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Determination of Some Characteristic Parameters of Treated Cellophane Membranes

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Abstract

Membrane potential, water permeation, and electrical resistance of a cellophane membrane treated with NaOH and HCl solutions have been measured. Some membrane properties, such as permselectivity, hydraulic permeability, and fixed charge concentration in the membrane, were calculated. Variation of hydraulic permeability and the concentration of fixed charge in the membrane with temperature have been also studied. In order to determine the influence of treatment, membrane potentials were measured for a untreated and three differently treated cellophane membranes. A comparation of the fixed charge concentration and permselectivity for treated and untreated membranes was also made. Variation of permselectivity with concentration was obtained.

INTRODUCTION

The study of liquid transport through artificial membranes has been greatly developed during the last years with the idea of determining the processes taking place in membranes when they are used as a barrier for transport, as well as to determine some characteristics of the membranes. Both aspects are important because of the potential use of membranes in various separation processes (*1*). Different transport phenomena through cellulosic membranes have long been studied. Permeation, electrokinetic phenomena, and membrane potentials of cellulose acetate and cellophane membranes with different electrolytes have been measured (*2–7*).

Permeation of water and alcohol-water mixtures through cellophane membranes has been extensively studied (*8–12*). It was found that the permeability characteristics of cellophane membranes can be altered significantly by solvent treatment, heating, irradiation, etc.

The purpose of this work was to study some properties of cellophane-treated membranes and to determine possible changes in the permselectivity and the concentration of the fixed charge of these membranes due to treatment with NaOH and HCl solutions. For that reason, membrane potentials for an untreated and three differently treated cellophane membranes were measured. Using the membrane potential expression based on TMS theory, the concentrations of fixed charges for treated and untreated membranes were calculated. From the membrane potential values, the variation of permselectivities versus concentration was also obtained for all membranes.

Variations of hydraulic permeability and fixed charge concentration with temperature for one of the treated membranes were also studied.

THEORY

The electrical potential difference between the two sides of a membrane separating electrolyte solutions of different concentrations, or "membrane potential," has been widely studied by means of the TMS theory. This theory assumes that the membrane potential, $\Delta\Phi$, is due to the sum of a Donnan potential at each membrane/solution interface plus a diffusion potential within the membrane. The membrane potential for a 1-1 electrolyte and negatively charged membranes can be written as

$$\Delta\Phi = \frac{RT}{F}\left[-\ln\frac{a_i}{a_e} + \ln\frac{(4a_i^2 + X^2)^{1/2} + X}{(4a_e^2 + X^2)^{1/2} + X} + U\ln\frac{(4a_i^2 + X^2)^{1/2} + UX}{(4a_e^2 + X^2)^{1/2} + UX}\right] \quad (1)$$

where a_1 and a_2 are the activities of solutions separated by the membrane, X is the fixed charge concentration in the membrane (which is assumed to remain constant at all values of the external solutions), R and F are the gas and Faraday constants, respectively, and T is the temperature of the system. The parameter U can be written as

$$U = (t_+/z_+) - (t_-/z_-)$$

with t_+ and t_- the transport numbers of the cation and anion in the membrane, and z_+ and z_- their valences, respectively.

Other important membrane processes are related to the mass flow passing through a membrane. When this flow, J, is due to a pressure difference between the two sides of a membrane, ΔP, the process is called permeation. The phenomenological equation between mass flow and pressure difference is given by

$$J = (q/\delta)A\Delta P \tag{2}$$

where q and δ are the cross-section and the thickness of the membrane, respectively, and A is the permeability coefficient.

Equations (1) and (2) allow us to determine some charcteristic parameters of membranes, such as the concentration of fixed charge in the membrane and the permeability, if the membrane potential or flow is known in each case.

EXPERIMENTAL

Material

The membranes used were cut from a sheet of Cellophane 600 P, supplied by Cellophane Española, S.A. Some of them were treated with a 10% sodium hydroxide solution and hydrochloric acid as described by Rastogi et al. (*13*). In this work the membranes were immersed for 3 min in each of six more progressively dilute solutions of NaOH (from 2.5 to 0.05 *M*), and then in dilute HCl for 6 min. After that, the membranes were repeatedly washed with conductivity water until the washed water had the same conductivity as pure water. These membranes will be called M_1 in the following sections. The polymer densities and the thicknesses of the membranes were determinated as in Ref. *14*, and the following values were obtained: $\rho = (0.68 + 0.04)$ g/cm^3, $\delta = (74 + 2)$ μm.

