculated from the water-transport rates for different Hy and Si-Hy contact lenses.

Figure 10. Relationship between the apparent diffusion coefficient of NaCl and the reciprocal of EWC(%) in pure water for the lenses studied. The line represents the fit between the limit values corresponding to NaCl diffusion in water and HEMA of 32.6% of water content for comparison.

Figure 11. NaCl permeability obtained from conductivity measurements as a function of (1/H)-1. Open symbols conventional hydrogel lenses. Filled symbols Si-Hy lenses.

Figure 12. Equilibrium partition coefficients, km, of NaCl in hydrogels and Si-Hy contact lenses as a function of equilibrium water content at 35ºC. Squares indicate the hydrogel lenses and rombs the Si-Hy contact lenses.
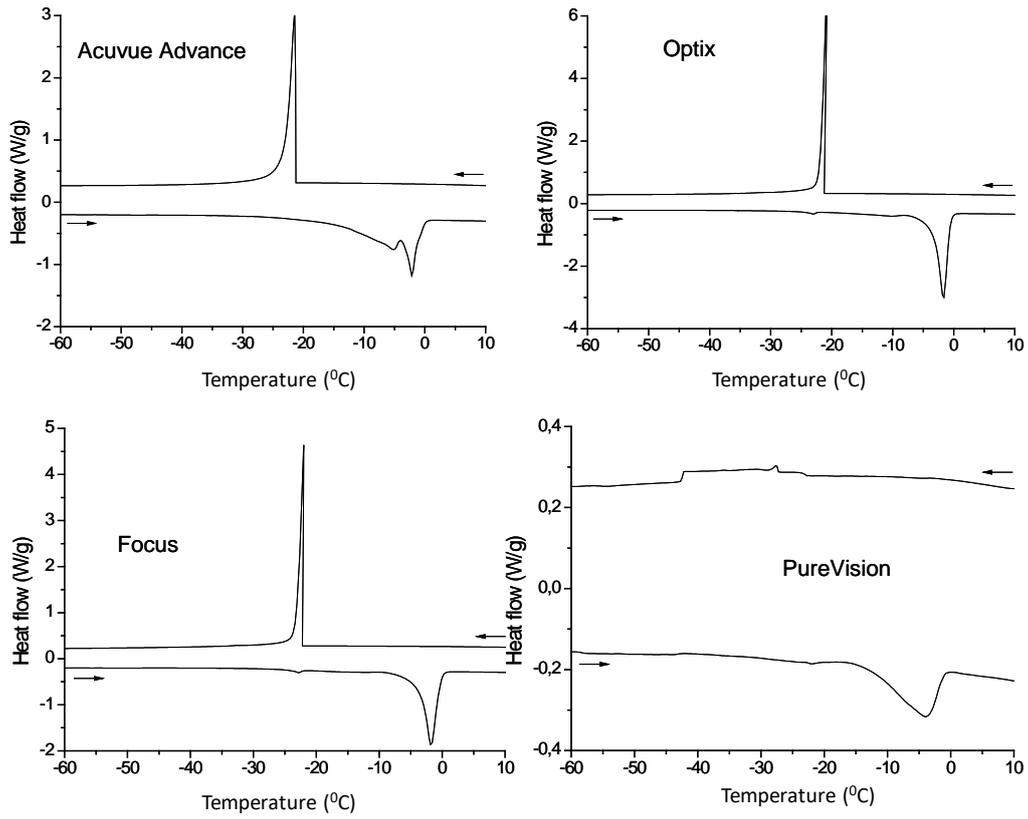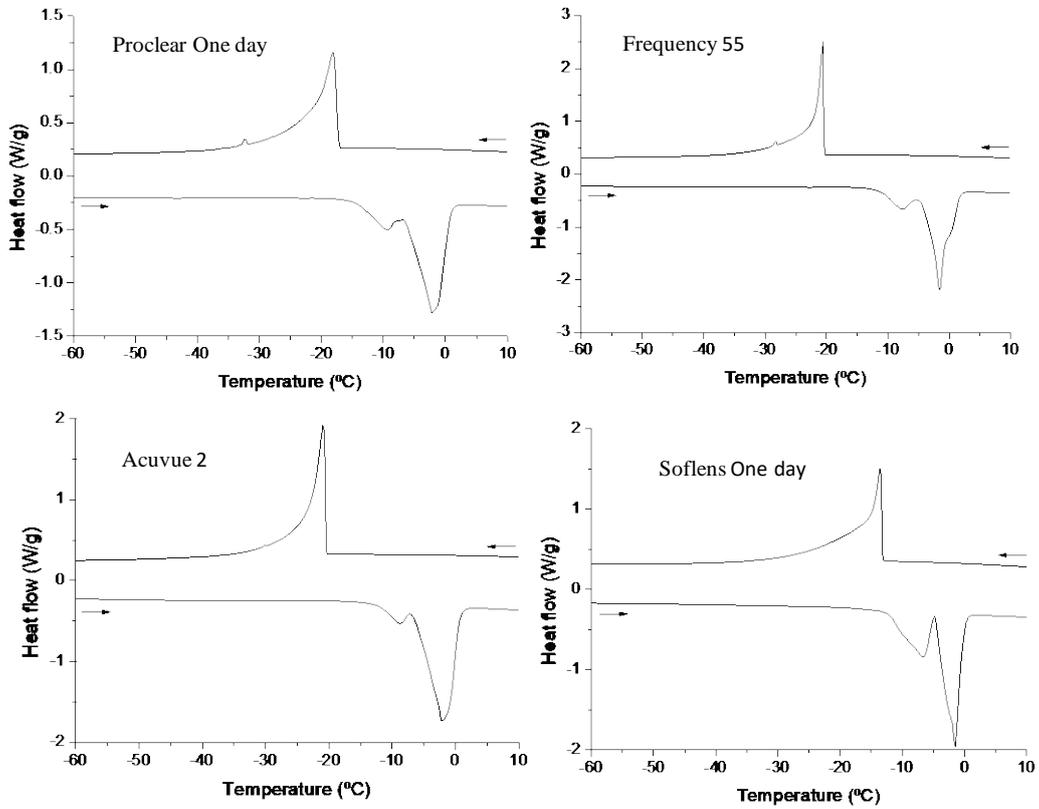
Figure 1

Figure 2
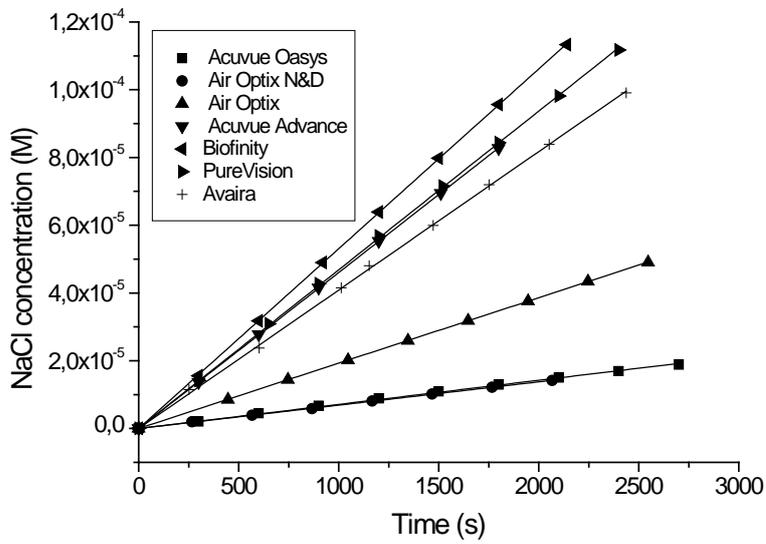
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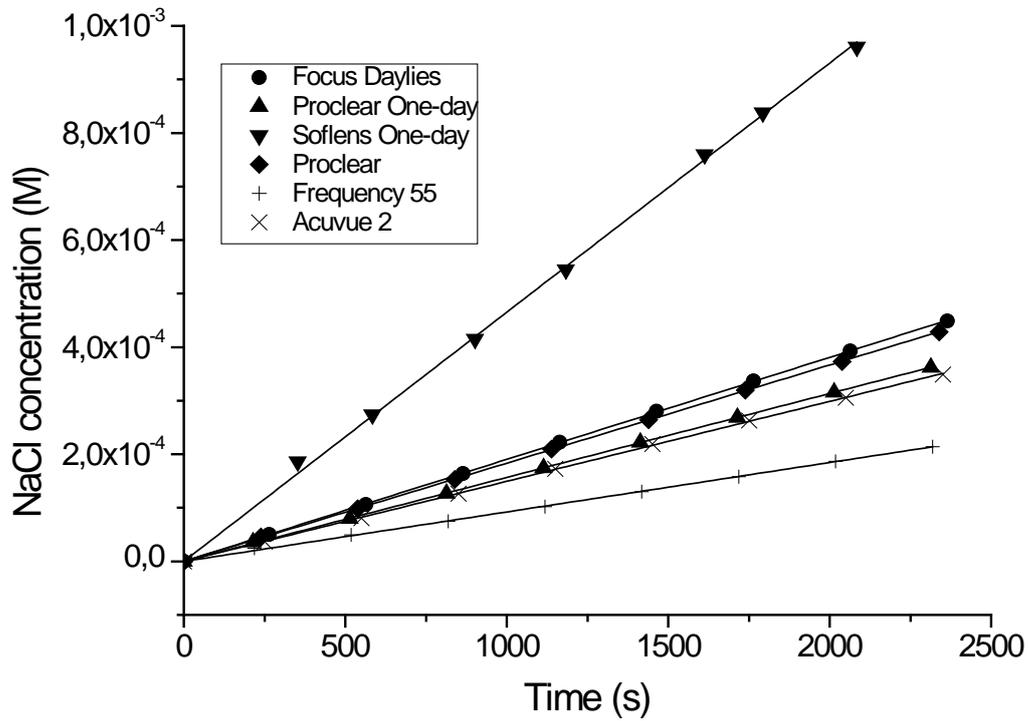
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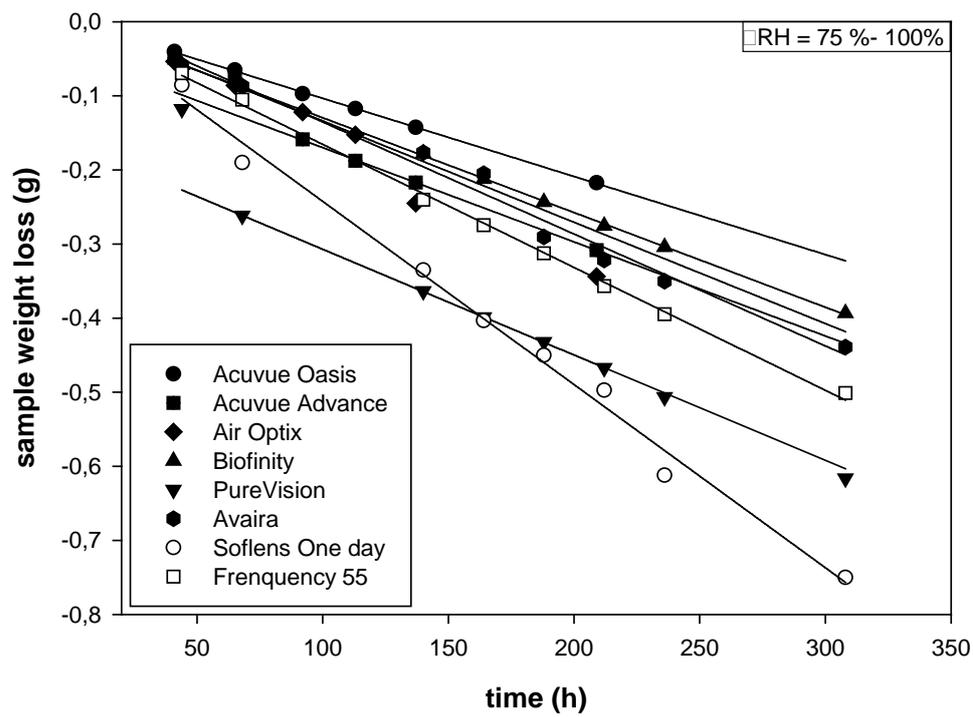
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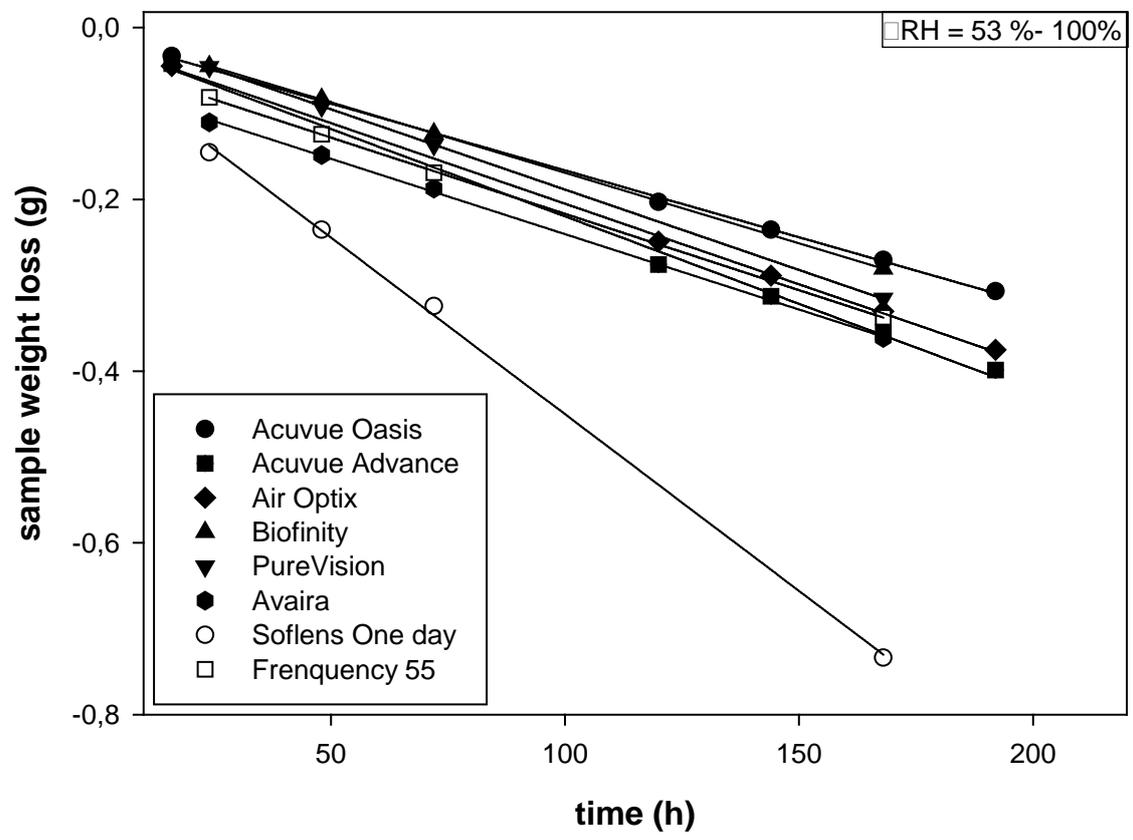
