ELASTO-OSMOMETRY

PROEFSCHRIFT

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Aan mijn ouders
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CONTENTS

CHAPTER 1

INTRODUCTION AND SURVEY OF NUMBER AVERAGE MOLECULAR WEIGHT METHODS

The task of the investigator who is concerned with the study of polymers is hampered by the fact that his materials are not well defined. This holds in particular with regard to the molecular weight which for synthetic polymers may vary between a few hundreds and a few millions. In view of the fact that many physical and mechanical properties are strongly molecular weight dependent, it is easily understood that research on rapid and sensitive methods for determining molecular weights and molecular weight distributions has become very intensive during the last decennia.

Now, even for a particular polymer sample, it is impossible to speak about *the* molecular weight because all actual samples are mixtures with a molecular weight distribution. As a consequence we may define several molecular weight averages which are, in a mathematical sense, moments of the distribution. In this thesis we are only concerned with the methods for determining the number average molecular weight, defined as

$$\overline{M}_n = \sum_i n_i M_i / \sum_i n_i \qquad (1.1)$$

where n_i is the number of molecules with molecular weight M_i. If the distribution can be considered to be continuous, we may write

$$\overline{M}_n = \int_0^\infty f(M)\, M\, dM \Big/ \int_0^\infty f(M)\, dM \qquad (1.2)$$

where $f(M)\, dM$ is the number of molecules having a molecular weight between M and $M + dM$.

In this average each molecule, regardless of its size, gives the same contribution. Therefore many methods for determining the number average are based on the colligative properties of solutions, that is, one "counts" the number of solute molecules and calculates the number average molecular weight from the known concentration[1]. To the colligative methods belong ebullioscopy, that is measuring of the boiling point elevation, cryoscopy, based on the measurement of the freezing point depression, vapour phase osmometry, in which the vapour pressure lowering as a result of

addition of a solute is measured, and membrane or regular osmometry, where the hydrostatic head built up between a solution and the pure solvent, separated by a semipermeable membrane, is measured.
The three first mentioned methods are no longer suitable if the molecular weight of the substance under investigation is larger than, say, 30,000 because in that case the effects to be measured are too small. Below this value they give excellent results and this is particularly true for the vapour phase osmometry. The ebullioscopic and cryoscopic methods possess some drawbacks due to the extreme temperatures one is forced to work at. Thermoelectric vapour phase osmometry [2,3], in which the vapour pressure difference between a solution and the pure solvent is converted into a temperature difference, can be used at each temperature between melting and boiling point of the solvent.

The osmotic pressure of solutions of polymers with molecular weight above 20,000 can be measured quite accurately, contrary to the effects mentioned above, and this holds up to molecular weights of the order of 500,000. Thus, the three methods mentioned before and membrane osmometry are complementary methods because the last one gives rise to erroneous results for molecular weights below about 20,000 due to diffusion of the solute through the membrane.

The investigations described in this thesis, are concerned with a relatively new method, the elasto-osmometry, which has a close resemblance with regular osmometry. The method is based on the phenomenon that the degree of swelling of a swollen gel, normally a crosslinked polymer network, is dependent on the activity of the swelling agent around the gel. A gel submerged in a pure solvent reaches a swelling equilibrium by absorption of solvent, in which the chemical potential of the solvent inside and outside the gel is equal. Replacement of the pure solvent by a polymer solution decreases the activity of the solvent around the gel and in course of time a new equilibrium is attained in which the chemical potentials are again equal, but the degree of swelling is lower. Thus, the swollen gel acts like the membrane in an osmometer, allowing solvent molecules to diffuse freely through while retarding the polymer molecules.
As a result of the decrease of the degree of swelling the volume of the gel also decreases. As early as 1945, Boyer [4] used this effect to determine number average molecular weights of polystyrenes up to 300,000 by weighing the amount of solvent in polystyrene-divinylbenzene gels, swollen in solutions of different concentrations. However, the variations of the dimensions of the gel turn out to be so small

in general that a method based on their measurement will be very insensitive or experimentally unfavourable.

Preliminary theoretical and experimental work by Hermans[5,6], Yamada[5], Prins[5,7] and Mieras[7] has demonstrated that if one keeps one of the dimensions, preferably the length, constant and considers the retractive force caused by the deswelling, this force is of such an order of magnitude that it can be measured quite accurately by the sensitive force indicators available at present.

The present study is concerned with an elasto-osmometer based on this principle, in which the sensitivity is comparable with or even better than the sensitivity of the best membrane osmometers. The theory of this type of elasto-osmometry is presented in Chapter 2, Chapter 3 gives a description of the apparatus and its operation. In Chapter 5 the experimental results are given and compared with theory.

Naturally, the determination of one of the averages of the molecular weight distribution of a polymer is not sufficient for a complete characterization in general, because the polymer behaviour will often be dependent on the shape of the distribution, especially in the case of wide distributions. Information about the distribution can be obtained by separating the sample into several fractions and by determining the molecular weight of each of these fractions. This method is, however, very time-consuming. For this reason one has tried to develop more rapid methods. One method is based on the permeability of the membrane in a conventional osmometer for low molecular weight substances[8,9]. If permeation occurs, the osmotic pressure decreases with time at a rate dependent on the diffusivity of the permeating molecules and thus on their size. A correct interpretation of this time effect provides the molecular weight distribution of the low molecular weight tail of the sample. Owing to the specific properties of the membranes, commonly used in osmometry, this method is restricted to relatively low molecular weights, roughly below 10,000.

In view of the analogy between membrane and elasto-osmometry one could expect that information about the molecular weight distribution could also be obtained from a detailed examination of the diffusion processes connected with permeation of low molecular weight substances into the gel of the elasto-osmometer. Owing to complications of both mathematical and practical nature this expectation has not been fulfilled for the greater part. It is possible, however, to determine the number average molecular weight in the case of penetration if the shape of the molecular

weight distribution is known. The theoretical aspects of the penetration effect are presented in Chapter 2 and Appendix I.

Finally, it must be mentioned that during the last few years a new technique has been developed which shows extremely favourable prospects for a rapid and accurate determination of molecular weight distributions, viz. gel permeation chromatography (GPC). This technique has been used in our investigation for the characterization of our polymer samples. It is described in some detail in Chapter 4. A disadvantage of GPC is the necessity of a calibration with samples of the same polymer as the polymer under investigation, but with a known distribution.

Chapter 4 also deals with the preparation of the various polymers used in our measurements. Together with GPC, vapour phase osmometry and membrane osmometry were used for their characterization.

CHAPTER 2

THEORY

2.1. EQUILIBRIUM THEORY FOR NON-PERMEATING SOLUTES.

2.1.1. *The chemical potential of the solvent in a swollen gel.*

A rubber or elastomer is commonly considered to consist of long, randomly coiling polymer chains connected to one another by covalent crosslinks. The whole network can be considered as one gigantic macromolecule. Such a material, brought into contact with a solvent*, will not dissolve but will form a gel by absorption of solvent.
The solvent content of the gel in equilibrium swelling is determined by the condition that the chemical potential of the solvent inside the gel must be equal to that outside the gel. The chemical potential inside the gel can be considered to contain two volume-dependent contributions. One is a consequence of the change in free energy due to mixing of the polymer network chains with solvent molecules, ΔF_m. The other contribution arises from the elastic or conformational free energy change, ΔF_c, which is a result of the shift in population of the chain conformations upon swelling. Thus

$$\mu_{1g} = \mu_1^o + \frac{\partial \Delta F_m}{\partial N_1} + \frac{\partial \Delta F_c}{\partial N_1} \qquad (2.1)$$

in which μ_1^o is the standard chemical potential of the solvent and N_1 is the number of moles of solvent in the gel.