In order to determine the effect of sodium hydroxide and hydrochloric acid on the membranes, measurements were made on two other samples from the same sheet of cellophane. One of them was immersed in NaOH only, in the manner and time indicated previously (M_2 membrane), and the other one in the hydrochloric dilute solution for 6 min (M_3 membrane). In both cases the membranes, after treatment, were washed as indicated above.

An untreated membrane, M_0, was also used for membrane potential measures.

Different NaCl dilute solutions were used for membrane potential and electrical resistance measurements, and pure water (twice distilled and deionized) in permeation experiments.

Membrane Potential

The membrane potential experimental set-up was essentially the same as that used in Refs. *12* and *15*, but there were some modifications: the solution tanks had a thermostatic jacket in order to maintain a constant temperature in the solution, and two small holes for platinum thermometers were made on both side of the membrane. A Crison 662/3 digital thermometer was used for temperature measurements.

Two different kind of membrane potential measurements were carried out: (i) The concentration of the solution on one side of the membrane (C_e) was kept constant while the concentration of the other side (C_i) was changed gradually. The constant concentration value was $C_e = 10^{-2}$ *M*, and C_i changed between 10^{-3} and 10^{-1} *M*. These measurements were made at 25°C with the M_0, M_1, and M_3 membranes. (ii) The concentrations of the solutions on both sides of the membrane were changed but the ratio of the concentrations was kept constant ($C_i/C_e = 2$). These experiments were carried out with the M_1 membrane at temperatures ranging between 25 and 65°C.

With both methods the electrode connected with the C_e solutions was grounded, so $\Delta\Phi = \Phi(C_i) - \Phi(C_e)$ for all measurements.

Resistance

The experimental device for measuring electrical resistance is similar to that described in Ref. *16*. In this case, alternate current via a Wayne-Kerr Bridge B905 with Ag/AgCl electrodes was used at four different frequencies. Measurements were made with the M_1 membrane in place in the membrane holder and without it. The difference between the values was taken as the membrane resistance. Two different concentrations (C), the same on both sides of the membrane, were used at 25°C ($C = 10^{-2}$ *M*, 5×10^{-2} *M*). Because of the considerable perturbations observed in resistance values during stirring, the measurements were made without stirring.

Hydraulic Permeability

The experimental arrangement for measuring the hydraulic permeability is described in Ref. *17*. A constant pressure method was used: the position of the air/water interface in a capillary tube on one side of the cell was read at different times while keeping the water level constant in a vertical capillary tube at the other side of the cell. The pressure difference ranged between 10 and 45 cm of water for each series of measurements. A different series of measurements was made with the M_1 membrane, and the temperature ranged between 40 and 65°C. Since the membrane hydraulic permeability is independent of the stirring rate (*4*, *14*), these measurements were carried out without stirring.

Equation (2) can be written

$$J = (dy/dt)(\rho q_0/M) = (q/\delta)A\Delta P \tag{3}$$

where ρ and M are the density and molecular weight of pure water, respectively; y is the position of the air/water interface in a horizontal capillary tube of cross-section q_0 at time t; and q, δ, and A have the meanings indicated previously.

By observing the air/water interface position in the horizontal capillary at different times, a set of pairs with values (y,t) were obtained for a given temperature. Measuring the slopes obtained with these values for each one of the series allowed us to obtain the hydraulic permeability of the membrane at that temperature.

RESULTS AND DISCUSSION

Figure 1 shows variations of the membrane potential with $\log (C_i/C_e)$ at $C_e = 10^{-2}\ M$ for the four membranes. Curves similars to these have been obtained by others with cellulose acetate and cellophane membranes (*6*, *18*). From Fig. 1 it can be seen that the values for membranes M_1 and M_2 are very similar, which means the main effect on membrane M_1 must be due to the NaOH treatment. There is also a big difference between the membrane potential values for these membranes and those for membranes M_0 and M_3, the latter being more negative.

