THE EFFECT OF CHEMICAL AND THERMAL TREATMENT ON PERMSELECTIVITY AND RESISTANCE VALUES OF CELLOPHANE MEMBRANES

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Membrane potentials through a chemically treated cellophane membrane have been measured at different temperatures. The results have been analysed on the basis of the Kobatake equation for the membrane potential, which permits the evaluation of some parameters related to the membrane structure. The influence of temperature on these parameters has been considered. The comparison among the permselectivity and electrical resistance values obtained at 25 °C with an untreated and two treated cellophane membranes, one chemically treated and another annealed, show a more significant loss of selectivity for the chemically treated membrane than for the annealed one, which can be attributed to a higher influence of the chemical treatment on the cellophane membrane structure than that due to the heating.

The study of the transport of electrolyte solutions through cellulosic membranes such as cellulose acetate or cellophane have received a great deal of interest for many years. Cellulose acetate membranes can be used for desalination purposes and cellophane ones are also utilized in some membrane devices separating different parts of the system or as the support for inorganic precipitates[1 – 5], and it is important to understand the influence of different treatments on the structure of these membranes. On the other hand, the different results found for the thermoosmotic permeability measured with similar cellophane membranes reported by different authors[6 – 7] may be attributed to the effect of both the chemical treatment and temperature on the structure of the cellophane membranes. In order to obtain a more precise characterization of these membranes their electrochemical properties have been studied, and it has been found that both cellulose acetate and cellophane membranes possess weak negative fixed charges[8 – 11]. The fixed charge density and the transport numbers in cellophane membranes have mainly been determined on the basis of the Teorell–Meyer–Sievers theory. These parameters are associated with the interaction between ions and the membrane matrix, because of which any change in the membrane structure could affect their values in the membrane. This change could be due to membrane treatment, chemical or thermal.

In this work the effect of both chemical treatment and temperature on the membrane structure and permselectivity of cellophane membranes have been studied. The membrane potential values measured at different temperatures have been analysed using the Kobatake equation[12]. This expression permits determination of a parameter related to the membrane structure and also the evaluation of the possible effect of temperature on the membrane matrix, which could be related with the different results found with thermoosmotic measurements for cellophane membranes indicated above. A comparison of the permselectivity (P_S) and the electrical resitance (R) values for chemically treated, untreated and annealed membranes, at a constant temperature (25 °C), indicates the influence of both treatments (chemical and thermal) on the P_S and R values for cellophane membranes, showing a loss of the selective behaviour of the treated membranes, which is more evident for those chemically treated.

EXPERIMENTAL

Materials

The membranes used were cut from a sheet of Cellophane 600 P (Cellophane Española, S.A.) and chemically treated with NaOH solutions (concentration from 2.5 mol dm^{-3} to 0.05 mol dm^{-3}) and then in diluted HCl following a procedure similar to that indicated by Rastogi et al.[7] . They were then repeatedly washed with conductivity water until its conductance remained unchanged. The membranes will hereafter be called M_{TR}.

In order to determine the effect of both, chemical treatment and temperature, on some electrochemical parameters two samples of cellophane membrane from the same sheet were taken: the first was annealed at 70 °C for 5 h (membrane M_H), the second was left untreated (membrane M_O). Geometric parameters of the membranes are stated in Table I. The thickness of the wet membranes was measured using a Militron–Compact instrument (1202-IC). ρ and ε values were determined as described elsewhere[13].

Experiments were carried out using NaCl (99.5% purity) aqueous solutions of various concentrations, which were obtained by dilution of the 2 M stock solution. Before measuring, the membranes were immersed in the 1 mM NaCl solution for at least 12 h.

Measurements

Membrane potential measurements: The experimental device used was similar to that one described recently[15], and basically consists of three parts: (i) two solution tanks of 1 dm^3 capacity each, surrounded by a thermostatic jacket; (ii) two circulatory systems, each with a centrifugal pump whose output was of the order of 600 cm^3 min^{-1}, to provide turbulent flow within the cell in order to minimize the effect of the solution boundary layers close to the membrane; (iii) the cell itself, which was formed by two half-cells made of methacrylate with approximate volume of 64 cm^3 each, had a membrane holder of 0.5 cm^2 area. The membrane was supported by rubber rings and the two half-cells were clamped together by a steel screw. To avoid a difference in the hydrostatic pressure between the two half-cells, which could cause a streaming potential across the membrane, each half-cell was provided with a vertical capillary tube acting as a reference manometer. The pressure of the two pumps was carefully adjusted so that the meniscus level in the two tubes were equal.