An expression for the free energy of mixing which has demonstrated its value in practice, is due to Flory[10] and Huggins[11]. In their derivation they make use of a liquid lattice model in which a polymer solution is considered as a homogeneous distribution of polymer segments and solvent molecules. This will only be the case in rather concentrated solutions, viz. a few percents if the molecular weight is not too low. Most swollen gels fulfil this condition because the volume fraction of polymeric material is seldom

* Diluent would be a more appropriate word. In elasto-osmometry, however, the polymer containing solvent phase around a swollen gel and not the gel itself is of chief interest. We will therefore use the word solvent throughout.

less than 5 percent. In the Flory-Huggins derivation the entropy and energy of mixing are treated separately. The entropy of mixing between the solution and its pure components is calculated under the assumption that it is independent of the interaction energy between polymer segments and solvent molecules. In order to calculate the energy of mixing, only first neighbour contacts are taken into account. This restriction is justified, because the forces between uncharged molecules decrease rapidly with the distance of separation. For a solution of N_2 moles of solute in N_1 moles of solvent the result arrived at, reads:

$$\Delta F_m = RT \left[N_1 \ln \phi_1 + N_2 \ln \phi_2 + \chi_{12} (N_1 + p_2 N_2) \phi_1 \phi_2 \right] \qquad (2.2)$$

In this equation R is the gas constant, T is the absolute temperature, ϕ_1 and ϕ_2 are the volume fractions of solvent and solute, respectively and p_2 is the molar volume of the solute divided by the molar volume of the solvent. In the original theory the Huggins interaction parameter χ_{12}, which ranges between 0 (very good solvent) and 0.5 (phase separation), is merely a function of the interaction energy between the two species. A more extensive study of the mixing process shows that χ_{12} should be regarded as a free energy parameter, $\chi_{12} = a + b/T$, because there may also be a contribution to the entropy of mixing from the interaction between the components of the solution. Besides, χ_{12} often turns out to be concentration dependent. However, if χ_{12} is considered as a semi-empirical parameter, the Flory-Huggins expression provides a satisfactory description of many polymer solutions.

The theory described above has originally been set up for solutions of polymers of finite chain length. Extension to swollen, crosslinked networks requires no essential alterations, however. We only have to take into account that in this case $N_2 = 1$, because the network can be regarded as one gigantic macromolecule.

Several theories have been proposed for the elastic free energy of elastomers [12,13,14]. In all theories the elastomer is considered to be mainly an entropy spring, the intermolecular forces usually being considered strain independent. Treating the network as an assembly of independent Gaussian chains leads to the following result:

$$\Delta F_c = RT \nu_e \left[\tfrac{1}{2} A (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - B \ln \lambda_x \lambda_y \lambda_z \right] \qquad (2.3)$$

where ν_e is the number of moles of elastically effective network chains between crosslinks; λ_x, λ_y and λ_z are the

relative deformations with respect to the so-called reference state in the x, y and z directions, respectively. The reference state is defined as that state in which the chains are unrestrained, that is in which the mean square end-to-end distance of the chains between crosslinks is the same as they would have in a solution of the same concentration. The factors A and B are here introduced to account for the fact that there are several versions of Equation (2.3) in the literature. Hermans[13] finds $A = B = 1$, Flory[12] $A = 1$, $B = \frac{1}{2}$, James and Guth[14] $A = \frac{1}{2}$, $B = 0$. The most recent experimental work[15] regarding this question, offers strong support for $A = \frac{1}{2}$, $B = \frac{1}{2}$, which is really Hermans' result, but with only half the number of effective network chains, as also predicted by Duiser and Staverman[16].

When the elastomer is allowed to swell in a solvent then the relative volume change is given by $\lambda_x\lambda_y\lambda_z = q/q_o$; q, the inverse volume fraction of gel material in the swollen state, is normally called the degree of swelling; q_o is the degree of swelling in the reference state.

In elasto-osmometry we consider the case of a swollen gel strip stretched in one, say x, direction from a length L_o in the reference state to a length L. Then $\lambda_x = L/L_o$ and $\lambda_y^2 = \lambda_z^2 = qL_o/q_oL$. Substitution of these λ-values into Equation (2.3) yields:

$$\Delta F_c = RT\nu_e \left[\tfrac{1}{2}A\left(\frac{L^2}{L_o^2} + \frac{2qL_o}{q_oL} - 3 \right) - B \ln \frac{q}{q_o} \right] \qquad (2.4)$$

The chemical potential of the solvent inside the gel can be readily obtained now by differentiating Equations (2.2) and (2.4) with respect to N_1. Taking into account that the volume fraction of network material, ϕ_2, is equal to $1/q$ and that $\phi_1 + \phi_2 = 1$, the result is:

$$\mu_{1g} = \mu_1^o + RT \left[\ln (1-q^{-1}) + q^{-1} + \chi_{1g} q^{-2} + \frac{1}{p_e}\left(Aq_o^{-1} \frac{L_o}{L} - Bq^{-1} \right) \right] \qquad (2.5)$$

where χ_{1g} is the interaction parameter for the solvent-network interaction.

In deriving Equation (2.5) it must be noted that $q = (V_d + N_1 v_1)/V_d$ in which V_d is the volume of network material and v_1 the molar volume of the swelling agent. For convenience the quantity $p_e = V_d/\nu_e v_1$ has been introduced. It

stands for the effective chain length between crosslinks, as measured in number of solvent lattice sites and has the advantage of being independent of the dimensions of the gel strip.

2.1.2. *Effect of the deswelling by polymer solutions on the retractive force.*

The state of a gel stretched in one direction in the presence of a swelling agent is determined by the variables T, V, L and N_{1g}. An infinitesimal change of the free energy of such a gel is given by

$$dF = -S\,dT - p\,dV + f\,dL + \mu_{1g}\,dN_{1g} \qquad (2.6)$$

From this equation it is apparent that the retractive force, f, is equal to

$$f = \left(\frac{\partial \Delta F_c}{\partial L}\right)_{T,V,N_{1g}} = ART\nu_e\left(\frac{L}{L_o^2} - \frac{qL_o}{q_o L^2}\right) \qquad (2.7)$$

if we employ Equation (2.4), ΔF_m being independent of L.

We are interested in the change of retractive force as a function of the concentration of the polymer solution outside the gel, c, at constant length. This change in force arises from the change in q due to a redistribution of solvent as the gel is brought from the pure solvent into the polymer solution.

From Equation (2.7) it follows that

$$\left(\frac{\partial f}{\partial c}\right)_L = \left(\frac{\partial f}{\partial q}\right)_L \left(\frac{\partial q}{\partial c}\right)_L = -\frac{ART\nu_e L_o}{q_o L^2}\left(\frac{\partial q}{\partial c}\right)_L \qquad (2.8)$$

The variation of q with c is governed by the condition that in equilibrium the chemical potentials of the solvent inside and outside the gel are equal:

$$\mu_{1g} = \mu_{1s} \quad \text{or} \quad \left(\frac{\partial \mu_{1g}}{\partial c}\right)_L = \frac{d\mu_{1s}}{dc}$$

so that

$$\left(\frac{\partial \mu_{1g}}{\partial q}\right)_L \cdot \left(\frac{\partial q}{\partial c}\right)_L = \frac{d\mu_{1s}}{dc} \quad \text{and thus} \quad \left(\frac{\partial q}{\partial c}\right)_L = \frac{d\mu_{1s}/dc}{(\partial \mu_{1g}/\partial q)_L} \qquad (2.9)$$

If we restrict ourselves to dilute solutions, the chemical

potential of the solvent in the solution outside the gel can be written as a virial series in the concentration:

$$\mu_{1s} = \mu_1^o - RT\left[(M_1/\bar{M}_n)c + A_2c^2 + \ldots\right] \quad (2.10)$$

Here the concentration c is expressed in terms of the weight of polymer per weight of solvent. It should be noted that if the solution is sufficiently concentrated for the Flory-Huggins approach (Equation 2.2) to be valid, the second virial coefficient A_2 is given by $A_2 = (\frac{1}{2}-\chi_{12})(\rho_1/\rho_2)^2$, in which ρ_1 and ρ_2 are the densities of the solvent and the dry polymer, respectively.
Using Equations (2.5) and (2.10) for calculating $(\partial q/\partial c)_L$ and introducing this result into Equation (2.8) finally leads to

$$\left(\frac{\partial f}{\partial c}\right)_L = ART\sigma_o\rho_1\left(\frac{L_o}{L}\right)^2\left(\frac{q}{q_o}\right)^2\frac{1-q^{-1}}{B(1-q^{-1})+p_e q^{-1}-2p_e\chi_{1g}q^{-1}(1-q^{-1})}\times$$

$$\times\left(\frac{1}{\bar{M}_n}+\frac{2A_2}{M_1}c+\ldots\right) =$$

$$= KRT\left(\frac{1}{\bar{M}_n}+\frac{2A_2}{M_1}c+\ldots\right) \quad (2.11)$$

where σ_o is the cross-section of the gel strip in the reference state. For practical purposes it is convenient to also have the integral form of Equation (2.11):

$$f - f_o = KRT\left(\frac{1}{\bar{M}_n}c+\frac{A_2}{M_1}c^2+\ldots\right) \quad (2.12)$$

where f_o stands for the retractive force when the gel strip is swollen in pure solvent.