Demish and Pusch (*6*) obtained the following expression for the fixed charge concentration in the membrane, X, by taking into account the

minimum condition ($d(\Delta\Phi)/dC_i = 0$) for the curve (electrolyte 1:1, and partition coefficient $k = 1$):

$$X = 2C_{i,\min}U/(1 - U^2)^{1/2} \tag{4}$$

where $C_{i,\min}$ is the concentration at the minimum and U is obtained from the slope of the right-hand branch of the curve. Values of X for all the membranes are shown in Table 1. Quite similar values were obtained for all the membranes, which have the same order of magnitude as those found in Ref. *12* with another cellophane membrane.

Permselectivity, which is a measure of a membrane's selectivity of the counterions over the co-ions, has been calculated for all the membranes. The permselectivity was obtained by the expression (*19*)

$$P_s = ((E/E_{\max}) + 0.5 - t_+^\circ)/(1 - t_+^\circ) \tag{5}$$

where E is the electrical potential difference measured between both sides of the membrane, $E_{\max} = -(RT/2F)$ ln (C_i/C_e), and t_+° is the cation transport number in free solution.

In Fig. 2, permselectivity versus log (C_i/C_e) is shown. P_s values decrease when C_i increases for all membranes. This decrease is quite strong for the three treated membranes and rather weak for the untreated membrane. For the M_0, M_1, and M_2 membranes, the permselectivity nearly reaches a constant value at high concentrations. This kind of behavior for P_s values must be due to a Donnan effect associated with the small fixed charge in the membrane, which can have some influence at low external concentrations ($C < X$). The sequence of permselectivities is $P_s(M_3) > P_s(M_0) > P_s(M_2) > P_s(M_1)$. It can be seen that the membrane treated by the Rastogi procedure and the one treated with NaOH have more similar permselectivity values, and both also exhibit less permselectivity than the

TABLE 1
Fixed Charge Concentration in the Membrane (X) and $C_{i,\min}$ Values for Different Cellophane Membranes Determined by Using Eq. (4)

Membrane	X (mol/L)	$C_{i,\min}$ (M)
M_0	1.33×10^{-2}	0.058
M_1	1.10×10^{-2}	0.036
M_2	1.03×10^{-2}	0.039
M_3	1.25×10^{-2}	0.053

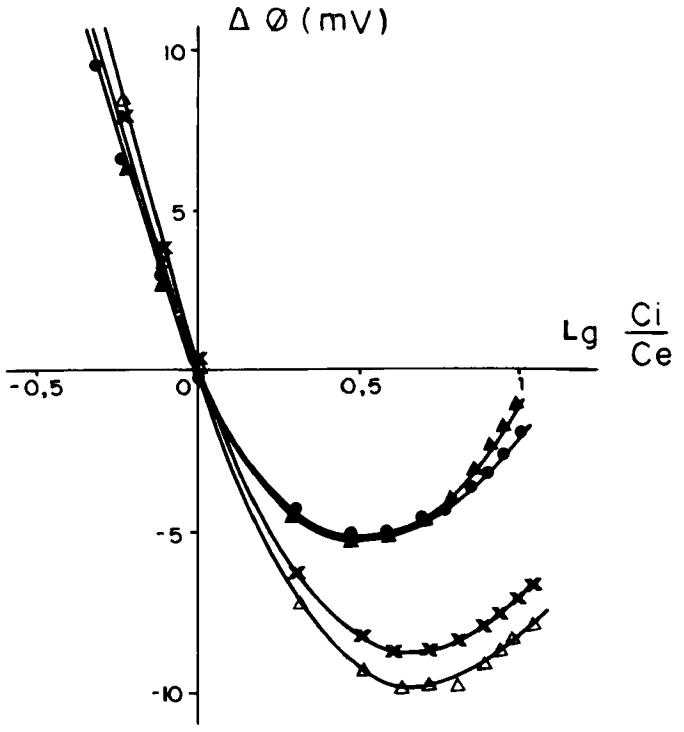

FIG. 1. Variation of membrane potential values versus log C_i/C_e. (×) M_0 membrane; (▲) M_1 membrane; (●) M_2 membrane; (△) M_3 membrane.

untreated membrane, while P_s values for the HCl-treated membrane are much higher than those for the untreated membrane at low concentration. Differences for the M_1 and M_2 membranes in membrane potential and permselectivity values, and those for the M_0 membrane, may be due to the higher porosity of the M_1 and M_2 membranes because of their treatment with NaOH solutions, as indicated by Rastogi et al. (*13*).

