

# Determination of lignosulfonate rejection from test results in the ultrafiltration of spent sulfite liquor

Kari Kovasin, Rauma-Repola Oy, Research Department, Rauma, Finland and Harry V. Nordén, Helsinki University of Technology, Department of Chemistry, Espoo, Finland.

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**SUMMARY:** A method is presented for the treatment of test results obtained in the ultrafiltration of spent sulfite liquor. The concentration polarisation model was utilized in the development of the method. The relative molecular mass distribution and its changes were taken into account in calculation of the mass transfer coefficient. The results of the procedure is the behavior of the membrane rejection of lignosulfonate in the course of ultrafiltration.

The method was adapted to the test results obtained at the ultrafiltration plant of Rauma Pulp Mill. The procedure is suitable for the processing of test results for plant design purposes.

**ADDRESSES OF THE AUTHORS:** K. Kovasin: Rauma-Repola Oy, Research Department, SF-26100 Rauma 10, Finland. H. V. Nordén: Helsinki University of Technology, Department of Chemistry, SF-02150 Espoo 15, Finland.

In membrane technology the quantity which describes the separation efficiency of the membrane is called the rejection of the solute. Rejection can be specified in two ways. The most common is according to eq. [1]:

$$R_{OBS} = 1 - c_p/c_b \quad [1]$$

The rejection of eq. [1] can be called the observed rejection because both solute concentrations  $c_p$  and  $c_b$  can be measured. In ultrafiltration and reverse osmosis, large circulation flows are used leading to practically a constant solute concentration on the concentrate side of the whole UF or RO unit. Therefore eq. [1] can also be called the rejection of the apparatus.

The rejection specified according to eq. [1] may, however, give a wrong picture of the separation properties of the membrane itself. In ultrafiltration, a concentration profile is developed on the concentrate side. The solute concentration increases when the distance to the membrane wall decreases (*fig. 1*). This phenomenon is called concentration polarisation. According to the symbols in *fig. 1*, the membrane rejection can be specified by eq. [2]:

$$R = 1 - c_p/c_w \quad [2]$$

The solute concentration in the close proximity of the membrane wall is very difficult to measure. If the concentration polarisation is strong, the rejections of eq. [1] and [2] differ markedly from each other. Under certain conditions, it is possible to calculate the solute concentration at the membrane wall,  $c_w$ , from test results. The membrane rejection can be estimated with eq. [2].

Nakao and Kimura (1) presented a method of calculating the membrane rejection from test results. If the pressure difference is constant between the concentrate and permeate side, a constant value can

be obtained for the membrane rejection, even though the observed rejection varies. This result is natural if the solute consists of one molecular size.

The lignosulfonates in spent sulfite liquor have a wide molecular size distribution. Therefore, it is evident that the membrane rejection changes when the molecular size changes. If the relative molecular mass distribution and its changes during ultrafiltration are taken into account, it is possible to establish the behavior of the membrane rejection in the course of ultrafiltration, e.g., as a function of the lignosulfonate purity in the concentrate.

If the behavior of the membrane and observed rejection are known from the ultrafiltration process, a simple method can be evolved for dimensioning full-scale systems for the ultrafiltration of spent sulfite liquor.

Test results are needed for the determination of the rejections; each sulfite mill has a spent liquor which is strictly speaking unique as regards ultrafiltration. Therefore, each spent liquor must be tested separately.

## Method for calculating membrane rejection

According to the concentration polarisation theory, the permeate flux can be calculated with eq. [3]:

$$J_v = k \ln[(c_w - c_p)/(c_b - c_p)] \quad [3]$$

When eq. [3] is solved for  $c_w$ , eq. [4] is obtained:

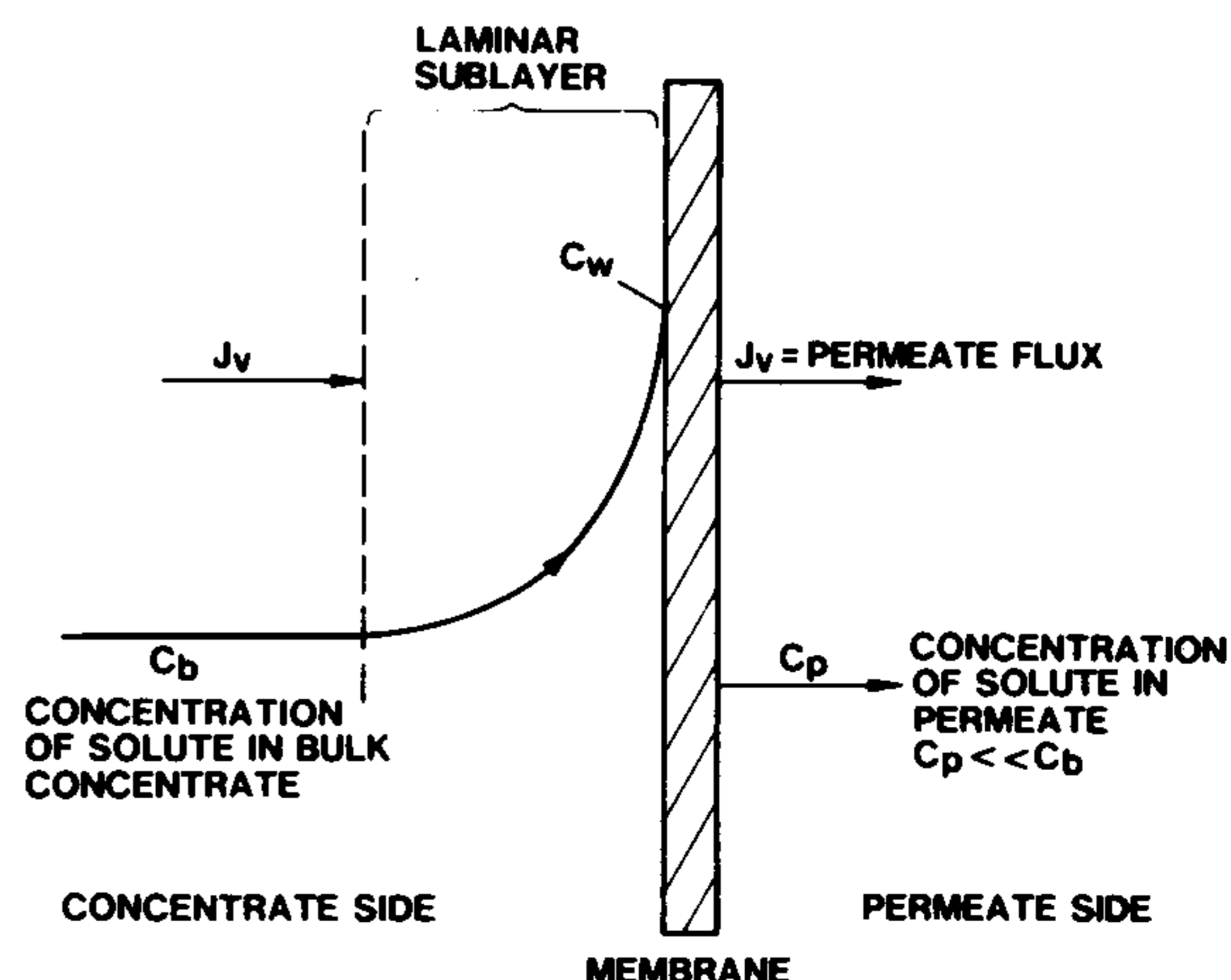
$$c_w = c_p + (c_b - c_p) \cdot \exp(J_v/k) \quad [4]$$

$c_p$ ,  $c_b$  and  $J_v$  can be obtained from test results. If the mass transfer coefficient can be calculated, the value of  $c_w$  and, after that, the membrane rejection can be calculated.

Numerous correlations have been presented for calculation of the mass transfer coefficient.

In the turbulent regime, the most widely used equation is the Deissler correlation (2), eq. [5]

$$Sh = 0.023 Re^{0.875} Sc^{0.25} \quad [5]$$



*Fig. 1. Concentration polarisation in ultrafiltration.*

While the Deissler equation is commonly accepted for the turbulent region, there are more alternative equations available for the laminar region.

