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A Study on the Variation with Temperature of Fixed Charge and Membrane Structure of Cellophane Membrane

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Abstract

Membrane potentials for a cellophane membrane at different temperatures (25–60°C) have been measured. Experimental results were analyzed on the basis of the Kobatake equation, and some characteristic parameters have been estimated. The activation energy was also obtained. A variation of the membrane structure at the highest temperature studied has been found.

INTRODUCTION

In previous works (*1*, *2*), treated and untreated cellophane 600 P membranes have been studied. Among other parameters, the concentration of fixed charge (X) and the average value of the apparent anion transport number ($t_-[\text{ap}]$) in the membrane were studied on the basis of the Teorell-Meyer-Sievers theory, by means of the Aizawa et al. (*3*) approximation, for the membrane potential equation (*4*, *5*); but this approximation is only valid when the external concentrations are much higher than the concentration of fixed charge in the membrane ($C \gg X$). Because the average value of X for both treated and untreated membranes was of the order of 10^{-2} M, only the membrane potential at relatively high concentrations was measured ($C > 4 \times 10^{-2}$ M).

On the other hand, some experiments carried out with cellophane membranes of similar characteristics have shown discrepancies in their results, mainly in those processes related to temperature dependence (*6*, *7*), which were attributed to the different experimental methods or membrane treatment. In our papers, a linear increase of the hydraulic permeability with temperature was found for both membranes, but no systematic variation of the fixed charge was obtained (only a slight decrease at 55°C with the treated membrane). In order to clarify the possible effects of temperature on the membrane–solution system, it will be interesting to know if the small changes are due to the variation of the solution with temperature or to the membrane itself.

In this work, membrane potentials ($\Delta\phi$) through a cellophane membrane for a wide interval of concentrations ($10^{-3}\ M < C < 10^{-1}\ M$) and different temperatures have been studied. The results have been analyzed by means of the Kobatake equation for the membrane potential (*8*). This equation shows a relationship between the membrane potential and three parameters: X, a, and β, which can be evaluated from the experimental values. The parameter β is related to the fixed charge in the membrane and a factor which depends on both the viscosity of the solution and the structural details of the membrane. For this reason, the Kobatake equation could be used to elucidate if the variations with temperature are due to the electrolyte solution or to changes in the membrane structure. In this study, an increase of the β value at 60°C, higher than that due to the viscosity of the solution, has been found. The fixed charge values obtained in this work are of the same order (but always higher) as those found in Ref. *2*, and the discrepancies are attributed to the different statements of both theories (effect of the water transport through the membrane). The activation energy and the average water transport number in the membrane at each temperature have also been obtained.

THEORY

Kobatake and coworkers (*8*), on the basis of the thermodynamics of irreversible processes and the integration of the flux equations, have obtained the following expression for the membrane potential when a negatively charged membrane separates two solutions of 1:1 electrolyte of concentrations C_1 and C_2 ($C_1 > C_2$):

$$\Delta\phi = (-RT/F)\{(1/\beta)\ln(C_1/C_2)[1 + (1/\beta) - 2a] \times \ln[(C_1 + a\beta\gamma)/(C_2 + a\beta\gamma)]\} \quad (1)$$

a and β, two parameters, are written as

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

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

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.

In order to determine the parameters X, a, and β when the concentration ratio has a constant value ($C_1/C_2 = \gamma$), two limiting forms of Eq. (1), depending on the concentration of the solutions, were derived. At low concentrations:

$$\Delta\phi = (-RT/F)[(1/\beta)\ln\gamma - ((\gamma - 1)/a\beta\gamma) \times (1 + (1/\beta) - 2a)(C_2/X)] \quad (4)$$

At high concentrations:

$$1/t_-[\mathrm{ap}] = [1/(1 - a)] + [(1 + \beta - 2a\beta) \times (\gamma - 1)a/2(1 - a)^2 \ln\gamma](X/C_2) \quad (5)$$

The apparent cation transport number at each pair of concentrations ($t_-[\mathrm{ap}]$) is obtained from the experimental data by

$$\Delta\phi = (RT/F)(1 - 2t_-[\mathrm{ap}])\ln\gamma \quad (6)$$

Equations (4) and (5) represent two linear relationships, one between $\Delta\phi$ and C_2, and another between $1/t_-[\mathrm{ap}]$ and $1/C_2$. By fitting of the experimental points to those expressions, the parameters X, a, and β can be determined.