From Eq. (1), and keeping constnat the concentration ratio on both sides of the membrane ($C_i/C_e = \gamma$ = constant), Aizawa et al. (*20*) obtained the following linear relationship between $\Delta\Phi$ and $1/C_e$:

$$\Delta\Phi = \frac{RT}{F}\left[(2t_- - 1)\ln\gamma + \frac{2(\gamma - 1)}{\gamma} t_-(1 - t_-)\frac{X}{C_e}\right] \qquad (6)$$

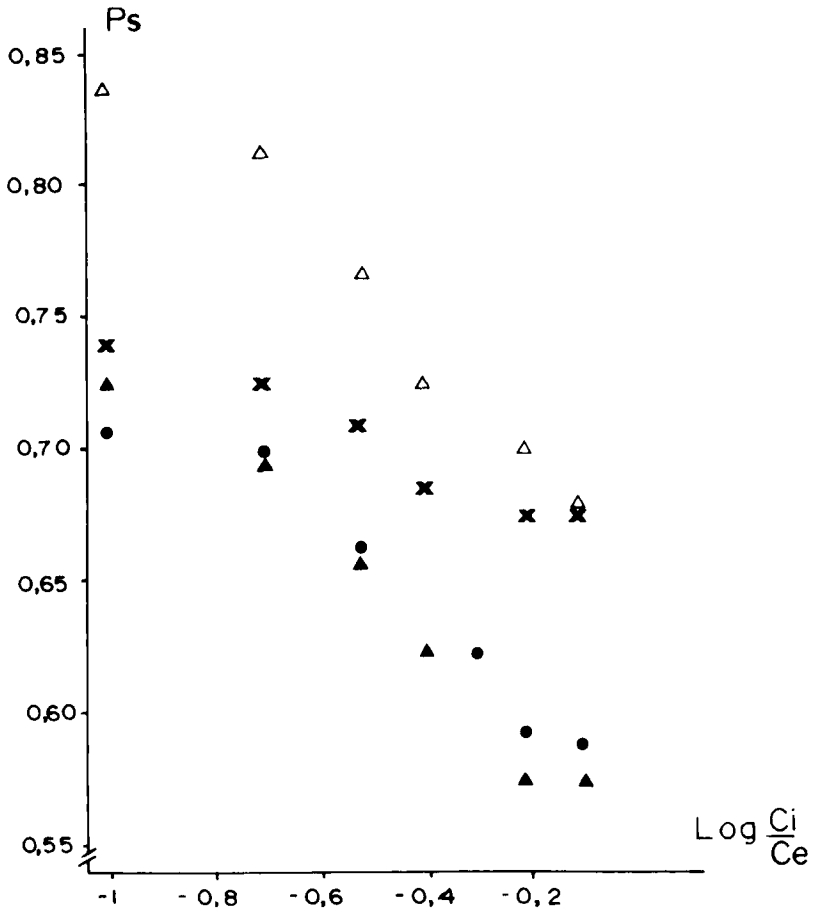

FIG. 2. Variation of permselectivity versus log C_i/C_e. (×) M_0 membrane; (▲) M_1 membrane; (●) M_2 membrane; (△) M_3 membrane.

where dilute solutions are considered and concentrations were used instead of activities.

The variation of $\Delta\Phi$ with concentration for the M_1 membrane at a constant ratio ($\gamma = 2$) and two different temperatures is shown in Fig. 3. Straight lines similar to these were found for all temperatures studied, with values ranging between 25 and 65°C. Equation (5) tells us that the average value of anions in the membrane, t_-, and the fixed charge concentration in the membrane, X, can be calculated from the origin on