2.2. EQUILIBRIUM THEORY FOR PERMEATING SOLUTES

2.2.1. *Distribution of the components over the two phases.*

The equilibrium between a swollen gel and a polymer solution, the solute molecules of which are able to penetrate into the gel, requires that the chemical potentials of all solution components are equal inside and outside the gel. In

order to calculate these chemical potentials we apply the Flory-Huggins approximation to both phases. The free energy of mixing of a solution of n components is generally given by[17]

$$\Delta F_m = RT \left[\sum_{i=1}^{n} N_i \ln \phi_i + \sum_{i=1}^{n} p_i N_i \sum_{i,j} \chi_{ij} \phi_i \phi_j \right] \quad (2.13)$$

where the summation over i and j is to be taken over all pairs $j > i$. From our point of view the most interesting case is that of a mixture of polymers of the same homologous series, chemically identical and differing in chain length only. For such a mixture the interaction parameter for all solvent-polymer pairs is equal ($\chi_{1i} = \chi_{1p}$) and the interaction parameter for all polymer-polymer pairs is equal to zero. Then the chemical potentials of the solvent (1) and a polymer component (k) in the solution are given by

$$\mu_{1s} = \mu_1^o + RT \left[\ln (1 - \sum_i \phi_{is}) + \sum_i (1 - \frac{1}{p_i}) \phi_{is} + \chi_{1p} (\sum_i \phi_{is})^2 \right] \quad (2.14)$$

$$\mu_{ks} = \mu_k^o + RT \left[\ln \phi_{ks} - (p_k - 1) + p_k \sum_i (1 - \frac{1}{p_i}) \phi_{is} + p_k \chi_{1p} (1 - \sum_i \phi_{is})^2 \right] \quad (2.15)$$

in which the summations are to be taken over all polymer components $i (i > 1)$.

The free energy of mixing of the gel is a function of the amounts of solvent, network material and all dissolved polymer components. As pointed out in Section 2.1.1 the total free energy, and thus the chemical potential, also contains a conformational free energy contribution. By differentiation with respect to the number of moles of the component in question we obtain for the chemical potentials inside the gel:

$$\mu_{1g} = \mu_1^o + RT \left[\ln (1 - q^{-1} - \sum_i \phi_{ig}) + q^{-1} + \sum_i (1 - \frac{1}{p_i}) \phi_{ig} + \chi_{1g} q^{-2} + \chi_{1p} (\sum_i \phi_{ig})^2 + (\chi_{1g} + \chi_{1p} - \chi_{pg}) q^{-1} \sum_i \phi_{ig} + \frac{v_1}{RTV_d} \left(\frac{\partial \Delta F_c}{\partial q} \right)_L \right] \quad (2.16)$$

$$\mu_{kg} = \mu_k^o + RT \left[\ln \phi_{kg} - (p_k - 1) + p_k q^{-1} + p_k \sum_i (1 - \frac{1}{p_i}) \phi_{ig} + p_k \chi_{1g} q^{-2} + p_k \chi_{1p} (1 - \sum_i \phi_{ig})^2 + \right.$$

$$- p_k(\chi_{1g} + \chi_{1p} - \chi_{pg})q^{-1}\left(1 - \sum_i \phi_{ig}\right) + \frac{p_k v_1}{RTV_d}\left(\frac{\partial \Delta F_c}{\partial q}\right)_L \Bigg] \quad (2.17)$$

χ_{pg} is the interaction parameter of the interaction between the dissolved polymer molecules and the network material. In the derivation of Equations (2.16) and (2.17) we have used the definition

$$q = (V_d + \sum_{i=1}^{n} p_i N_i v_1)/V_d \quad (2.18)$$

The equilibrium conditions $\mu_{1g} = \mu_{1s}$ and $\mu_{kg} = \mu_{ks}$ offer the possibility of expressing ϕ_{kg} in terms of ϕ_{ks} and $\sum_i \phi_{is}$. To this end we expand the logarithmic terms of μ_{1g} and μ_{1s} in powers of $\sum_i \phi_{ig}$ and $\sum_i \phi_{is}$. Then we substract $p_k \mu_{1g}$ and $p_k \mu_{1s}$ from μ_{kg} and μ_{ks}:

$$\mu_{kg} - p_k \mu_{1g} = \mu_{ks} - p_k \mu_{1s} \quad (2.19)$$

and after rearrangement we find:

$$\ln(\phi_{kg}/\phi_{ks}) = p_k \ln(1-q^{-1}) + p_k(\chi_{1g} + \chi_{1p} - \chi_{pg})q^{-1} + \\ + \textit{higher terms in } \sum_i \phi_{is} \quad (2.20)$$

It should be stressed that an explicit knowledge of the conformational part of the chemical potential is not required for the derivation of Equation (2.20).
Even at concentrations of several percents the higher terms in the volume fraction of dissolved polymer are negligible, so that in the concentration range normally employed the ratio between the volume fractions of a polymer component of a certain chain length, inside and outside the gel is a constant for a given gel. Although the derivation is based on the Flory-Huggins expression for the free energy of mixing part, it is conceivable and even probable that this result has a much greater validity. This is, however, not easy to prove for the general case.
The ratio between the volume fractions of solvent is given in first approximation by

$$\frac{\phi_{1g}}{\phi_{1s}} = \frac{1 - q^{-1} - \sum_i \phi_{ig}}{1 - \sum_i \phi_{is}} \approx 1 - q^{-1} \quad (2.21)$$

2.2.2. *Influence of permeation on the retractive force increment.*

For permeating solutes the change in retractive force of a gel strip as a function of the concentration of the surrounding polymer solution is again given by Equation (2.8). In the present calculation of $(\partial q/\partial c)_L$ from the condition $\mu_{1g} = \mu_{1s}$ we have to take into consideration that now μ_{1g} is not only a function of q but also of the volume fractions of the polymer components in the gel. Henceforward, for convenience, we shall denote $\sum_i \phi_{ig}$ by Φ_g and $\sum_i \phi_{is}$ by Φ_s. Hence

$$\left(\frac{\partial \mu_{1g}}{\partial q}\right)_{L,\Phi_g} \left(\frac{\partial q}{\partial \Phi_s}\right)_L + \left(\frac{\partial \mu_{1g}}{\partial \Phi_g}\right)_{L,q} \frac{\partial \Phi_g}{\partial \Phi_s} = \frac{d\mu_{1s}}{d\Phi_s} \qquad (2.22)$$

and thus

$$\left(\frac{\partial q}{\partial c}\right)_L = \frac{\rho_1}{\rho_p}\left(\frac{\partial q}{\partial \Phi_s}\right)_L = \frac{\rho_1}{\rho_p} \cdot \frac{(d\mu_{1s}/d\Phi_s) - (\partial \mu_{1g}/\partial \Phi_g)_{L,q}(\partial \Phi_g/\partial \Phi_s)}{(\partial \mu_{1g}/\partial q)_{L,\Phi_g}} \qquad (2.23)$$

where ρ_p is the density of the solute and c the total weight of solute per unit weight of solvent.
In elasto-osmometry we are chiefly interested in dilute solutions, i.e. $\Phi_s \to 0$ and thus $\Phi_g \to 0$. Introduction of these limiting conditions simplifies the mathematical treatment of the problem considerably. For a dilute solution the chemical potential is in first approximation linearly dependent on the concentration (see Equation (2.10)) and thus on the volume fraction of polymer:

$$\mu_{1s} = \mu_1^o - RT \frac{M_1}{\bar{M}_n} c = \mu_1^o - RT \frac{1}{\bar{p}_n} \Phi_s \qquad (2.24)$$

so that

$$\left(\frac{d\mu_{1s}}{d\Phi_s}\right)_{c \to o} = -\frac{RT}{\bar{p}_n} \qquad (2.25)$$

$\bar{p}_n$ is the number average chain length of the solute as expressed in number of solvent molecules.
As a consequence of the diffusion into the gel each polymer component i will reach there a certain volume fraction ϕ_{ig}. This affects the chemical potential of the solvent, again in first approximation, by an amount $-RT\,\phi_{ig}/p_i$. Summation over all species i yields for the chemical potential μ_{1g} (compare also Equation (2.5)):

$$\mu_{1g} = \mu_1^o + RT \left[\ln(1-q^{-1}) + q^{-1} + \chi_{1g} q^{-2} + \right.$$
$$\left. + \frac{1}{\bar{p}_e} \left(A q_o^{-1} \frac{L_o}{L} - B q^{-1} \right) - \sum_i \frac{1}{\bar{p}_i} \phi_{ig} \right] \qquad (2.26)$$