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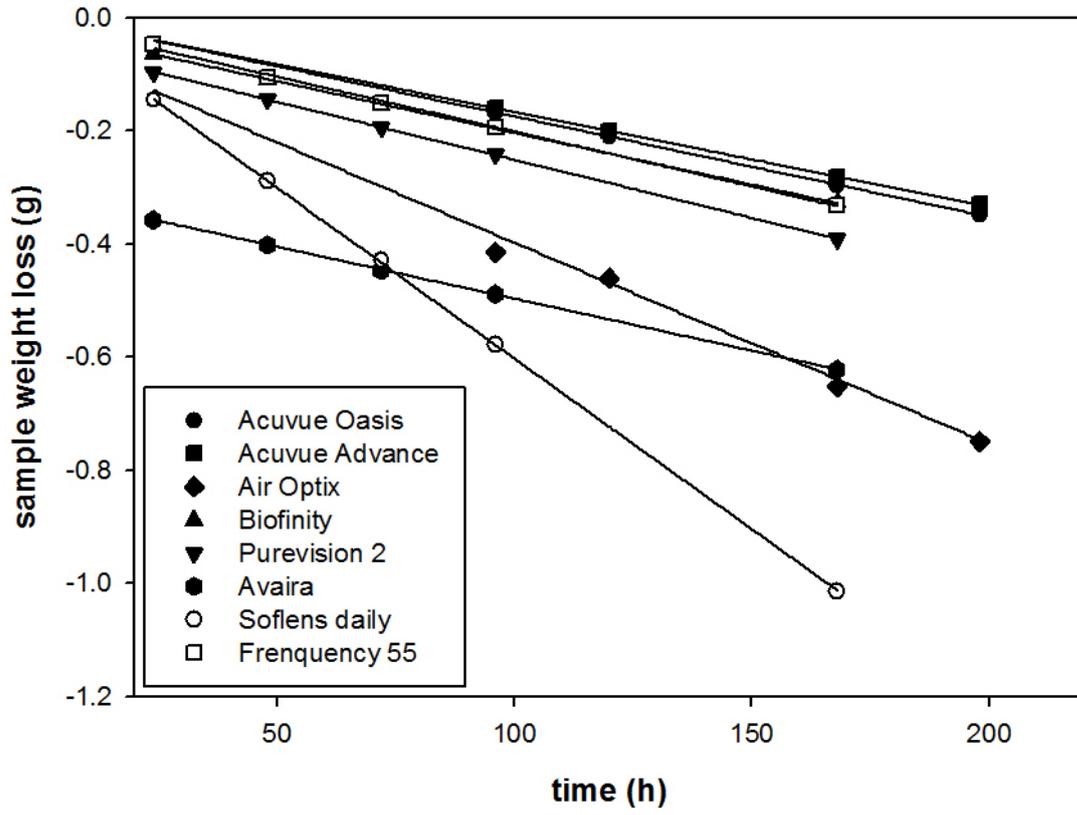

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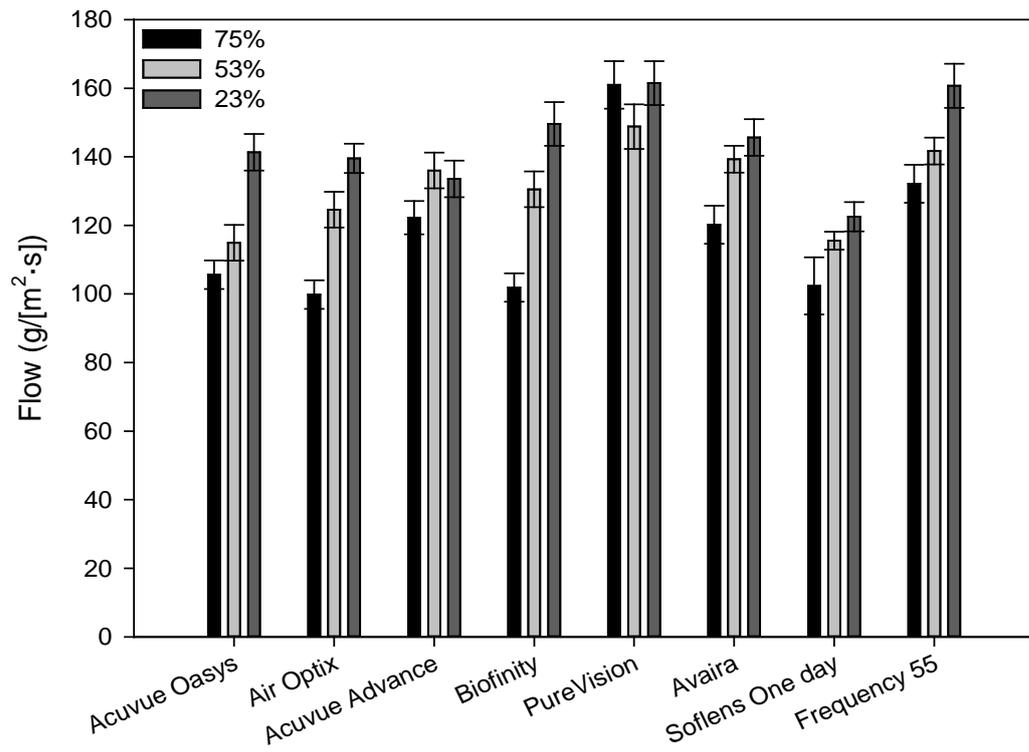
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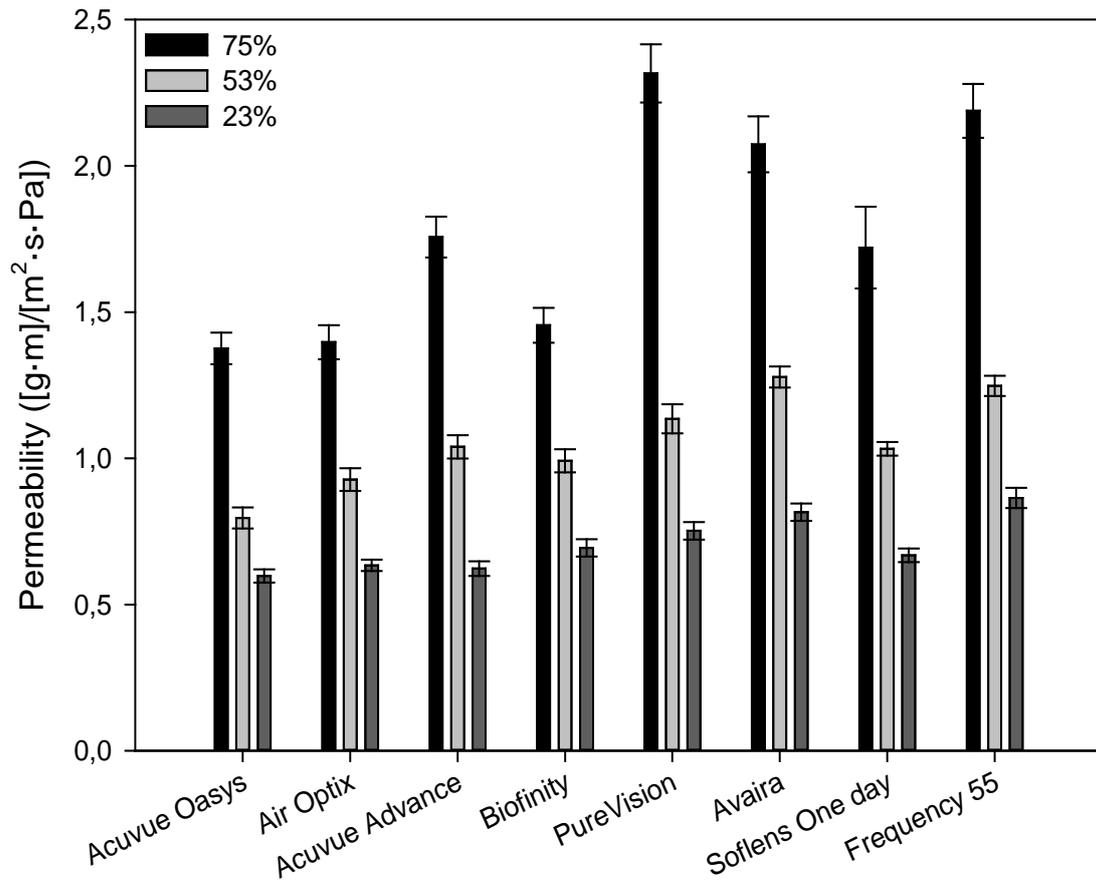
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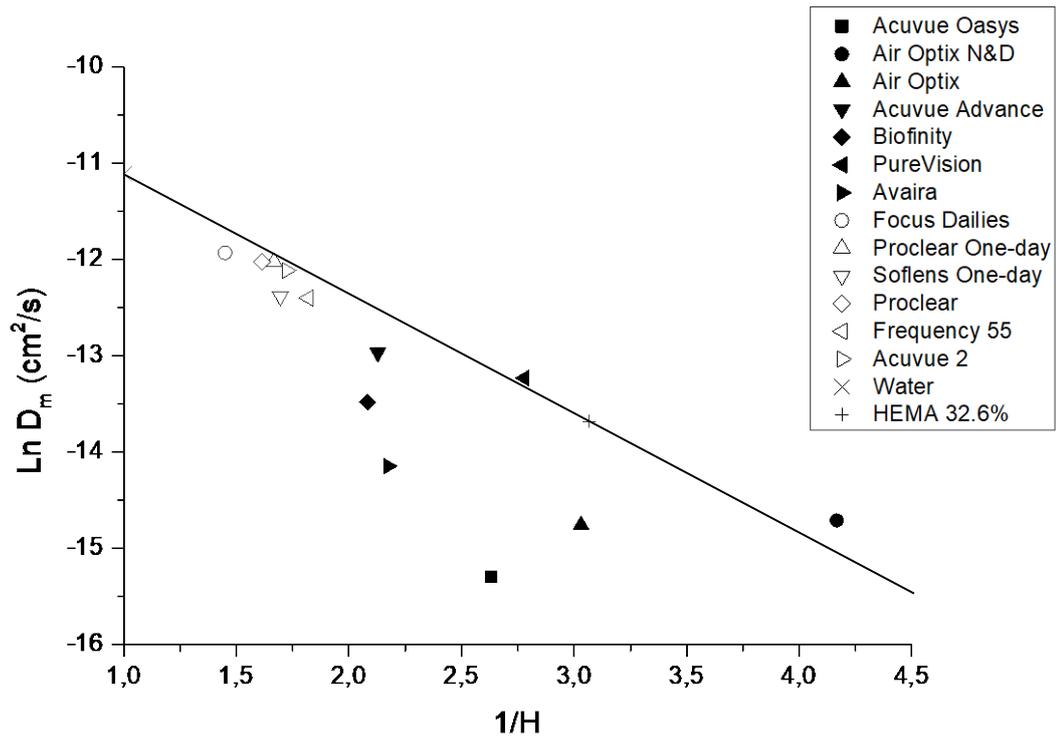
