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Measurement of the ionic conductance of regenerated cellulose membranes in alkaline solutions with attention to current refraction

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A novel cell is described for making measurements of membrane conductivity by an a.c. technique. Membrane resistance was determined from measurements of the cell resistance for various numbers of membrane layers. Plots of resistance vs. membrane thickness were curved due to current refraction into the region clamped between the mating faces of the cell. A non-empirical correction was made for this refraction which linearized the data and enabled accurate values of membrane conductance to be achieved. Conductance and thickness values for regenerated cellulose membranes in CsOH, KOH, NaOH and LiOH over a wide range of concentrations are reported.

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1. Introduction

This paper describes one aspect of a programme of work aimed at improving the understanding of the behaviour of films of regenerated cellulose in strongly alkaline solutions. The original interest of the authors arose from the importance of such membranes as separators in some alkaline battery systems [1]: the work has wider implications and in particular is relevant to the mercerization of cotton, an important process in the textile industry.

Sixty years ago Neale [2] recognized that the swelling of cellulose in alkaline solutions arises from osmotic pressure generated via a Donnan equilibrium. Consequently, it is important to study the ions and solvent within the cellulose to gain additional insight. Such investigations include the measurement of anionic and cationic concentrations [3], transference numbers of ions and solvent [4] and ionic conductivity. The present paper concerns the last aspect.

2. Experimental details

The conductivity cell, shown in Fig. 1 was constructed from methyl methacrylate (Perspex). Electrodes were platinized platinum bonded at the rear to threaded steel rods. The water jacket, which was fed from a water bath at 25° C was in four sections, the water being pumped from one section to the next and finally back to the bath. The cell consisted of two almost identical halves which when separated allowed the membrane to be placed between the ground faces. Alignment of the two parts was achieved via close fitting pegs and matching holes in those faces.

Holes were punched through presoaked membranes using a template for positioning. Where measurements involved more than one layer of membrane the pieces were lightly rolled on a flat plate to expel gas bubbles and excess electrolyte trapped between the layers. The cell was then assembled and the four through bolts evenly tightened to a final torque of 0.5 N m using a torque screwdriver (Torqueleader Quick-Set) with appropriate head.

Electrolyte was introduced to each side of the membrane using a hypodermic syringe. Measurements of cell resistance were then made using a Wayne-Kerr Autobalance Universal a.c. bridge type B642 operating at 1592 Hz. Marks on each half of the cell allowed the change in electrode separation due to incorporation of the membrane to be measured with a cathetometer.

The regenerated cellulose used was PUDO 193 manufactured by Du Pont: it contained no additives or softener and had a thickness on receipt of approximately 28 μm. Electrolyte solutions were prepared by dissolution of (i) KOH (Analar grade, BDH), (ii) NaOH (Analar grade, Fisons), (iii) LiOH (Laboratory reagent, BDH) or (iv) CsOH (99 + %, Aldrich) in singly-distilled water. Pieces of membrane were never exposed to more than one solution of a particular alkali and given concentration. Soaking times were at least one day at 25° C in a sealed container.

3. Results and discussion

The conductivity cell described above had some features in common with that of Lorimer *et al.* [5] with the additional advantages of an integral thermostated water jacket and through-bolts tightened to a reproducible torque. As a result, once assembled the cell could be operated on the bench exposed to the air at

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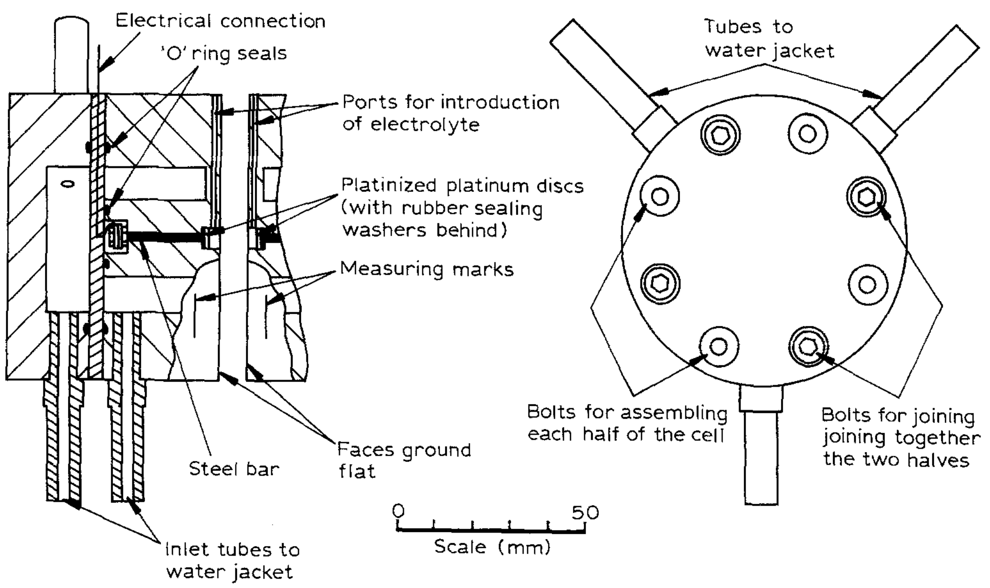