From this equation we obtain:

$$\left(\frac{\partial \mu_{1g}}{\partial \Phi_g} \right)_{L,q} = - RT \frac{\partial}{\partial \Phi_g} \sum_i \frac{1}{\bar{p}_i} \phi_{ig} \qquad (2.27)$$

and

$$\left(\frac{\partial \mu_{1g}}{\partial q} \right)_{L,\Phi_g} = RT \left[\frac{q^{-2}}{1 - q^{-1}} - q^{-2} - 2\chi_{1g} q^{-3} + \frac{1}{\bar{p}_e} B q^{-2} \right] \qquad (2.28)$$

By introducing Equations (2.25), (2.27) and (2.28) into Equations (2.23) and (2.8) we find:

$$\left(\frac{\partial f}{\partial c} \right)_{L,c \to o} = KRT \frac{\rho_1}{\rho_p M_1} \left(\frac{1}{\bar{p}_n} - \frac{\partial}{\partial \Phi_s} \sum_i \frac{1}{\bar{p}_i} \phi_{ig} \right) \qquad (2.29)$$

where K has the same meaning as in Equation (2.11).

In Section 2.2.1 we derived an expression for the relation between the volume fractions of polymer inside and outside the gel strip. According to Equation (2.20) the ratio between these two is a constant which is equal to:

$$\frac{\phi_{ig}}{\phi_{is}} = \left[(1-q^{-1}) \exp \left\{ (\chi_{1g} + \chi_{1p} - \chi_{pg}) q^{-1} \right\} \right]^{p_i} = \epsilon^{p_i} \qquad (2.30)$$

This, together with the circumstance that for a given polymer sample $d\Phi_s/\Phi_s = d\phi_{is}/\phi_{is}$, means that

$$\partial \sum_i \frac{1}{\bar{p}_i} \phi_{ig} / \partial \Phi_s = \sum_i \frac{1}{\bar{p}_i} \phi_{ig} / \Phi_s \qquad (2.31)$$

Thus we finally arrive at:

$$\left(\frac{\partial f}{\partial c} \right)_{L,c \to o} = KRT \frac{\rho_1}{\rho_p M_1} \left(\frac{1}{\bar{p}_n} - \frac{\sum_i \frac{1}{\bar{p}_i} \epsilon^{p_i} \phi_{is}}{\sum_i \phi_{is}} \right) \qquad (2.32)$$

This expression has little practical utility, however, even if the sample consists of polymer molecules of the same chain length. Of course, in this limiting case, ϵ can always be obtained by a calibration with samples of known molecular weight. The chain length of an unknown sample can then be found by means of a numerical calculation. However, this procedure is not applicable if the sample possesses a molecular weight distribution, as is normally the case. The only possibility for making Equation (2.32) accessible for this general case lies in a series expansion of ϵ^{P_i}. This is permitted only if $p_i \ln \epsilon$ is small compared to one and this will be the case if the degree of swelling is sufficiently high and/or $(\chi_{1g} + \chi_{1p} - \chi_{pg})$ is large. The latter condition will be fulfilled if the swelling agent is a relatively poor solvent for both the network polymer and the dissolved polymer. At first sight this seems contradictory to the requirement of a high degree of swelling, but it is indeed possible to have high degrees of swelling even in poor solvents, viz. if the crosslinking has taken place in solution. Introduction of the series expansion into Equation (2.32) finally leads to

$$\left(\frac{\partial f}{\partial c}\right)_{L,c\to o} = KRT \frac{\rho_1}{\rho_p M_1} \left[-\ln \epsilon - \tfrac{1}{2} (\ln \epsilon)^2 \overline{p}_w - \ldots.\right]$$

$$= KRT \frac{\rho_1}{\rho_p M_1} \left[-\ln \epsilon - \frac{\rho_1 (\ln \epsilon)^2}{2\rho_p M_1} \overline{M}_w - \ldots.\right] \quad (2.33)$$

in which $\overline{M}_w$ is the weight average molecular weight of the dissolved polymer, defined as:

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\int_o^\infty f(M)\, M^2\, dM}{\int_o^\infty f(M)\, M\, dM} \quad (2.34)$$

It frequently occurs that only a part of the polymer sample, i.e. the low molecular weight tail, is able to penetrate into the gel. Let us suppose that the critical chain length for penetration is p_c. Then the summation in Equation (2.32) only contains contributions of the components of chain length shorter than p_c:

$$\left(\frac{\partial f}{\partial c}\right)_{L,c\to o} = KRT \frac{\rho_1}{\rho_p M_1} \left(\frac{1}{\overline{p}_n} - \frac{\sum_{i=2}^{c} \frac{1}{p_i} \epsilon^{P_i} \phi_{is}}{\sum_{i=2}^{n} \phi_{is}} \right) \quad (2.35)$$

where n is the total number of components.
If we proceed in the same way as in the derivation of Equation (2.25), we obtain the following result:

$$\left(\frac{\partial f}{\partial c}\right)_{L,c\to o} = KRT\left[\frac{1}{\overline{M}_n} - \left\{\frac{1}{(\overline{M}_n)_c} + \frac{\rho_1 \ln \epsilon}{\rho_p M_1} + \right.\right.$$
$$\left.\left. + \frac{\rho_1^2(\ln \epsilon)^2}{2\rho_p M_1^2}(\overline{M}_w)_c + \ldots\right\}\psi\right] \qquad (2.36)$$

In this equation ψ is the weight fraction polymer which is able to penetrate:

$$\psi = \frac{\sum_{i=2}^{c} \phi_{is}}{\sum_{i=2}^{n} \phi_{is}} = \frac{\int_o^{M_c} f(M)\ M\ dM}{\int_o^{\infty} f(M)\ M\ dM} \qquad (2.37)$$

$(\overline{M}_n)_c$ and $(\overline{M}_w)_c$ are the number and weight average molecular weights, respectively, of the penetrating part of the solute:

$$(\overline{M}_n)_c = \frac{\int_o^{M_c} f(M)\ M\ dM}{\int_o^{M_c} f(M)\ dM} \quad \text{and} \quad (\overline{M}_w)_c = \frac{\int_o^{M_c} f(M)\ M^2\ dM}{\int_o^{M_c} f(M)\ M\ dM} \qquad (2.38)$$

It is apparent from Equation (2.36) that a correction for the penetration of the low molecular weight tail of a given polymer sample is only possible if the type of molecular weight distribution and ϵ are both known. In order to obtain ϵ a calibration with a fully penetrating solute of known molecular weight and a known, narrow molecular weight distribution will be necessary.

In one respect the elasto-osmotic method for evaluation of the molecular weight of a partially penetrating solute, as described in this Section, differs considerably from the analogous method in membrane osmometry. In elasto-osmometry the equilibrium state is considered, whereas in membrane osmometry the equilibrium state offers no information, because then the penetrating part of the solute does not contribute to the osmotic pressure. In the latter case the prob-

lem is solved by a suitable extrapolation to zero time. The extrapolated osmotic pressure is proportional to the theoretical osmotic pressure, i.e. the pressure if the membrane were ideally semipermeable. The proportionality constant, which is normally called the reflection coefficient[18], is a very complex function of among other things the molecular weight. As a result a direct association with a simple average molecular weight is virtually impossible in most cases[19].

2.3. DIFFUSION PHENOMENA IN ELASTO-OSMOMETRY.

In Section 2.2 we studied the influence of solute penetration on the equilibrium degree of swelling. The establishment of equilibrium takes a certain amount of time, which is determined by the diffusion rates and the concentrations of the components of the solute. In view of the fact that the diffusion coefficients of the various solute components are directly related to their molecular weights, we might expect a detailed study of the deswelling as a function of time to furnish some information about the molecular weight distribution. Such a treatment would at first sight appear to be analogous to the treatment of penetration data in membrane osmometry[8,9].

The problem of interest here is a special case of the problem of diffusion out of a plate into an infinite medium or vice versa. This is so because the volume of the gel strip is very small compared to the amount of solution around the gel and because the diffusion flows through the sides of the strip can be neglected since the width is much larger than the thickness.