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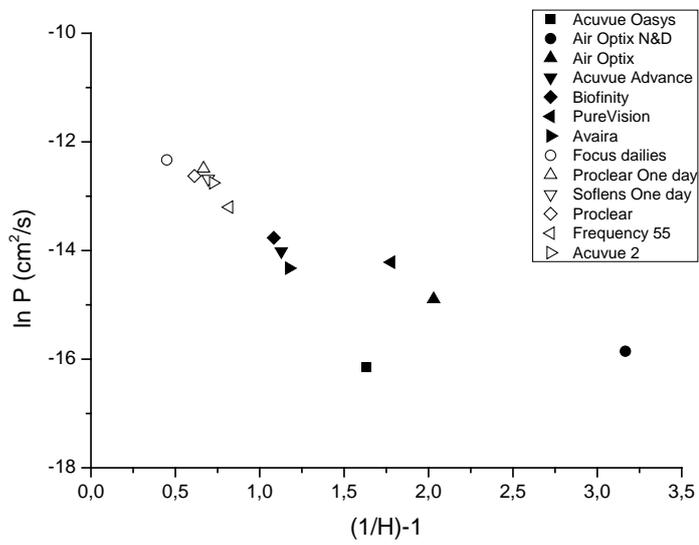
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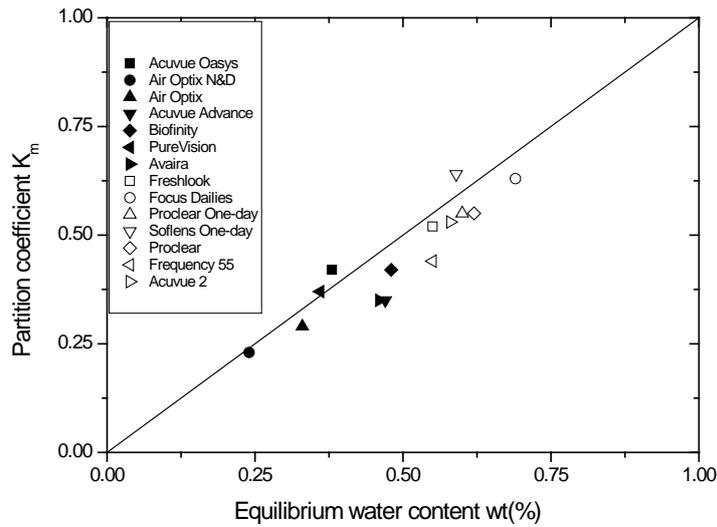
Figure 12

1. Nicolson PC, Vogt J. Soft contact lens polymers: an evolution. Biomaterials 2001;22(24):3273-3283.
2. Nicolson PC, Baron RC; Extended wear ophthalmic lens patent EP0819258 (A1). 2001.
3. Willis SL, Court JL, Redman RP, Wang JH, Leppard SW, O'Byrne VJ, Small SA, Lewis AL, Jones SA, Stratford PW. A novel phosphorylcholine-coated contact lens for extended wear use. Biomaterials 2001;22(24):3261-3272.
4. Tighe B. Silicone Hydrogels: structure, properties and behaviour. In: Sweeney DF, editor. Silicone Hydrogels: Continuous Wear Contact Lenses. Oxford: Butterworth-Heinemann; 2004.
5. Guan L, Jimenez MEG, Walowski C, Boushehri A, Prausnitz JM, Radke CJ. Permeability and Partition Coefficient of Aqueous Sodium Chloride in Soft Contact Lenses. Journal of Applied Polymer Science 2011;122(3):1457-1471.
6. Refojo MF. Mechanism of gas-transport through contact-lenses. Journal of the American Optometric Association 1979;50(3):285-287.