EXPERIMENTAL

Material

Measurements have been carried out with a cellophane 600 P membrane with characteristics similar to those indicated in Ref. *1*. Before use, the membrane was washed several times and it was maintained 48 h in twice distilled and deionized water. Before carrying out each series of measurements, the membrane was immersed for at least 12 h in a 10^{-3} M solution of NaCl. The NaCl solutions had a purity of 99.5%, and they were obtained by diluting a 2-M stock solution.

Experimental Device

The membrane potential experimental device is similar to that used in Ref. *1*, and it is schematically shown in Fig. 1. It basically consists of three parts: 1) Two solution tanks of 1 L capacity, each one surrounded by a thermostatic jacket to maintain the temperature of the solutions constant; 2) two circulatory systems, each one with a centrifugal pump (the output was of the order of 600 cm^3/min), which provides a turbulent flow within the cell in order to disturb the polarization layer in the solution near the membrane; 3) the cell itself, which was formed by two half-cells made of methacrylate, each with an approximate volume of 64 cm^3, and a membrane holder of 0.5 cm^2 area. The membrane was supported by rubber rings. The two half-cells were clamped together by a steel screw.

The membrane potential was measured by calomel electrodes placed close to the membrane and in contact with the solutions via KCl saline bridges, and joined to a digital voltmeter. For temperature measurements, a platinum thermometer was placed in each half-cell, which was connected to a Crison 662/3 digital thermometer.

The membrane potential measurements were carried out by keeping the concentration ratio of the solutions constant on both side of the membrane, $C_1/C_2 = \gamma = 2$, for the interval of concentrations (10^{-3} $M < C < 10^{-1}$ M). In all cases $\Delta\phi = \phi(C_1) - \phi(C_2)$. Measurements were made at different temperatures (25–60°C).

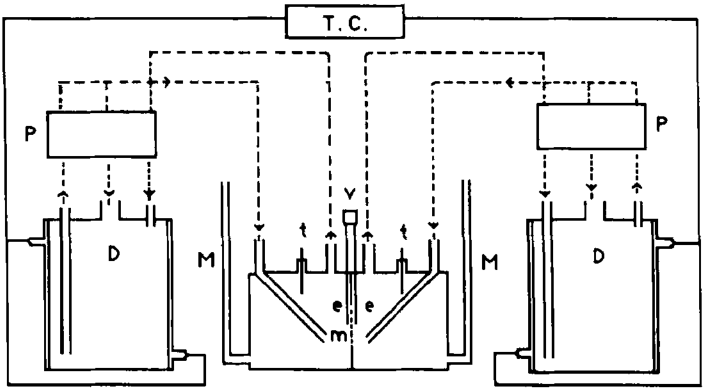

FIG. 1. Experimental apparatus. m: membrane, e: calomel electrode; M: manometer; P: pump; t: thermometer; D: tank; V: voltmeter; T.C.: temperature control.

RESULTS AND DISCUSSION

The membrane potential values measured between both sides of the cellophane membrane have been rescaled by dividing by the factor RT/F and calling these new dimensionless values $\Delta\phi^*$. Figure 2 shows the variation of $\Delta\phi^*$ with $1/C_2$, when C_2 ranges between 2×10^{-3} M and 10^{-1} M at different temperatures. A nonlinear behavior for the whole interval of concentration exists, and two different zones, which depend on the C_2 values, can be seen. This picture indicates, that the two limiting equations derived above (Eqs. 3 and 4) for the membrane potential could be applied to this membrane.

In Fig. 3, $\Delta\phi^*$ versus C_2 for low external concentrations at different temperatures has been drawn. The fitting of the experimental points, using the least-squares method, permits us to obtain the parameter β at each given temperature from the value of the origin ordinate of the straight line corresponding to that temperature.