The Leveque correlation has often been suggested for the laminar region (3):

$$Sh = 1.62 [Re Sc(d_H/L)]^{0.33} \quad [6]$$

According to López-Leiva (4), the following type of equation gives the best correlation in the laminar region:

$$Sh = A \cdot Re^{0.5} Sc^{0.33} \quad [7]$$

$A$  is a constant which acquires different values depending on the structure and dimensions of the equipment in question.

Goldsmith (5), for example, gave an equation of the same type as eq. [7].

To calculate the mass transfer coefficient from these dimensionless equations requires knowledge of such physical properties as the diffusion coefficient of lignosulfonate in spent sulfite liquor and the viscosity and density of the spent liquor.

These physical properties are affected by the dry solids content, lignosulfonate purity, temperature and, especially when the diffusion coefficient is concerned, the relative molecular mass distribution of the lignosulfonates.

Yearn et al. (6) postulated that the diffusion coefficient of lignosulfonates depend on the molecular mass according to eq. [8]

$$D_{298K}/(m^2/s) = 4.5 \cdot 10^{-9} [M/(kg/kmol)]^{-0.33} \quad [8]$$

Eq. [8] has been solved for sodium lignosulfonate obtained from spruce. The temperature at which eq. [8] is valid is 25°C. The diffusion coefficient at other temperatures can be estimated using eq. [9].

$$D\eta/T = \text{constant} \quad [9]$$

The dependence of the viscosity and density of spent sulfite liquor on dry matter content, lignosulfonate purity and temperature is readily demonstrable if enough liquid samples are collected during ultrafiltration. The results of the viscosity and density measurements are fitted to the appropriate equations by regression analysis.

### Estimation of the average molecular mass

In order to utilize eq. [8] for the diffusion coefficient

Table 1. The cumulative mass distribution during ultrafiltration of spent sulfite liquor

Lignosulfonate content in concentrate, wt.-% of dry matter	Portion $\phi$ of mass below relative molecular mass $M$ (kg/kmol), %				
	< 5 000	< 10 000	< 20 000	< 30 000	< 40 000
48.8	53.0	65.6	76.1	82.3	86.6
77.7	34.4	50.5	64.0	72.9	78.7
96.5	21.1	37.6	54.4	64.7	72.0