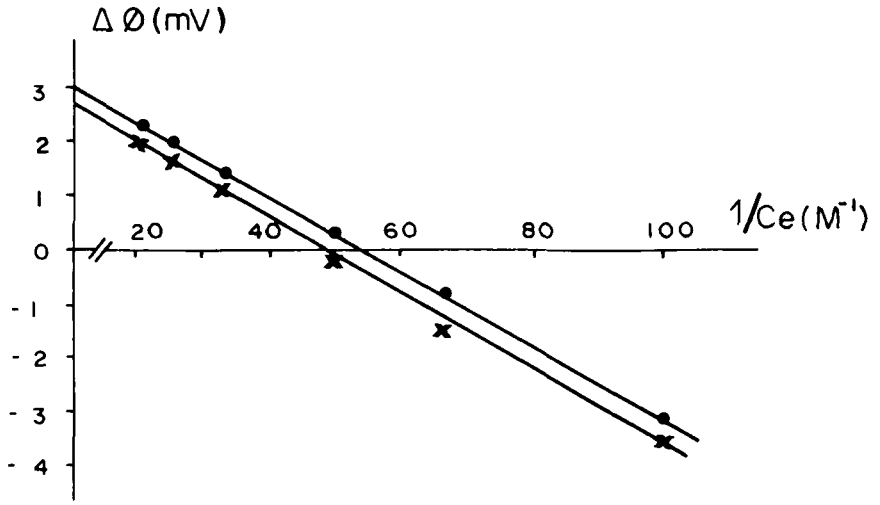

FIG. 3. Membrane potential values versus $1/C_e$ for the M_1 membrane: (●) at 25°C, (×) at 55°C.

the ordinate and the slope of the fitting of the experimental values to Eq. (6), respectively. The least-squares method was used, and the correlation coefficients obtained were higher than 0.99 for all temperatures. Table 2 shows the variation of t_- and X with temperature. No systematic variations of t_- and X values with temperature have been found; the smallest value was obtained at 55°C.

Electrical resistance values for the M_1 membrane at four frequencies are shown in Table 3. A decrease of resistance values with increasing

TABLE 2
Variation of Transport Number (t_-) and Fixed Charge Concentration in the Membrane (X) with Temperature for Membrane M_1 (Eq. 6)

T (°C)	t_-	X (mol/L)
25	0.61 ± 0.03	$(-1.12 \pm 0.05) \times 10^{-2}$
40	0.61 ± 0.02	$(-1.37 \pm 0.03) \times 10^{-2}$
50	0.58 ± 0.04	$(-1.10 \pm 0.07) \times 10^{-2}$
55	0.59 ± 0.03	$(-0.89 \pm 0.06) \times 10^{-2}$
60	0.60 ± 0.03	$(-1.28 \pm 0.06) \times 10^{-2}$
65	0.56 ± 0.08	$(-1.02 \pm 0.05) \times 10^{-2}$

TABLE 3
Electrical Resistance of M_1 Membrane at Four Different Frequencies and Two NaOH Concentrations

f (Hz)	$C = 10^{-2}$ M, R (Ω)	$C = 5 \times 10^{-2}$ M, R (Ω)
10^2	125	23
4×10^2	115	20
10^3	115	19
10^4	115	20
dc	160[a]	30[a]

[a]Values obtained with dc current and stirring.

concentration is observed, which agrees with the results found in Refs. *6* and *19*. In Table 3, the electrical resistance obtained with dc current is also presented. There is not a big difference between the electrical resistance values found by using both methods, but the values obtained with ac current are lower than those found with dc current. This could be due to the different methods used (capacitative effect with ac current, etc.), or because there is a different concentration value in the layers closer to the membrane with respect to the bulk solution when the system is not stirred.

Figure 4 shows the experimental relation between $J\delta/q$ and ΔP at two different temperatures for the M_1 membrane. Straight lines similar to these were obtained at the other temperatures. The hydraulic permeability at one given temperature was calculated from the slope of each one of these lines, as given by Eq. (2). In general, A values increase when the temperature increases, and a very high value of A was obtained at 65°C. Experimental results are drawn in Fig. 5.

Haase et al. (*21*) found a linear increase of hydraulic permeability when the temperature increases, and a strong increase of A values at temperatures higher than 70°C for Cellophane 600 membranes (untreated) with characteristics similar to those used in this work. They also found a deviation from linearity at temperatures very close to 60 and 65°C. Those values were not considered correct by the authors. In this work, slight changes in the membrane fixed charge concentration and in the hydraulic permeability values were found at 55°C. This could indicate a change in the membrane characteristic for the interval $55°C < t < 65°C$ (depending on the membranes) instead of an experimental error. Because of that, measurements of hydraulic permeability for temperature intervals of 2°C are being made.