The membrane potential, $\Delta\Phi$, was measured by calomel electrodes placed close to the membrane and in contact with the solutions via saturated KCl saline bridges, and joined to a digital voltmeter of 1 000 MΩ input impedance. For temperature measurements a platinum thermocouple was placed in each half-cell, which was connected to a Crison 662/3 digital thermometer. Four temperatures were considered: 25, 40, 50 and 60 °C.

The membrane potential measurements were carried out keeping constant the concentration ratio of the solutions on both sides of the membrane, $c_1/c_2 = \gamma = 2$ (for the interval of concentrations ranging from 10^{-3} to 10^{-1} mol dm^{-3}). In all cases, $\Delta\Phi = \Phi(c_1) - \Phi(c_2)$, and $\Delta\Phi$ values were corrected to compensate for electrode asymmetry but not for the liquid junction potentials at the tips of the saline bridges.

Electrical resistance measurements: The experimental device for measuring electrical resistance was described in ref.[16]. In this case, alternating current via a Wayne Kerr Bridge B905 with Ag/AgCl electrodes was used at four different frequencies: 100 Hz, 400 Hz, 1 kHz and 10 kHz. Measurements were made at 25 °C with the membranes placed in the membrane holder and without them; the difference between these values was taken as the membrane resistance.

RESULTS AND DISCUSSION

Membrane potentials, $\Delta\Phi$, versus c_1 dependencies for the chemically treated cellophane membrane at the four temperatures studied are shown in Fig. 1. It is seen from the picture that a linear relationship between $\Delta\Phi$ and c_1 exists at low values of concentration, however, the linear character disappears at higher concentrations ($c_1 > 0.02$ mol l^{-1}).

For this reason, it is possible to analyse these results on the basis of the Kobatake equation for the membrane potential[12] measured through a negatively charged membrane separating two solutions of 1 : 1 electrolyte of concentrations c_1 and c_2, ($c_1 > c_2$):

$$\Delta\Phi = (-RT/F)\,((1/\beta)\ln(c_1/c_2)\,(1 + (1/\beta) - 2\alpha)\ln((c_1 + \alpha\beta\gamma)/(c_2 + \alpha\beta\gamma))) \quad (1)$$

α and β are two parameters written as:

$$\alpha = u/(u + v) \quad (2)$$

$$\beta = 1 + (KFX/u)\,, \quad (3)$$

where u and v are the cationic and anionic mobilities in the membrane, respectively, F is the Faraday constant, X is the fixed charge concentration in the membrane and K is a parameter dependent upon the viscosity of the solution and the structure of the membrane matrix.

TABLE I
Wet thickness (δ), density (ρ), and fractional void volume (ε) of the three membranes studied

Membrane	δ, μm	ρ, g cm^{-3}	ε, %
M_O[a]	62 ± 2	0.73 ± 0.05	47
M_{IR}	74 ± 2	0.68 ± 0.04	59
M_H	70 ± 4	0.65 ± 0.05	55

[a] Values from ref.[14].

Two limiting forms of Eq. (*1*), depending on the concentration of the solutions, were derived[12]: Eq. (*4*) for low and Eq. (*5*) for high concentrations, respectively.

$$|\Delta\Phi| = (RT/F)\,((1/\beta)\ln\gamma - ((\gamma-1)/\alpha\beta\gamma)\,(1+(1/\beta)-2\alpha)\,(c_1/X)) \qquad (4)$$

$$1/t_- = (1/(1-\alpha)) + ((1+\beta-2\alpha\beta)\,(\gamma-1)\,\alpha/2\,(1-\alpha)^2\ln\gamma)\,(X/c_1)\,, \qquad (5)$$

where t_- is the apparent anion transport number in the membrane (no water flux has been considered). Because celophane membranes are weakly negatively charged[15], at high concentrations t_- values are obtained from the experimental data by the diffusion potential expression (it can be used at high concentration when the possible effect of the fixed charge is neglected, $c_1 >> X$) (ref.[17]).

$$\Delta\Phi = (RT/F)\,(1-2t_-)\ln(c_1/c_2) \qquad (6)$$

Equations (*4*) and (*5*) represent two linear relationships, one between $\Delta\Phi$ and c_1, and another between $1/t_-$ and $1/c_1$. By fitting the experimental points to those expressions, the parameters X, α and β, which characterize the membrane, can be determined.