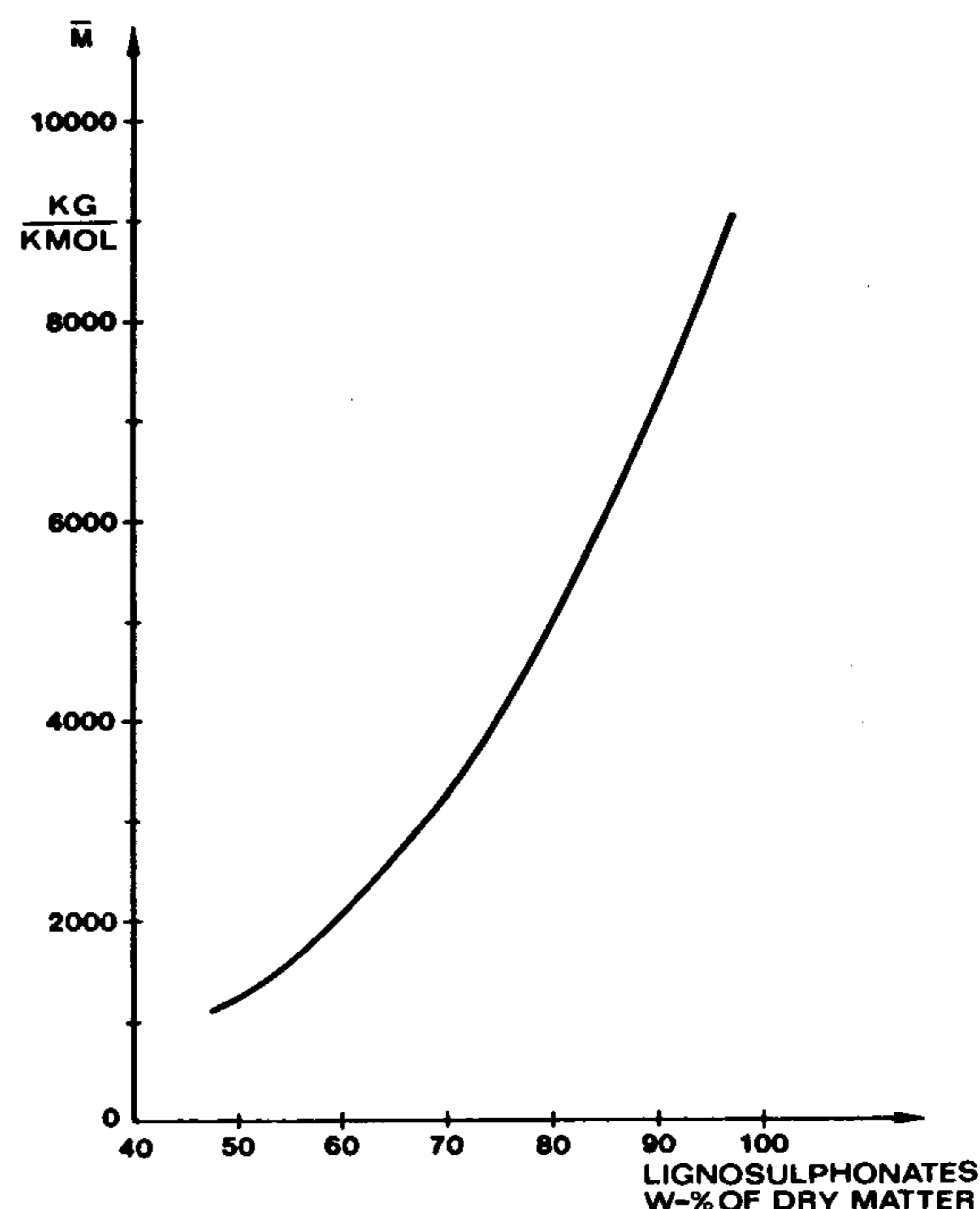


Fig. 2. Average relative molecular mass  $\bar{M}$  (kg/kmol) of lignosulfonate during ultrafiltration of spent sulfite liquor.

the behavior of the relative molecular mass distribution throughout ultrafiltration must be known.

One method is to calculate the average molecular mass as a function of the lignosulfonate purity.

Table 1 presents the cumulative mass distribution  $\phi$  as a function of relative molecular mass for three lignosulfonate purities from samples obtained during ultrafiltration of spent sulfite liquor. The analysis method for the relative molecular mass distribution was gel chromatography.

From table 1, it is possible to determine with regression analysis the corresponding distribution functions which are of the form

$$\phi(M) = a + b \ln M \quad [10]$$

$a$  and  $b$  are constants which have different values depending on the lignosulfonate content of the liquor. The distribution functions are defined between certain numerical values  $M_1$  and  $M_2$ , which also depend on the LS purity. The constants  $a$ ,  $b$ ,  $M_1$  and  $M_2$  are tabulated in table 2 and correspond to the

Table 2. The parameters in the cumulative mass distribution function  $\phi$ , eq. [10]

Lignosulfonate content in concentrate, wt.-% of dry matter	$a$	$b$	$M_1$	$M_2$
			kg/kmol	kg/kmol
48.8	-0.829454	0.160359	176	90083
77.7	-1.45166	0.211455	958	108431
96.5	-1.8749	0.244609	2123	127140

distributions in table 1. The correlation coefficient of regression analysis was between 0.999 and 0.9999.

The density functions of the distributions are obtained by taking the first derivative of eq. [10]:

$$f(M) = b/M \quad [11]$$

the average relative molecular mass is finally obtained from eq. [12]. Eq. [12] defines the average relative molecular mass as the ratio of total mass to total amount of moles. The formula should be used when average mass-transfer coefficients are calculated.

$$\bar{M}^{-1} = \int_{M_1}^{M_2} f(M)M^{-1}dM \quad [12]$$

Fig. 2 presents the average relative molecular mass as a function of the lignosulfonate purity of the dry matter in the liquor. The correlation of fig. 2 is utilised in eq. [8]. Eq. [12] presumes that  $\phi(M_2) - \phi(M_1) = 1$ .