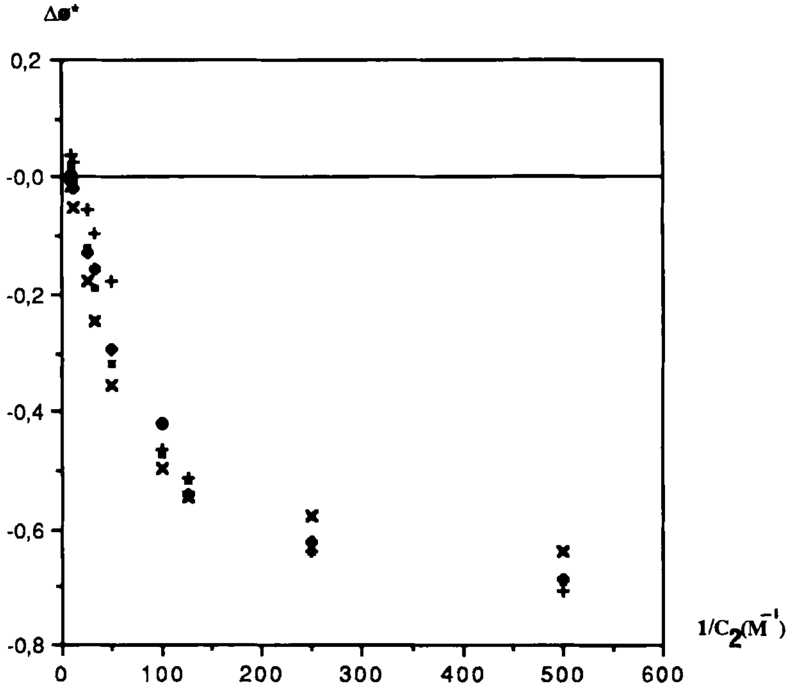

FIG. 2. Variation of $\Delta\phi^*$ with $1/C_2$ for the whole interval of concentrations at different temperatures: (+) 25°C; (◇) 40°C; (■) 50°C; (×) 60°C.

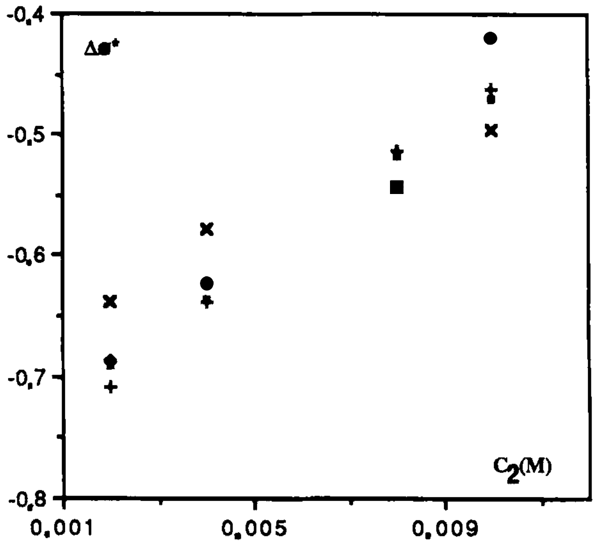

FIG. 3. Δφ* versus C_2, for low values of the concentration C_2, at different temperatures: (+) 25°C; (◇) 40°C; (■) 50°C, (×) 60°C.

Figure 4 shows $1/t_-[\mathrm{ap}]$ as a function for C_2 at high values of the salt concentration. From the intercept of these straight lines, the value of a at each temperature was determined. By means of Eq. (2) the values of the mobility ratio of the ions in the membrane, u/v, were calculated, and the results are shown in Table 1. These values do not differ very much from those corresponding to a free solution for the same interval of concentrations and temperatures.