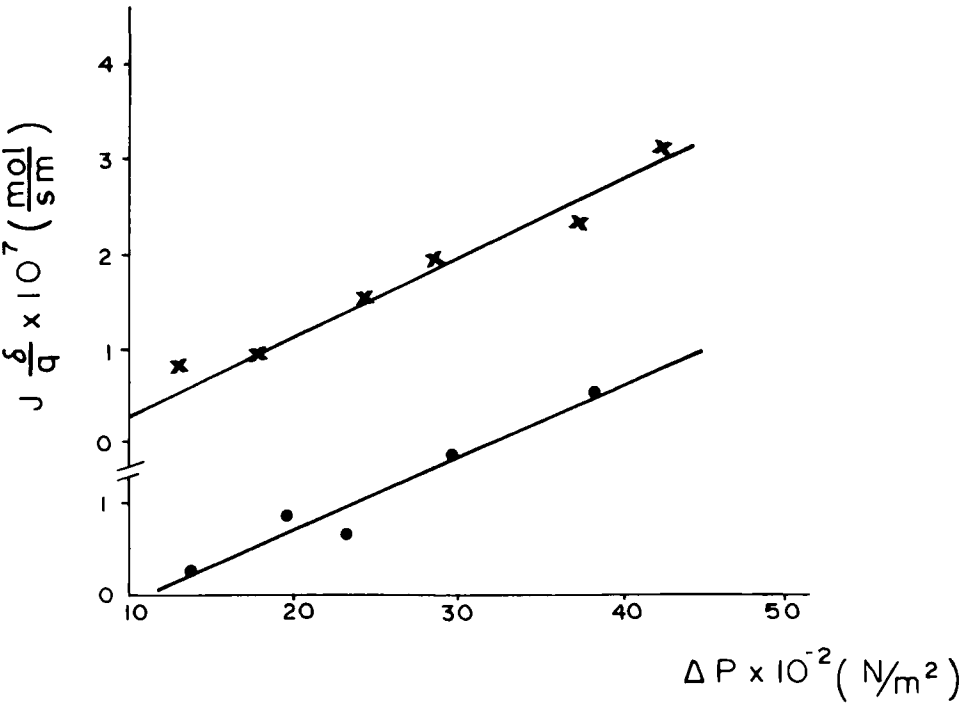

FIG. 4. Variation of $J\delta/q$ values with ΔP: (●) at 40°C, (×) at 55°C.

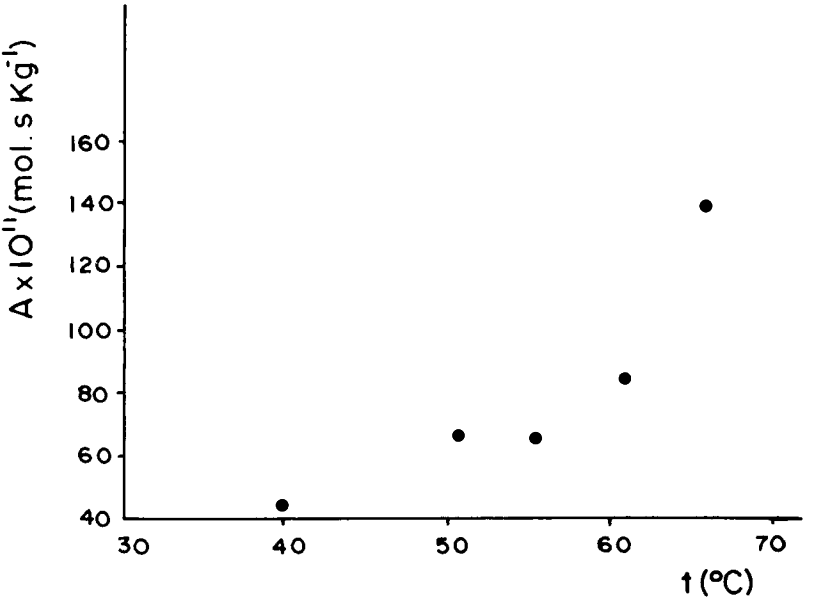

FIG. 5. Hydraulic permeability versus temperature.

As a result of this work, a higher porosity for cellophane membranes treated with NaOH solution is assumed, but no other changes in parameters were found.

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