### Calculation of rejection from test results

The test material was obtained from the ultrafiltration plant of Rauma Pulp Mill. The equipment was delivered by the Danish company DDS and was of the type DDS 35-42-7. The membrane was polysulfonic membrane GR 60 P.

The ultrafiltration line was continuous and had a nominal capacity of 0.3 t/h calculated on a dry matter basis. The lignosulfonate purity of the product was 95% of the dry solids. The spent sulfite liquor

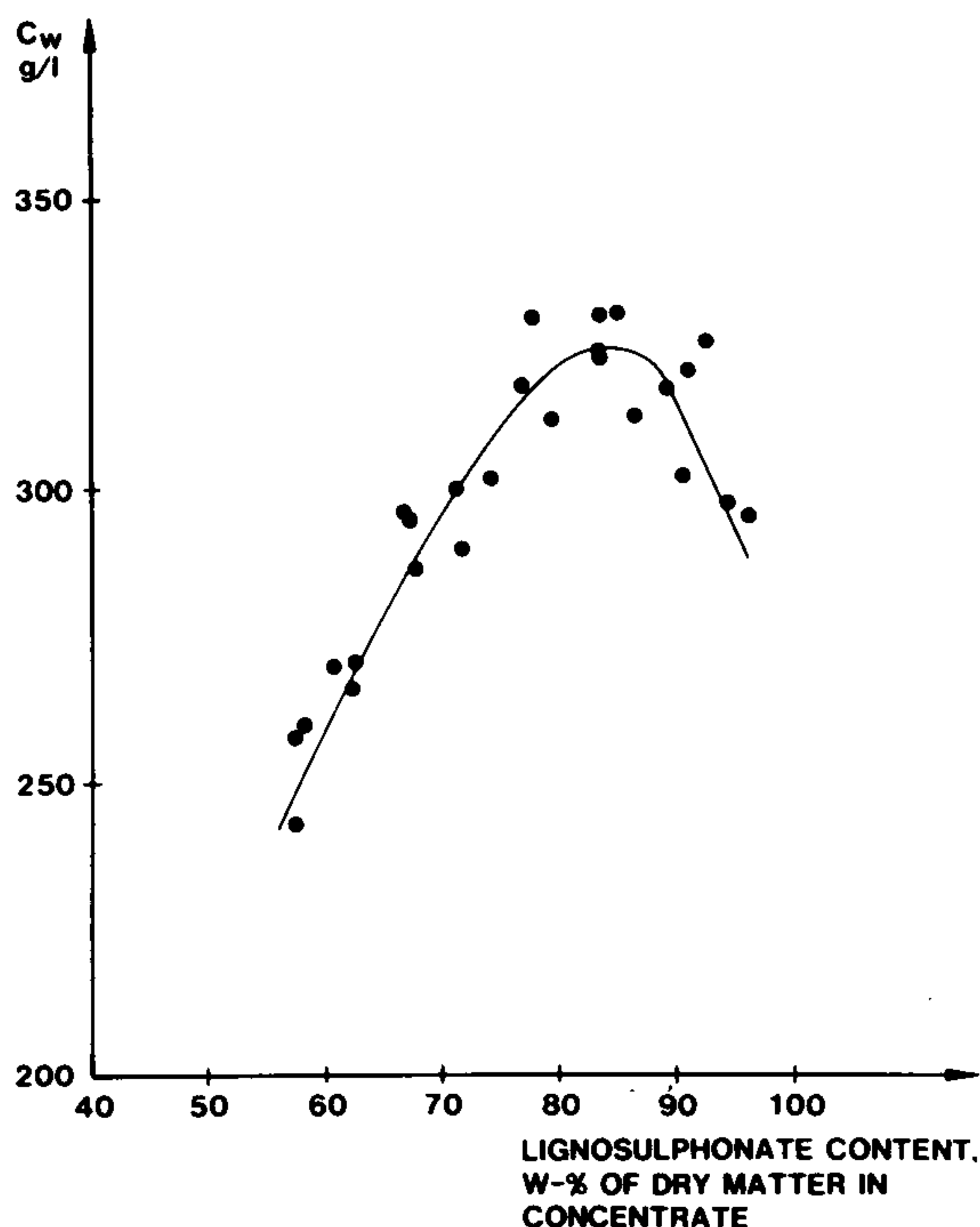


Fig. 3. Lignosulfonate concentration on the membrane wall during the ultrafiltration of SSL.

came from the acid cooking stage of the three-stage Rauma process which produces dissolving pulp from softwood.