Once a and β values are known, the concentration of fixed charge in the membrane at low concentrations (X_p) and high concentrations (X_g) can be obtained from the slopes of the straight lines represented in Figs. 3 and 4, respectively. X_p and X_g values are also shown in Table 1. Quite good agreement between these values has been found, but the results obtained at low concentrations are always lower. Similar behavior have been indicated in the literature for cellulose acetate membranes (*9*). A linear plot of ln X_g versus $1/T$ is shown in Fig. 5, the slope of which gives the activation energy, E_a, as required by the Arrhenius equation. The E_a value obtained was 3 kcal/mol.

In Table 1, the X values obtained by the Aizawa approximation (from Ref. *2*) are also presented. A comparison of X and X_g (both measured at the same interval of concentrations) indicates that X_g values are 3 to 4 times higher than X. These discrepancies can be attributed to the different

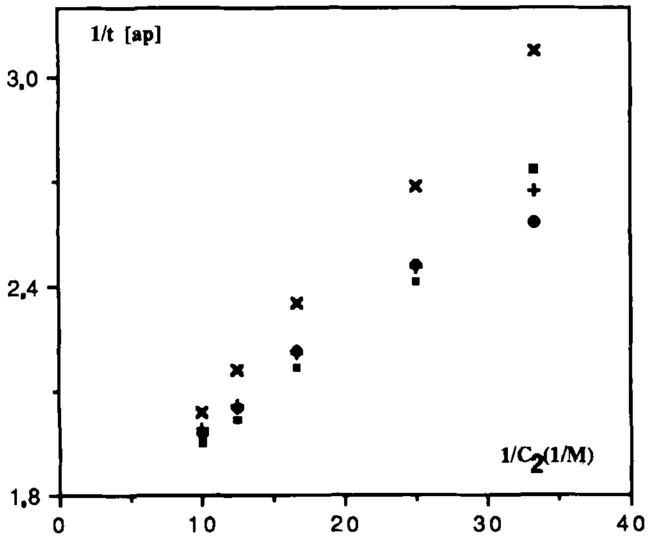

FIG. 4. Variation of $1/t_-$[ap] with $1/C_2$, at different temperatures and high values of the external concentrations: (+) 25°C; (◇) 40°C; (■) 50°C; (×) 60°C.

statements for both theories. One of the most evident differences between the TMS and the Kobatake equations for the membrane potential comes from the fact that the TMS theory does not take into account the transport of water through the membrane. For this reason, knowledge of the water transport number for the cellophane membrane could give us an idea of the relative importance of this effect on the membrane potential. For an 1:1 electrolyte, the apparent and true transport numbers are related by *(10)*

$$t_+[\mathrm{ap}] = t_+ - 10^{-3} M t_w \langle m \rangle \tag{7}$$

TABLE 1

Variation with Temperature of the Ionic Mobility Ratio (u/v), the Membrane Fixed Charge ($|X_p|$), ($|X_g|$) and (X) (from Eqs. 4 and 5 and Ref. 2, respectively), and the Average Water Transport Number (t_w)

t (°C)	u/v	$\lvert X_p\rvert(M)$	$\lvert X_g\rvert(M)$	$\lvert X\rvert(M)$	t_w
25	0.695	4.05×10^{-2}	4.10×10^{-2}	1.48×10^{-2}	115
40	0.739	3.98×10^{-2}	4.66×10^{-2}	1.50×10^{-2}	125
50	0.628	4.26×10^{-2}	6.07×10^{-2}	1.70×10^{-2}	135
60	0.652	5.53×10^{-2}	6.80×10^{-2}	1.70×10^{-2}	150

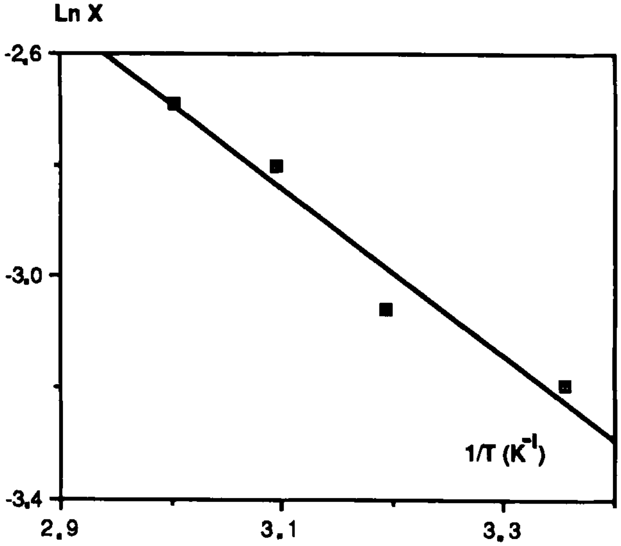

FIG. 5. Arrhenius plot of fixed charge.