In the solution as well as the gel phase the diffusion process is governed by Fick's second law, which can be written in our case as:

$$\frac{\partial \phi_{ig}}{\partial t} = D_{ig} \frac{\partial^2 \phi_{ig}}{\partial x^2} \quad \text{and} \quad \frac{\partial \phi_{is}}{\partial t} = D_{is} \frac{\partial^2 \phi_{is}}{\partial x^2} \qquad (2.39)$$

We start from a gel, swollen in the pure solvent. This means that the initial volume fraction of solvent is equal to $(\phi_{1g})_o = 1 - q_b^{-1}$, in which q_b is the degree of swelling of the gel in pure solvent. The initial volume fractions of the polymer components in the gel, $(\phi_{ig})_o$, are equal to zero. At zero time the gel is brought into contact with a polymer solution with a total volume fraction of polymer of $\sum_{i=2}^{n} (\phi_{is})_o$, so that

the initial volume fractions of solvent and solute components are $(\phi_{1s})_o = 1 - \sum_{i=2}^{n} (\phi_{is})_o$ and $(\phi_{is})_o$, respectively. After the deswelling equilibrium has been reached, the volume fractions are fixed by the equilibrium conditions described in Section 2.2.1:

$$(\phi_{1g})_{t=\infty} = \alpha_1 (\phi_{1s})_o \quad \text{and} \quad (\phi_{ig})_{t=\infty} = \alpha_i (\phi_{is})_o,$$

in which $\alpha_1 = 1 - q^{-1}$ and $\alpha_i = \epsilon^{Pi}$.
In order to solve the diffusion equations we also need the conditions for the boundary between the gel and the solution. One boundary condition is that the diffusion flow out of the gel must be equal to the diffusion flow into the solution. In the second place the relation between the volume fractions at the boundary must be known. It seems logical to assume that in this region the equilibrium conditions, described in Section 2.2.1. are maintained from the first beginning of the diffusion process onward. As a result the ratio between the volume fractions at the boundary is a constant throughout:

$$(\phi_{1g}/\phi_{1s})_{x=\pm d} = \alpha_1 \quad \text{and} \quad (\phi_{ig}/\phi_{is})_{x=\pm d} = \alpha_i$$

if the thickness of the gel strip is equal to $2d$.

The diffusion equations (2.39) can be solved by using Laplace transformations. A full treatment of the procedure is given in Appendix I. One obtains the volume fractions of solvent and polymer inside the gel as a function of the distance to the centre of the strip, x, and time, t. The distribution of the solvent and the polymer components at a given time is not uniform over the thickness of the strip. As a consequence the degree of swelling and thus the retractive force vary with the distance to the centre. Thus, the strip should be considered as a continuous assembly of parallel springs of varying modulus all held at the same extension rate. Such an assembly is equivalent to a spring with a cross-section which is equal to the sum of the cross-sections of the component springs and with a modulus which is the average of all moduli. For the calculation of the average degree of swelling we need the average volume fractions of the solvent and the polymer components. These follow directly from Equations (A.17) and (A.18) in Appendix I:

$$\langle \phi_{1g} \rangle = \frac{1}{2d} \int_{-d}^{+d} \phi_{1g} \, dx =$$

$$= (\phi_{1g})_o \left[1 - \frac{2}{d} \frac{\sqrt{D_{1g} D_{1s}} \left\{ 1 - \alpha_1 (\phi_{1s})_o / (\phi_{1g})_o \right\}}{\alpha_1 \sqrt{D_{1g}} + \sqrt{D_{1s}}} \sqrt{t} \times \right.$$

$$\left. \times \sum_{n=o}^{\infty} \left(\frac{\alpha_1 \sqrt{D_{1g}} - \sqrt{D_{1s}}}{\alpha_1 \sqrt{D_{1g}} + \sqrt{D_{1s}}} \right)^n \left\{ \text{ierfc} \frac{nd}{\sqrt{D_{1g} t}} - \text{ierfc} \frac{(n+1)d}{\sqrt{D_{1g} t}} \right\} \right] \quad (2.40)$$

$$\langle \phi_{ig} \rangle = \frac{1}{2d} \int_{-d}^{+d} \phi_{ig} \, dx =$$

$$= (\phi_{is})_o \frac{2}{d} \frac{\alpha_i \sqrt{D_{ig} D_{is}}}{\alpha_i \sqrt{D_{ig}} + \sqrt{D_{is}}} \sqrt{t} \times$$

$$\times \sum_{n=o}^{\infty} \left(\frac{\alpha_i \sqrt{D_{ig}} - \sqrt{D_{is}}}{\alpha_i \sqrt{D_{ig}} + \sqrt{D_{is}}} \right)^n \left\{ \text{ierfc} \frac{nd}{\sqrt{D_{ig} t}} - \text{ierfc} \frac{(n+1)d}{\sqrt{D_{ig} t}} \right\} \quad (2.41)$$

where D_{1g} and D_{1s} are the diffusion coefficients of the solvent molecules in the gel phase and the solution phase, respectively, and D_{ig} and D_{is} those of a polymer component i. The complete solutions provide no possibility of obtaining the diffusion coefficients from the experimental curves. Possibly, in some cases, a way out is afforded by retaining only the first term of the ierfc-summation, which is equal to $1/\sqrt{\pi}$. For not too large diffusion coefficients this may be allowed at small t-values.
If this approximation is valid, Equations (2.40) and (2.41) become:

$$\langle \phi_{1g} \rangle = (\phi_{1g})_o \left[1 - \frac{2}{d\sqrt{\pi}} \frac{\sqrt{D_{1g} D_{1s}} \left\{ 1 - \alpha_1 (\phi_{1s})_o / (\phi_{1g})_o \right\}}{\alpha_1 \sqrt{D_{1g}} + \sqrt{D_{1s}}} \sqrt{t} \right] \quad (2.42)$$

and

$$\langle \phi_{ig} \rangle = (\phi_{is})_o \frac{2}{d\sqrt{\pi}} \frac{\alpha_i \sqrt{D_{ig} D_{is}}}{\alpha_i \sqrt{D_{ig}} + \sqrt{D_{is}}} \sqrt{t} \quad (2.43)$$

The average reciprocal degree of swelling depends on these average volume fractions through:

$$\langle q^{-1} \rangle = 1 - \langle \phi_{1g} \rangle - \sum_{i=2}^{n} \langle \phi_{ig} \rangle \quad (2.44)$$

The retractive force at constant length (Equation (2.7)), however, contains $\langle q \rangle$. Owing to the fact that the variations of q over the thickness of the strip are less than 10 percent, the error introduced by writing $\langle q \rangle = \langle q^{-1} \rangle^{-1}$ is negligible. Inserting Equations (2.42), (2.43) and (2.44) into Equation (2.7) we get:

$$f = ARTv_e \left[\frac{L}{L_o^2} - \frac{L_o}{q_o L^2} \left(1 - (\phi_{1g})_o + \right. \right.$$
$$+ \frac{2}{d\sqrt{\pi}} \left\{ \left[(\phi_{1g})_o - \alpha_1 (\phi_{1s})_o \right] \frac{\sqrt{D_{1g} D_{1s}}}{\alpha_1 \sqrt{D_{1g}} + \sqrt{D_{1s}}} + \right.$$
$$\left. \left. \left. - \sum_{i=2}^{n} (\phi_{is})_o \frac{\alpha_i \sqrt{D_{ig} D_{is}}}{\alpha_i \sqrt{D_{ig}} + \sqrt{D_{is}}} \right\} \sqrt{t} \right)^{-1} \right] \qquad (2.45)$$

Because we restrict ourselves to small t-values and dilute solutions this equation, by means of a series expansion of the denominator, can be approximated by

$$f = f_o + \frac{2ARTv_e L_o q_b}{q_o L^2 d\sqrt{\pi}} \left[\left\{ (\phi_{1g})_o - \alpha_1 (\phi_{1s})_o \right\} \frac{\sqrt{D_{1g} D_{1s}}}{\alpha_1 \sqrt{D_{1g}} + \sqrt{D_{1s}}} + \right.$$
$$\left. - \sum_{i=2}^{n} (\phi_{is})_o \frac{\alpha_i \sqrt{D_{ig} D_{is}}}{\alpha_i \sqrt{D_{ig}} + \sqrt{D_{is}}} \right] \sqrt{t} \qquad (2.46)$$

Unfortunately, even this simple, approximate expression offers no possibility of obtaining the diffusion coefficients of the permeating components. This is in contrast to a corresponding expression in membrane osmometry for the osmotic pressure as a function of time, as derived by Hoffmann and Unbehend[9]. In membrane osmometry the osmotic pressure depends on the concentration difference between the solutions on both sides of the membrane. In elasto-osmometry, however, the volume fractions inside the gel determine the retractive force. As a result the slope of the curve, obtained by plotting $(f-f_o)$ versus $\sqrt{t}$, contains both the diffusion coefficients and the volume fractions of the components. There is no means of separating these two contributions. Another, more practical, difficulty has already been mentioned before, i.e. Equation (2.46) is valid only at small t. Anticipating the experimental results described

in Chapter 5, it turns out that for the case of moderately swollen gels this condition is by no means fulfilled.