Fig. 1. End view and cross-sectional view of the membrane conductivity cell.

room temperature. The diameter of the orifice defining the area of membrane exposed to electrolyte was measured using a cathetometer as 6.15 mm.

In an initial test the separation of the cell halves was measured with an increasing number of layers of presoaked membrane (Fig. 2). A linear regression analysis indicated a membrane thickness in 7.1 M KOH of 87.5 ± 3.5 μm: this compared with measurements made on single layers using a thickness gauge [3] of 84 ± 3 μm. This showed that within experimental error the separation of the cell electrodes was increased by an amount equal to the membrane thickness and confirmed the proper functioning of the cell.

Some measurements made of membrane resistance are shown in Fig. 3 in a normalized format. The points shown as circles represent the primary data and fall on curved lines when plotted against membrane thickness. The objective was to determine a value of the ionic conductivity of the membrane from each curve.

The curvature on these plots was due to current refraction into the region of the membrane clamped between the ground faces surrounding the active orifice of the conductivity cell (Fig. 4) as was pointed out by Tye [6]. The true ionic conductivity of the membrane may be determined from the slope of the tangent to the curve at zero membrane thickness. However, it is difficult to determine this slope accurately and consequently it is more satisfactory to correct the points for refraction to reveal a straight line of the required slope. A satisfactory analysis not previously applied to the correction of membrane

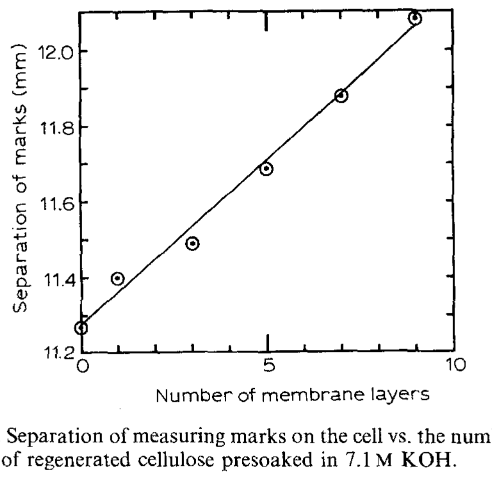

Fig. 2. Separation of measuring marks on the cell vs. the number of layers of regenerated cellulose presoaked in 7.1 M KOH.

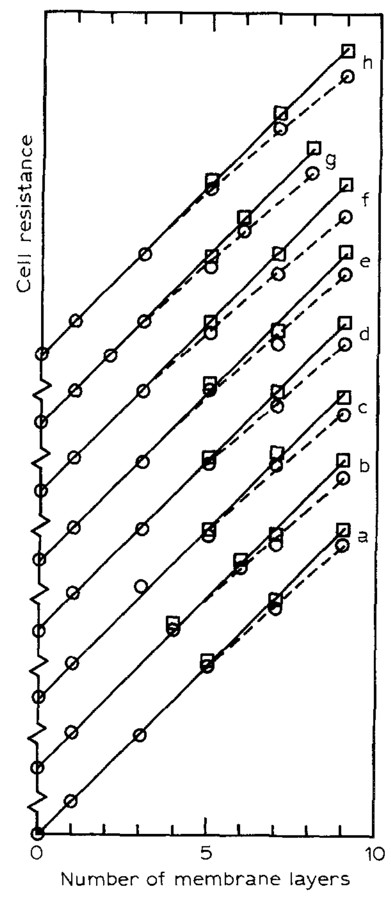

Fig. 3. Resistance measurements for membrane in KOH solutions. Solution molarity, intercept (Ω), slope (Ω) per layer: (a) 0.09, 49.6, 4.84; (b) 0.48, 10.7, 0.981; (c) 1.09, 4.97, 0.480; (d) 1.94, 3.22, 0.331; (e) 3.60, 2.15, 0.205; (f) 5.27, 1.86, 0.164; (g) 5.95, 1.79, 0.159; (h) 6.99, 1.82, 0.174. These numbers apply to the best lines through values corrected for refraction. (○) Primary data; (□) corrected data.