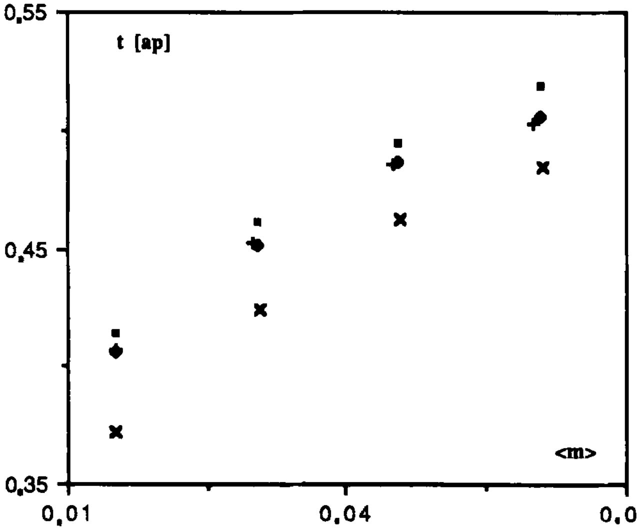

FIG. 6. t_+[ap] versus mean molality of both external solutions at different temperatures: (+) 25°C; (◇) 40°C; (■) 50°C; (×) 60°C.

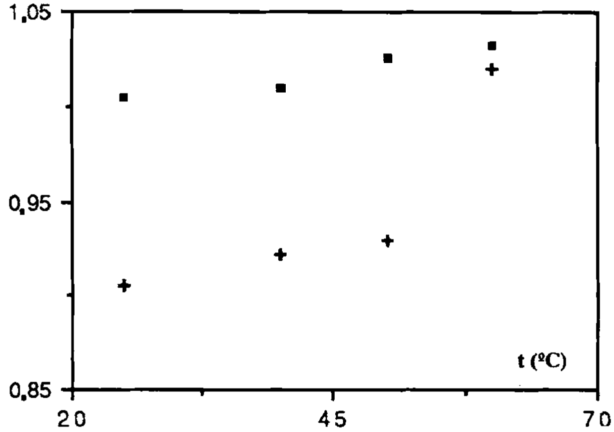

FIG. 7. Variation with temperature of (+) β parameter and (■) relative viscosity of the solution.

where t_+ is the cation transport number in the membrane, t_w is the water transport number, M is the molecular weight of water, and $\langle m \rangle$ is the average molality of the solutions separated by the membrane.

A plot of t_+[ap] versus $\langle m \rangle$ for different temperatures has been drawn in Fig. 6. From the slopes of these straight lines, the average value of t_w for the interval of concentrations studied was obtained. These results are also written in Table 1. The relatively high values obtained for t_w indicate that water transport across the cellophane membrane could be important, and it could explain the differences between X and X_g values, as was indicated above.

Variation of the parameter β with temperature is shown in Fig. 7. From 25 to 50°C a linear increase of β with temperature exists, which could be related to the linear increase of the relative viscosity with temperature for that interval of concentrations (which is also drawn in Fig. 7), but at 60°C a high value of β was obtained. Taking into account Eq. (3) and using the calculated values for X_p, the ratio K/u has been estimated. For the interval of temperatures between 25 and 50°C, the average value was $(4.90 + 0.18) \times 10^{-4}$, but at 60°C the value was 3.83×10^{-4}, which differs appreciably. Because this difference cannot be attributed to the change of u with temperature, it could be due to the parameter K.

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