CHAPTER 3

DESCRIPTION AND OPERATION OF THE ELASTO-OSMOMETER

3.1. DESIGN OF THE ELASTO-OSMOMETER.

In designing an elasto-osmometer there are two main points to consider. In the first place we desire the highest possible sensitivity and in the second place the construction should be such that the length of the elastomer strip is kept as constant as possible. The latter condition is important because the equations describing the elasto-osmotic effect (Chapter 2) are derived under the assumption of constant length. All force measuring devices, however, inherently need a small displacement for measuring the exerted force. When this displacement is too large the length of the strip and thus its retractive force diminishes to a considerable extent (see Section 3.3.1). For strain gauges, as used in the instruments of Yamada[5] and Mieras[7], this effect can lead to reductions in signal up to 20%.
A much better instrument for measuring forces at constant length is an inductive transducer. Such a force indicator displays a much smaller displacement than a strain gauge. For our instrument (Type Q1/10-50, Hottinger, Darmstadt, Germany) this displacement amounts to only 30 microns at a maximum load of 10 grams.

Another disadvantage of the elasto-osmometers of Yamada and Mieras is that the gel strip is directly connected to the strain gauge. This arrangement prohibits the use of very sensitive measuring devices because these have a small maximum load. The absolute force level is sometimes fairly high because, in order to avoid slack and other irreversible non-elastic behaviour, the strip has to be given a degree of elongation of 5 to 10 percent. For moderately swollen strips this can lead to forces of 10 to 40 grams.
For this reason an elasto-osmometer was developed in which the gel strip is connected to one end of a balance, whereas the inductive force pick up is attached to the other arm of the balance.

Figure 1 shows a photograph of the instrument, a schematic diagram can be found in Figure 2. In this diagram the balance arm is marked with the symbol A, the transducer and the gel strip with B and E, respectively.

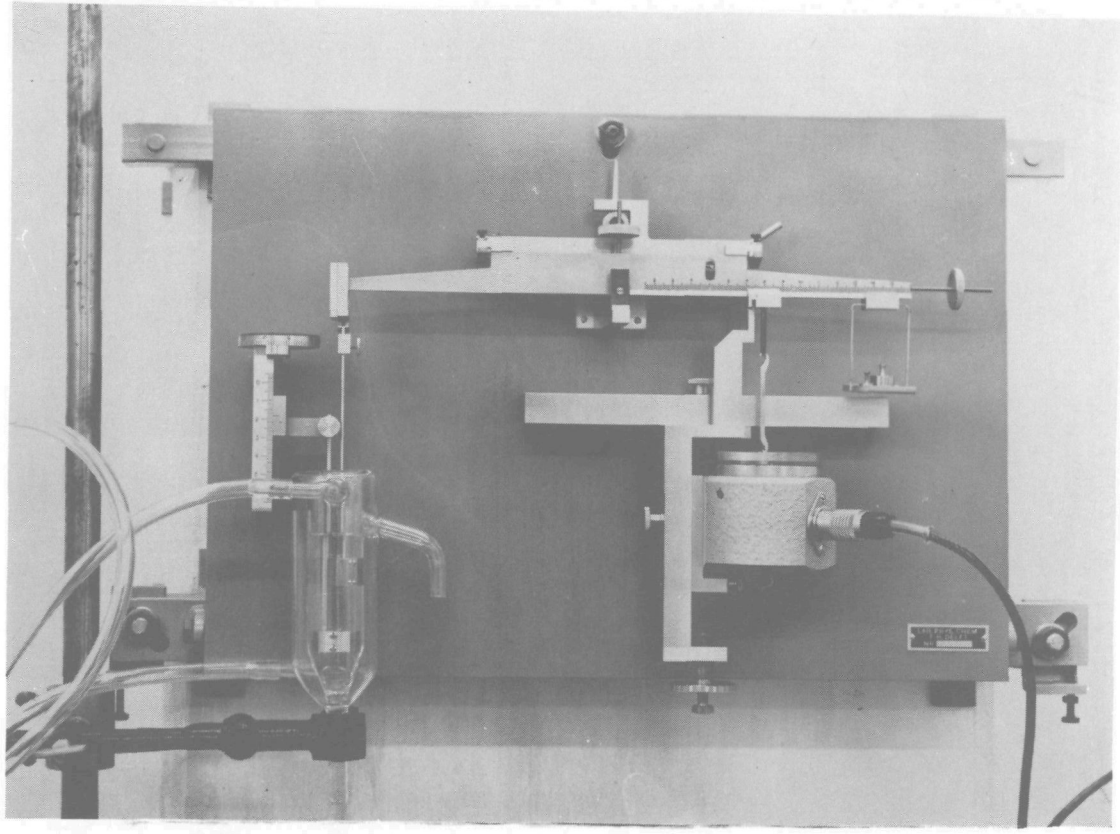

Figure 1. Photograph of the elasto-osmometer.

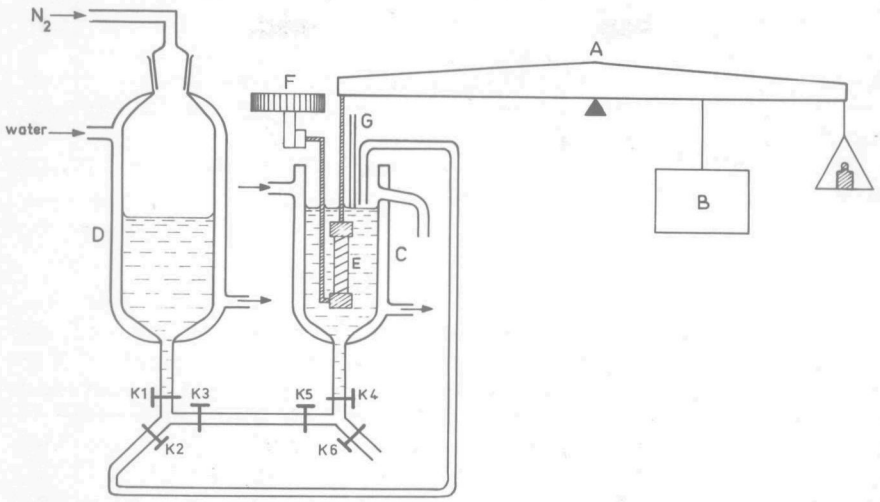

Figure 2. Schematic diagram of the elasto-osmometer. A = balance; B = inductive force pick up; C = thermostated measuring cell; D = thermostated solution vessel; E = swollen gel strip; F = micrometer, connected to lower clamp of strip; G = adjustment device for constant immersion level; K1-6 = metal stopcocks for introduction, replacing and draining of polymer solutions.

In order to keep friction as low as possible the knife-edges of the balance and their bearings are made of agate. By placing a counterweight at the same side as the transducer the initial force due to the stretching can be compensated. A second advantage of a balance-type design is that an additional amplification can be obtained by moving the point of attachment of the force pick up closer to the centre of the balance.

The output of the transducer is supplied to an amplifier (Type KWS/II-50, Hottinger), connected to a 4 Volt recorder (Goerz Servogor, type RE 511, Vienna, Austria).

A condition for attaining a high sensitivity is that the instrument should be well isolated from mechanical vibrations. For example, in our case measuring at night-times, rather than day-time, reduced the noise level about tenfold.

The gel strip is held between two clamps of which the upper one is connected to the balance arm by means of an Invar rod. The lower clamp is attached to the base plate of the balance, also by means of an Invar rod. A micrometer

(F in Figure 2) moves this lower clamp in order to adjust the length of the strip. The strip, together with its clamps, is immersed in a swelling agent or a polymer solution in the measuring cell C. This vessel has a volume of about 60 ml and is thermostated by a water jacket to exclude temperature influences.

The whole instrument is enclosed in a perspex box to avoid disturbance by air draughts.