The UF line consisted of seven units in series, the ultrafiltration process was a combination of concentration and diafiltration. The concentrate and permeate samples were gathered from different units throughout the line. The dry solids content was determined by drying the sample; the lignosulfonate content was analyzed by means of UV-absorbancy. The permeate flux and temperature of the unit in question were determined at the time of sampling.

The pressure was 11.5 bar (abs.) when the concentrate entered the module; the outlet pressure was 6.0 bar (abs.).

The test material was collected at the beginning of the ultrafiltration test run periods so that the effect of fouling could be eliminated.

When the rejections were calculated the mass transfer correlation used was the Leveque equation (eq. [6]). Reynolds number varied between 700 and 1300 so that the flow regime was clearly laminar.

The concentration of lignosulfonate at the membrane wall,  $c_w$ , which is obtained from eq. [4], is presented in fig. 3 as a function of the lignosulfonate content in the concentrate during ultrafiltration.

The membrane and observed rejections calculated from about 50 measurements are presented in fig. 4. The observed rejections increased quite linearly from 0.8 to 0.91 when the lignosulfonate purity increased from 66 to 95% during the ultrafiltration. The membrane rejection did not vary so much and also behaved quite linearly.

The information from fig. 4 can be utilized by finding suitable mathematical representations for  $R$