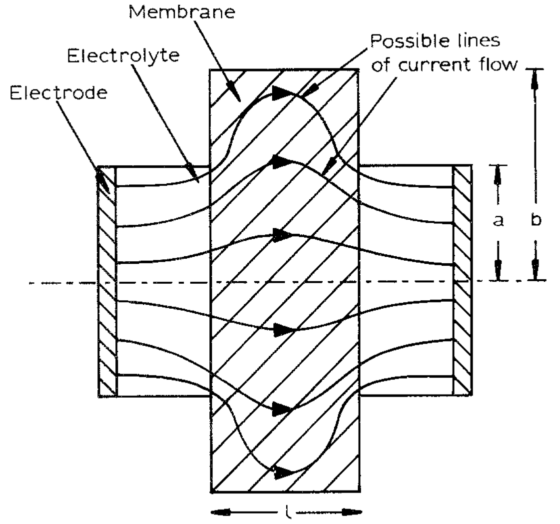

Fig. 4. Representation of current refraction in the membrane. l is the membrane thickness; a and b are the electrode and membrane radius, respectively.

conductivity data, may be formulated by applying the mathematical treatment of Barrer *et al.* [7]. It should be noted that the theoretical analysis [7] assumes constant flux per unit area over the membrane: the experimental tests of the theory carried out by Barrer *et al.* indicated that the error introduced by this assumption was negligible.

The results of the computations carried out in the present work are presented in Fig. 5. This shows the reduction factor F, which is the factor by which the measured resistance of the membrane is reduced as a result of current refraction, plotted against l/a the dimensionless membrane thickness (l, a and b are defined in Fig. 4). It should be noted that with the large b/a values appropriate to typical conductivity cells the reduction factor is insensitive to the precise value of b/a as was shown by Barrer *et al.* and confirmed here by the shaded points.

The data in Fig. 5 are accurately represented by the equation

$$F = 1 - 0.313(l/a) + 0.017(l/a)^2 \qquad (1)$$

This equation may be used for correcting membrane resistance measurements when $l/a < 1.0$ and $b/a \geqslant 4$. As such it covers the range appropriate to most membrane conductivity work. It is noteworthy that to a first approximation the points in Fig. 5 are linear in accordance with Tye's earlier [6] observation.

The correction given by Equation 1 was made to the data by applying the following equation

$$R_l' = \frac{R_l - R_0}{F} + R_0 \qquad (2)$$

R_l and R_0 are the measured cell resistances with and without the membrane respectively and R_l' is the cell resistance corrected for refraction. It is arguable that application of Equation 2 is excessively dependent upon the value of R_0 which itself might be significantly in error. This point will now be briefly considered.

The membrane resistivity is determined from the slope of the straight line resulting from plotting cell resistance corrected for refraction vs. membrane thickness. In the following analysis the fractional change in this slope is determined as a result of an error ΔR_0 in the cell resistance with zero membrane thickness bringing the observed value to $R_0 + \Delta R_0$. Two points are considered, at membrane thicknesses l_1 and l_2 and observed cell resistances of R_1 and R_2 respectively. If the error in $R_1' - R_2'$ resulting from the error ΔR_0 in R_0 is written as $\Delta(R_1' - R_2')$, i.e. bringing the calculated value to $(R_1' - R_2') + \Delta(R_1' - R_2')$, then it follows by application of Equation 2 that

$$\Delta(R_1' - R_2') = -\Delta R_0\left(\frac{1}{F_1} - \frac{1}{F_2}\right) \qquad (3)$$

F_1 and F_2 are the reduction factors appropriate to membrane thicknesses l_1 and l_2 respectively. To a first approximation F is linearly related to l (Fig. 5) so that the following equation may be written

$$F = 1 - m\left(\frac{l}{a}\right) \qquad (4)$$

where m is a constant approximately equal to 0.31. Invoking the binomial expansion and ignoring second and higher order terms Equation 4 becomes

$$\frac{1}{F} = 1 + m\left(\frac{l}{a}\right) \qquad (5)$$

Substituting from Equation 5 into 3 it follows that

$$\Delta(R_1' - R_2') = -\frac{m}{a}\Delta R_0(l_1 - l_2) \qquad (6)$$

If the membrane resistivity is written as ρ then

$$R_1' - R_2' = (l_1 - l_2)\rho/\pi a^2 \qquad (7)$$

And from Equations 6 and 7

$$\frac{\Delta(R_1' - R_2')}{R_1' - R_2'} = -\pi a m \Delta R_0/\rho \qquad (8)$$