3.2. OPERATION PROCEDURE.

At the beginning of an experiment the measuring cell is usually filled with pure solvent. After establishment of the swelling equilibrium the solvent is replaced by a polymer solution of known concentration from the storage vessel D (see Figure 2) by applying a small nitrogen pressure and operating the metal stopcocks K1, K3, K5 and K4. This replacing process must not be carried out too fast in order to avoid too much mixing of the original and the new solution. A reasonable time for this process is 10 minutes. During the replacing process the new swelling equilibrium begins to establish itself. In most cases it is attained in 15 tc 20 minutes in the case of non-permeating solutes and in about the same time or a little longer for permeating solutes. If the solution in the measuring cell has to be replaced by a solution of lower density, this latter solution is introduced via stopcocks K1 and K2, whilst the original solution is drained off by way of stopcocks K4 and K6.

In view of the buoyancy effect on the Invar rod of the upper clamp it is important to adjust the liquid level always at precisely the same height. This is achieved by first lowering the liquid level, after the replacement, to below the end of a narrow steel tube G (Figure 2) and after that making it rise again slowly until the liquid surface takes hold of the end of the tube.

3.3. SENSITIVITY OF THE METHOD AND SOURCES OF ERROR.

The accuracy and sensitivity of the elasto-osmotic method is affected by three sources of errors. In the first place the construction of the balance and the inductive transducer may be the origin of imperfections such as irreproducebility and non-linearity. Secondly, the measuring cell, together with the gel strip, the clamps, etc. can be a possible source of error. Finally, errors may originate from the procedure

for replacement of the solutions.

3.3.1. *The balance-transducer-recorder combination.*

In order to obtain information concerning the sensitivity of the mechanical and electrical part, the instrument was calibrated by means of known weights. The arrangement during this calibration was such that the distance between the point of attachment of the pick up and the centre of the balance was 0.6 times the distance between the point of attachment of the strip and the centre. In section 3.1 the possibility of an amplification of the force exerted on the transducer, by moving the point of attachment closer to the centre, was mentioned. However, due to an increasing influence of mechanical vibrations the overall sensitivity does not increase beyond a certain point. In our instrument the value 0.6 can be regarded as an optimum value. Moreover, the decrease in retractive force originating from the fact that the length of the gel strip decreases as a result of the displacement of the transducer, is the greater the more the point of attachment approaches the pivot, as pointed out at the end of this Section.

A calibration was carried out on the 1 μ, 2 μ, 5 μ and 10 μ scale of the amplifier. These displacement values correspond with forces of 0.13, 0.26, 0.65 and 1.30 grams, respectively. In all ranges the deviations from non-linearity are less than 0.4%. The reproducebilities for the two most sensitive ranges, which are of most interest from an experimental point of view were both found to be about 1 mg. This sensitivity is less than that of an analytical balance (0.1 mg). The reason is that, although the assembly resembles an analytical balance, its equilibrium position depends on the transducer rather than on the weight of the beam and the location of the centre of gravity with respect to the pivot.

The effect of the extensibility of the transducer will now be subjected to a closer inspection (see Figure 3).

The equations describing the change in retractive force as a function of the concentration of the polymer solution outside the gel are derived under the assumption that the length of the strip, L, is equal before and after the deswelling. In that case the transducer measures a force k which is related to the retractive force of the strip, f, by

$$k = (a/b)f \qquad (3.1)$$

Because of the displacement of the transducer the length

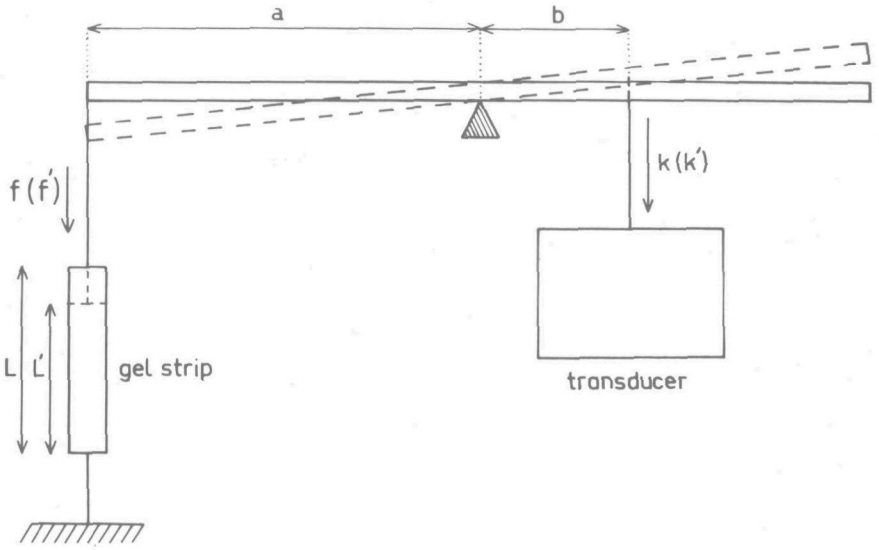

Figure 3. Effect of the extensibility of the transducer.

of the strip in reality changes to L'. The corresponding retractive force becomes f' and the transducer measures a force k':

$$k' = (a/b)\, f' \tag{3.2}$$

Since we want to calculate the deviation resulting from the displacement effect in the case of a given solute concentration and thus a given chemical potential of the solvent, we are interested in

$$\Delta k = k - k' = \frac{a}{b} \left(\frac{\partial f}{\partial L} \right)_{\mu_{1g}} \Delta L \tag{3.3}$$

where $\Delta L = L - L'$.
By differentiating f, as given by Equation (2.7), with respect to L, we get:

$$\left(\frac{\partial f}{\partial L} \right)_{\mu_{1g}} = ARTv_e \left[\frac{1}{L_o^2} + \frac{2qL_o}{q_o L^3} - \frac{L_o}{q_o L^2} \left(\frac{\partial q}{\partial L} \right)_{\mu_{1g}} \right] \tag{3.4}$$

Noting that

$$\left(\frac{\partial q}{\partial L}\right)_{\mu_{1g}}\left(\frac{\partial L}{\partial \mu_{1g}}\right)_{q}\left(\frac{\partial \mu_{1g}}{\partial q}\right)_{L} = -1 \text{ and thus } \left(\frac{\partial q}{\partial L}\right)_{\mu_{1g}} = -\frac{(\partial \mu_{1g}/\partial L)_{q}}{(\partial \mu_{1g}/\partial q)_{L}} \tag{3.5}$$

we obtain, if we employ Equation (2.5) for the chemical potential of the solvent:

$$\left(\frac{\partial f}{\partial L}\right)_{\mu_{1g}} = ART\nu_{e}\left(\frac{1}{L_{o}^{2}} + \frac{2qL_{o}}{q_{o}L^{3}} - \frac{K}{\sigma_{o}\rho_{1}L^{2}}\right) \tag{3.6}$$

where K has the same meaning as in Equation (2.11).
k' is related to the displacement of the transducer which in our case is equal to $(b/a)\Delta L$, through δ, the displacement of the transducer per unit force:

$$k' = \frac{b}{a}\frac{\Delta L}{\delta} \tag{3.7}$$

δ is a constant for a given transducer.
Combining Equations (3.3), (3.6) and (3.7) we finally arrive at:

$$\frac{\Delta k}{k'} = ART\nu_{e}\delta\left(\frac{a}{b}\right)^{2}\left(\frac{1}{L_{o}^{2}} + \frac{2qL_{o}}{q_{o}L^{3}} - \frac{K}{\sigma_{o}\rho_{1}L^{2}}\right) \tag{3.8}$$

Owing to the fact that the deviation is proportional to the force itself, the slope of the experimental f-c curve will be too small and consequently the molecular weight calculated from the slope at its limit of infinite dilution will be too high. For a poly(dimethyl siloxane) strip an estimate has been obtained by substituting a ν_{e}-value obtained from the swollen modulus and assuming A and q_{o} to be unity. It turns out that $\Delta k/k' = 2.48\times10^{-3}(a/b)^{2}$ in this case. This means that for $b/a = 0.6$ the deviation is only 1.5%, but for $b/a = 0.1$ the deviation amounts to 25%.
It appears from Equation (3.8) that the deviation increases with increasing ν_{e} and thus with increasing modulus. Therefore a correction for the effect will be necessary in general. Fortunately, it will be obvious from the foregoing that we can get round the difficulty by a calibration of the instrument

with solutions of known activity.