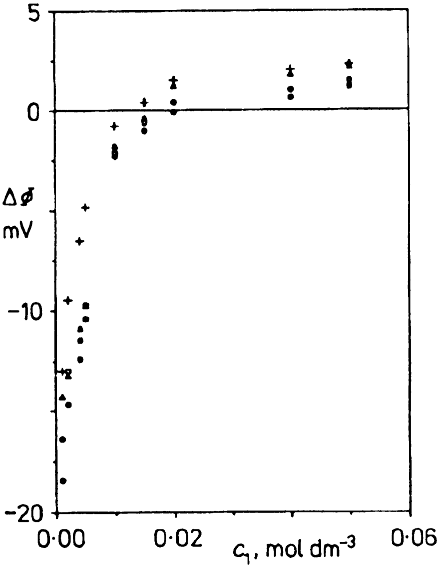

FIG. 1

Variation of the membrane potential $\Delta\Phi$ with concentration c_1 for the M_{TR} cellophane membrane at different temperatures. + 25 °C; ● 40 °C; ○ 50 °C; ▲ 60 °C

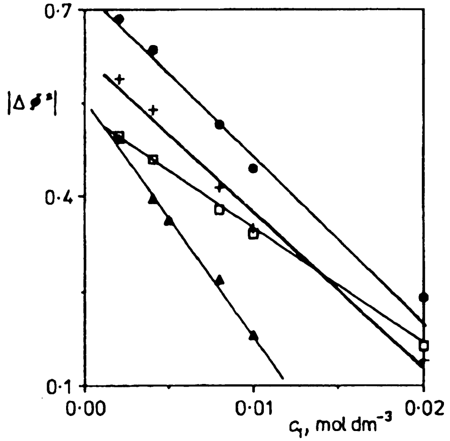

FIG. 2

Variation of the dimensionless parameter $|\Delta\Phi^*| = |(F/RT)\Delta\Phi|$ with c_1 for the M_{TR} cellophane membrane, at low concentrations, for different temperatures. ▲ 25 °C; ● 40 °C; + 50 °C; □ 60 °C

In Fig. 2, the values of the dimensionless parameter $\Delta\Phi^* = (F/RT)\Delta\Phi$ versus c_1 for low concentrations of the external solutions are shown for the different temperatures considered. Fitting the experimental points using the least squares method, yields the parameter β, at each given temperature, from the value of the origin ordinate of the straight line corresponding to that temperature. Figure 3 shows $1/t_-$ as a function of $1/c_1$, at high values of salt concentration. From the intercept of these straight lines the value of α at each temperature was determined. Once α and β values are known, the fixed charge concentration in the membrane at low concentrations (X_p) and at high concentrations (X_g), were obtained from the slopes of the straight lines drawn in Figs 2 and 3, respectively, and are shown in Table II. It is seen that, in both cases, the fixed charge values are almost constant for the interval 40 – 60 °C, but at 25 °C low values of X_p and X_g were obtained, which could be related to a change in the membrane structure for a temperature between 25 and 40 °C. On the other hand, the values of X_g agree quite well with those previously obtained[15] at high concentrations using the approximation to the TMS theory proposed by Aizawa et al.[18].

TABLE II
Variation of the fixed charge densities X_p and X_g, and the parameter $\langle K\rangle/u_+$ with temperature

t, °C	$\lvert X_p\rvert$, mol dm^{-3}	$\lvert X_g\rvert$, mol dm^{-3}	$\langle K\rangle/u_+$
25	$2.9 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$11.1 \cdot 10^{-5}$
40	$5.6 \cdot 10^{-2}$	$2.1 \cdot 10^{-2}$	$1.1 \cdot 10^{-5}$
50	$5.1 \cdot 10^{-2}$	$1.8 \cdot 10^{-2}$	$3.5 \cdot 10^{-5}$
60	$5.5 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$	$8.4 \cdot 10^{-5}$

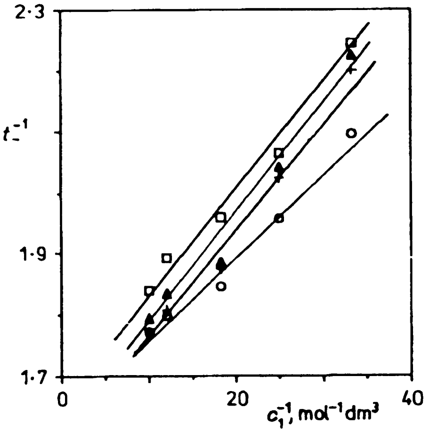

FIG. 3
Variation of the apparent anion transport number in the M_{TR} cellophane membrane, t_-^{ap}, at high concentrations, for different temperatures. ○ 25 °C; + 40 °C; □ 50 °C; ▲ 60 °C

The parameter K can be calculated by Eq. (3) as a function of the cationic mobility in the membrane. $\langle K \rangle / u_+$ values, at the different temperatures studied, are also shown in Table II, where $\langle K \rangle$ means the average value of K obtained using X_p and X_g values in Eq. (3). A significant difference between $\langle K \rangle / u_+$ values at 25 °C and those corresponding to the other temperatures exists, and because this difference is too big to be assigned to changes of u_+ or the solution viscosity (on which the parameter K also depends), this fact can be attributed to changes in the membrane structure due to the temperature.