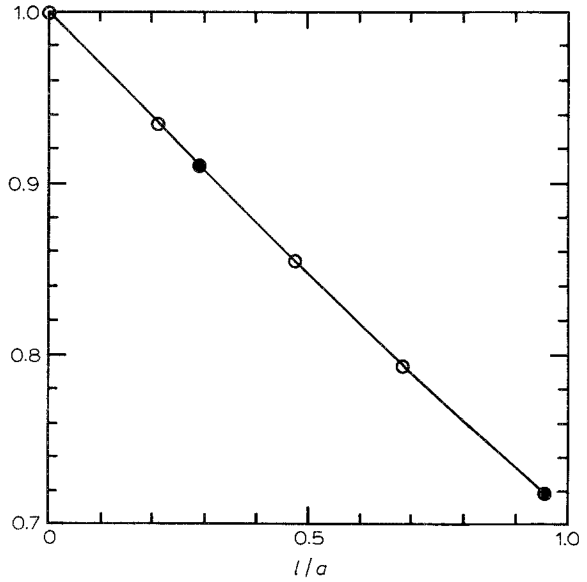

Fig. 5. Resistance reduction factor, F against l/a. (○) $b/a = 4$; (●) $b/a = 4$ or 13.

Table 1. Statistical analysis of correlation coefficients, r

Alkali	*(1 − r)/10⁻⁵*	
	Uncorrected data	*Corrected data*
CsOH	40 ± 10	7 ± 2
KOH	80 ± 9	35 ± 10
NaOH	139 ± 32	131 ± 34
LiOH	30 ± 10	10 ± 4

Results are shown as mean ± standard deviation of the mean.

Equation 8 shows that the fractional error in the calculated membrane resistance is directly proportional to ΔR_0. This indicates that the cell should be designed to minimize R_0 which in turn would tend to minimize ΔR_0: this is achieved in practice by siting the electrodes as close as is practicable to the membrane-solution interfaces. The error arising as quantified by Equation 8 was examined for the data in Fig. 3 together with that shown later in Table 2. It was assumed that to a first approximation ΔR_0 could be equated to the difference between the measured value of R_0 and that determined from the intercept of the best straight line through the points based upon the corrected data. A statistical analysis on the calculated values of $\pi a m \Delta R_0 / \rho$ revealed a standard deviation of 7×10^{-4} with a mean close to zero (3×10^{-5}) as expected. Thus it is concluded that errors in the determined values of the membrane conductivity due to errors in R_0 were negligible.

Table 2. Thickness and conductance values, the latter derived from data corrected for current refraction

Solution (M)		*Thickness per layer (μm)*	*Conductance per layer ($\Omega^{-1} cm^{-2}$)*
0.20	CsOH	59	1.47
1.28		81	8.82
3.10		82	15.3
5.70		88	18.7
8.22		77	12.7
0.09	KOH	55	0.697
0.48		60	3.44
1.09		66	7.02
1.94		72	10.2
3.60		79	16.5
5.27		109	20.5
5.95		110	21.2
6.99		87	19.4
9.79		79	13.5
11.90		90	10.9
14.59		119	7.80
0.40	NaOH	72	2.34
1.02		81	5.85
5.63		115	14.0
6.99		105	12.5
9.02		94	6.98
11.05		88	4.29
13.05		90	3.58
14.75		95	2.76
0.22	LiOH	66	1.16
1.79		95	9.16
3.80		134	15.6

Data corrected according to Equations 1 and 2 are shown as the squares in Fig. 3. Examination of the plots indicates that in most cases correction for refraction resulted in a marked improvement in linearity of the data. This was checked by carrying out linear regression analyses on both the uncorrected and corrected data. Analysis on the corrected data provided the slope and intercept of the best line shown as a continuous line in each case in Fig. 3. The analyses also provided values for the correlation coefficient, *r* (Table 1) which confirmed that there is indeed an improvement in linearity when the correction is applied to the results in CsOH, KOH and LiOH. In NaOH the analysis indicates no improvement: this result is thought to arise from the generally poorer quality of the data, as demonstrated by the greater deviation of *r* from unity, in these solutions. The likely error arising from not correcting for refraction for a maximum l/a value of only 0.35 is approximately 10%. Thus for typical experimental conditions, errors due to refraction can be substantial.

The conductance data for regenerated cellulose in the various alkaline solutions are presented in Table 2 together with thickness values determined previously [3]. All results, including those relating to NaOH have been corrected for current refraction as described above. The full significance of these ionic conductance data will be considered in a forthcoming publication [8].

4. Conclusions

The novel cell described enabled precise measurements of membrane conductivity to be made. Membrane resistance vs. thickness plots were curved due to a current refraction effect. The data were linearized by application of a non-empirical correction factor. This led to a substantial improvement in the accuracy of the measured membrane conductance.

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