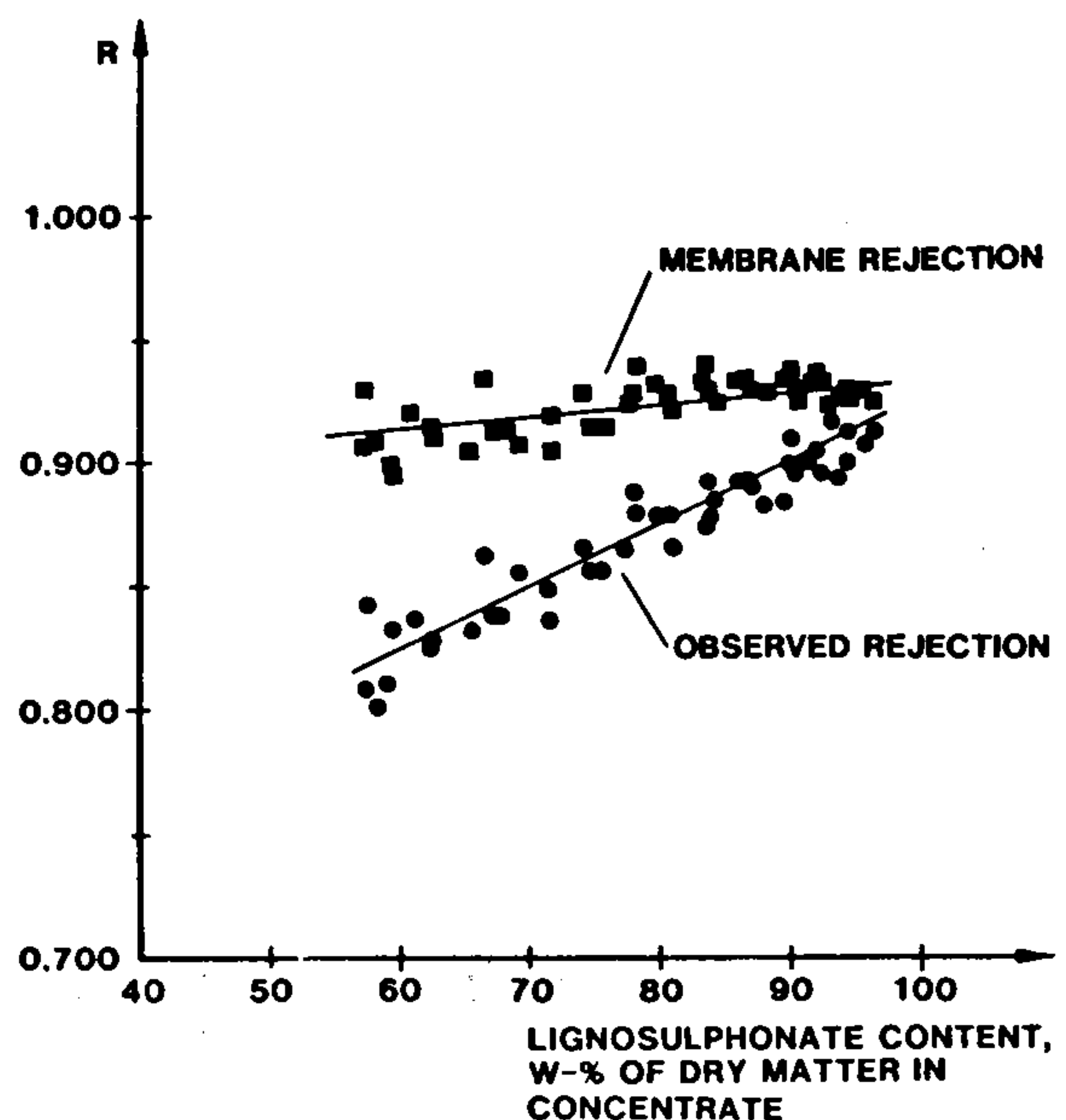


Fig. 4. Observed rejection and membrane rejection of lignosulfonates during the ultrafiltration of SSL.

and  $R_{OBS}$  as functions of lignosulfonate purity. In the present case, linear expressions were suitable.

Applying eqs. [1] and [2], it was possible to re-write eq. [3]:

$$J_v = k \ln \left\{ \frac{R(1 - R_{OBS})}{R_{OBS}(1 - R)} \right\} \quad [13]$$

Eq. [13] can be used as design equations for calculating permeate flux. The rejections  $R$  and  $R_{OBS}$  are correlated from experimental results and an appropriate mass transfer correlation is used for the mass transfer coefficient.

Further information is needed to allow for fouling of the membranes. The fouling can be seen as the decline of permeate flux in the course of ultrafiltration. By plotting the flux measured in standard conditions as a function of the running time from the beginning of UF period, the effect of fouling can be obtained.

## Conclusions

The method presented in this publication can be used to analyse ultrafiltration test data to establish the mass transfer parameters prevailing in the ultrafiltration of spent sulfite liquor.

The relative molecular mass distribution and its changes in the course of ultrafiltration must be taken into account because the molecular size influences the whole mass transfer behavior through the diffusion coefficient.

Further design calculations can be greatly simplified when the behavior of observed and membrane rejections are known.

## Symbols

- $a, b$  = constants  
 $c_b$  = lignosulfonate concentration in concentrate, g/l  
 $c_p$  = lignosulfonate concentration in permeate, g/l  
 $c_w$  = lignosulfonate concentration at the membrane wall, g/l  
 $D$  = diffusion coefficient of lignosulfonate,  $m^2/s$

$D_{298K}$  = diffusion coefficient of lignosulfonate at 25°C,  $m^2/s$

$d_H$  = hydraulic diameter of the flow channel, m

$f$  = differential mass distribution function or density function, kmol/kg

$J_v$  = permeate flux,  $m^3/(m^2s)$

$k$  = mass transfer coefficient, m/s

$L$  = length of flow channel on the membrane, m

$M$  = relative molecular mass, kg/kmol

$R$  = lignosulfonate rejection, dimensionless

$R_{OBS}$  = observed rejection, dimensionless

$Re$  = Reynolds number =  $w d_H \rho / \eta$

$Sc$  = Schmidt number =  $\eta / \rho D$

$Sh$  = Sherwood number =  $k d_H / D$

$T$  = temperature, K

$w$  = velocity in the flow channel, m/s

## Greek letters

$\phi$  = unit cumulative mass distribution as a function of the molecular size

$\rho$  = density,  $kg/m^3$

$\eta$  = viscosity, kg/(ms)

## Literature

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