Comparison of the Permselectivity for Thermal and Chemically Treated Membranes

The permselectivity, P_S, of the treated cellophane membrane, which is a measure of the membrane selectivity of the counter-ions over the co-ions, has been determined for the temperatures studied and the interval of concentration between 0.02 mol l^{-1} and 0.1 mol l^{-1}. P_S values were obtained by the expression[19],

$$P_S = (t_+ - t_+^0)/(1 - t_+^0)\,, \tag{7}$$

where t_+ and t_+^0 are the cation transport number in the membrane and in free solution, respectively. The variation of permselectivity with the average concentration, $\langle c \rangle$, is shown in Fig. 4, at 25 °C. No significant variations of P_S values were found at the different temperature studied, which indicates that temperature hardly affects the permselectivity of the treated cellophane membranes. However, a decrease in the membrane permselectivity when the external concentration increases can be observed from this picture, which is due to an uptake of the co-ions into the membrane at high external concentrations and, therefore, a loss of its selectivity.

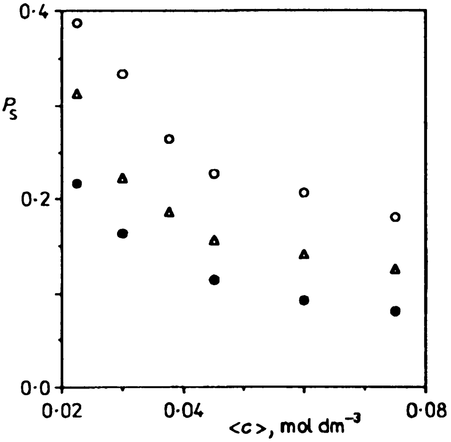

FIG. 4

Variation of the permselectivity for three cellophane membranes with the average concentration, at the same temperature t = 25 °C. ○ M_O; Δ M_H; ● M_{TR}

In order to determine the effect of both chemical treatment and heat on the structure of cellophane membranes, the membrane potential and the electrical resistance have been measured, at 25 °C for two other cellophane membranes: one of them was previously annealed at 70 °C (M_H), and the other one was an untreated membrane (M_O). Figure 4 also shows the variation of P_S with concentration for these three membranes, and a decrease of the permselectivity can be observed when the concentration increases, which is similar to that indicated above for the chemically treated membrane. In this figure, the loss of permselectivity of the treated membranes as compared with the untreated ones is significant and it remains almost constant for the whole interval of concentrations. The sequence of decrease for P_S values is: $P_S(M_O) > P_S(M_H) > P_S(M_{TR})$, which indicates a higher effect of the chemical treatment on the membrane than that due to the heat. These results also agree with those found for the geometric parameters of these membranes written in Table I, where a slightly high influence of the chemical treatment on the thickness and fractional void volume of the cellophane membranes is shown.

Electrical Resistance for Untreated, Heated and Chemically Treated Membranes

Variation of the electrical resistance, R, with concentration is drawn in Fig. 5, for M_O, M_H and M_{TR} membranes. For the three membranes a very slight increase of R with frequency was found, and the values shown in Fig. 5 correspond to those measured at $f = 1$ kHz. From this picture, lower values of R for both treated membranes can be observed, and also for this parameter the sequence of values is: $R(M_O) > R(M_H) > R(M_{TR})$.

It can be concluded that both chemical and thermal treatment affects the cellophane membrane structure, which may be an explanation of the differences in results reported

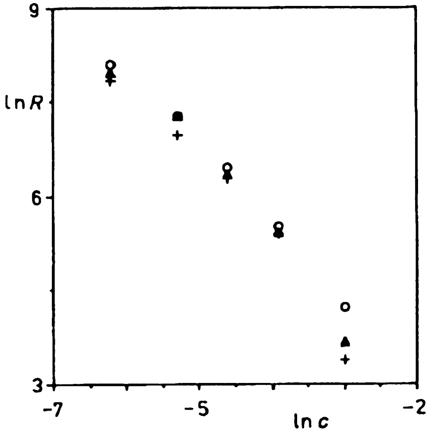

FIG. 5

ln R versus ln c for three cellophane membranes at a given temperature t = 25 °C. + M_O; ▲ M_H; ○ M_{TR}

by various authors working on temperature related processes with cellophane membranes as it was indicated above (thermoosmosis, mainly[6 – 7]). However, the chemical treatment seems to have a higher influence on the changes in the cellophane membrane structure.

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