3.3.2. *Errors due to variations in buoyancy.*

The buoyancy of the gel strip, the upper clamp and the rod which connects this clamp to the balance can be affected by two effects. One is the deviation of the liquid level from its proper height, influencing the rod only, the other is found in the change in density of the solution around the gel upon its replacement by a solution of higher concentration.

The deviation brought about by variations in the liquid level can easily be calculated from the diameter of the Invar rod which forms the connection between the upper clamp and the balance arm. Because in our instrument the diameter is 2 mm, a variation of the liquid level of 1 mm gives a difference in buoyancy of 3 mg, if the density of the solution in the measuring cell is 1 g/cm^3. By means of the adjustment device, described in Section 3.1, the liquid level can be adjusted to within 0.2 mm. This reduces the error to about 0.6 mg which is well within the sensitivity of the instrument.

The difference in density between a polymer solution and the solvent may exercise more influence. The volume of the gel strip, the upper clamp and that part of the rod which is immersed in the liquid amounts to 1.75 cm^3. For a 1% solution of polystyrene in toluene of which the density difference with regard to the solvent is 0.0017 g/cm^3, the buoyancy difference is equal to 3 mg. This example shows that, generally speaking, this effect is not negligible. However, in molecular weight determinations one usually performs measurements on a series of solutions of different concentrations in order to eliminate non-ideality by extrapolating to infinite dilution. This extrapolation also eliminates the density effect which is in first approximation linearly proportional to the concentration. On the other hand, if one is interested in the second virial coefficient of the polymer solution (A_2 in Equation (2.10)), a correction will be necessary.

3.3.3. *Reliability of the replacement procedure.*

During the introduction of a solution from the storage vessel into the measuring cell, concentration changes may occur by mixing with the original solution in the cell.
In order to get an impression about the magnitude of the differences in concentration between the storage vessel and the

measuring cell, the replacement procedure was carried out with aqueous solutions of ammonium thiocyanate. The experiments were performed using two solutions, differing 0.0018 g/cm^3 in density. In one experiment the dilute solution was brought into the measuring cell and subsequently replaced by the more concentrated solution in about 10 minutes. From the overflow of the cell 10 ml aliquots were collected, in which the concentrations were determined by volumetric titration with a standard silver nitrate solution. In a second experiment the measuring cell contained the more concentrated solution, whereas the dilute solution was introduced at the top of the cell, as described in Section 3.2.

In both experiments a boundary layer of not more than about 5 ml volume was observed. The concentrations in all aliquots, except the one containing the boundary layer, agreed with those of the original solutions to within 1%. In view of the fact that the density difference of these test solutions is comparable with that of the dilute polymer solutions normally employed in elasto-osmometry, we may assume that in the latter case the concentration remains constant as well.

3.4. THE GEL STRIPS.

For use in elasto-osmometry an overwhelming variety of possible elastomers is at our disposal. In principle, the only demand we make on the elastomers is that they exhibit a certain degree of swelling in a suitable swelling agent. Of course, the gel strips must also be manageable in this respect that their consistency allows them to be mounted into the clamps and to be stretched to about 10%.
However, in order to obtain a high sensitivity it will be profitable to aim our research at strips with a high K-value (Equation (2.11)). An a priori prediction of K requires knowledge of all network parameters, some of which are not so easy to obtain. Besides, in the derivation of Equation (2.11) the elastomer was solely regarded as an entropy spring. Energy effects may also play a role, however. This altogether makes the search to a certain extent a question of trial and error.

In order to get an impression of the properties which govern the efficiency, strips of varying chemical composition and degree of crosslinking have been used in our investigations. Measurements have been carried out with strips of poly(dimethyl siloxane) (General Electric Co., Schenectady, N.Y., U.S.A.), poly(cis-isoprene), poly(cis-butadiene),

poly(butadiene-co-styrene), containing 23% styrene and poly-(butadiene-co-acrylonitrile), containing 36% acrylonitrile (courtesy of the Shell Plastics Laboratory, Delft, The Netherlands).

All strips were crosslinked in the dry state. This has the advantage that q_0 has a low value, because the chains in such a dry crosslinked polymer should have conformations which are close to those in the non-crosslinked, unrestrained state. As the volume fraction of network material in the dry state is close to 1, $q_0 \approx 1$. According to Equation (2.11) K is largest when q_0 has a minimal value.

Before crosslinking the strip materials were formed into thin sheets of about 0.2 mm thickness. This was performed by pressing the material, after a preliminary diminution of the thickness by means of a calender, in a steel press at a pressure of about 10,000 atm*. During the pressing the press was heated to about 100°C by steam. Although K is linearly dependent on the cross-section of the gel strip, it is not advisable to use much thicker strips, as the time of attainment of equilibrium increases with increasing cross section. So one has to find a compromise between the sensitivity and the speed of the instrument.

The crosslinking was accomplished by γ- or β-irradiation. The irradiation normally gives rise to several types of reactions like chain scission, gas evolution and crosslinking[21]. For our purpose the crosslinking effect must be predominant. All materials used in our investigations could readily be crosslinked by irradiation without too much damaging.

For the irradiation of poly(dimethyl siloxane) and poly(cis-isoprene) use was made of a Co^{60} source with a dose rate of 0.1 megarads per hour. During the irradiation the strips were kept under nitrogen in sealed glass tubes. In the case of poly(dimethyl siloxane) a dose of 10 megarads turned out to be sufficient to produce an insoluble network of reasonable strength. For poly(cis-isoprene) the proportion between the reactions leading to crosslinking and the chain scission reactions is less favourable and here doses of 30 to 40 megarads are necessary.

The strips consisting of the other materials mentioned above were crosslinked by irradiation with electrons (energy 0.5 MeV) from a Van de Graaff generator**. This source has the advantage that the intensity and the effectiveness

* The assistance of Rubberinstituut TNO, Delft, is gratefully acknowledged.

** The author is grateful to Dr. W.A.Cramer, Reactor Instituut, T.H., Delft, for his assistance.

of the radiation is much greater than that of a Co^{60} source, so that the radiation times are shortened considerably.

In Table I the doses and the properties of the resulting elastomers are listed. The degree of swelling q was determined by measuring under a microscope the dimensions of a piece of crosslinked polymer before and after swelling in the swelling agent, which in all cases was toluene.

Table I

Gel material	Dose (megarads)	q	Young's modulus in the dry state (dynes/cm^2)	Young's modulus in the swollen state (dynes/cm^2)
poly(dimethyl siloxane)	10	6.23	1.55×10^6	5.2×10^5
poly(cis-isoprene)	30	7.34		1.62×10^6
	42	5.96		1.85×10^6
poly(cis-butadiene)	15	3.87	1.15×10^7	7.52×10^6
poly(butadiene-co-styrene)	15	5.72		3.34×10^6
poly(butadiene-co-acrylonitrile)	7.5	2.85		8.53×10^7

In most cases the original polymer material contained a smaller or larger amount of additives like stabilizers and dyes. Also, some low molecular weight, soluble material is formed through side reactions during the irradiation. For this reason all strips were subjected to an extraction with toluene for several days.

All gel strips, prepared in this way, behaved well in this respect that they could be easily mounted into the clamps and that after a short initial period the retractive force at a certain degree of elongation remained constant.

CHAPTER 4

PREPARATION AND CHARACTERIZATION OF THE POLYMERS

In order to investigate the possibilities and limitations of the elasto-osmotic technique a calibration with well defined polymer materials is of prime importance. To this end three different types of polymers were used, viz. polystyrenes, poly(vinyl acetates) and poly(oxypropylene)glycols.

4.1. PREPARATION

A number of polystyrenes were prepared at Kunststoffeninstituut TNO, Delft, The Netherlands, by anionic polymerization of styrene using a technique described by Szwarc [22]. In this method the reactants and the conditions are chosen such that (i) the rate of initiation is much greater than the propagation rate and (ii) termination does not occur during polymerization. Under these circumstances the polymer chains, after a simultaneous initiation, grow at equal rates. When all the monomer is consumed they will all have nearly the same length. As a result the polymer, after termination, will have a very narrow molecular weight distribution.

Similar polystyrene samples were also obtained from ArRo Laboratories Inc., Joliet (Illinois), U.S.A., in a later stage of this study.

The poly(oxypropylene)glycols were obtained from Dow Chemical Co., Rotterdam, The Netherlands (trade name: Voranol) and Shell Chemie Nederland N.V., The Netherlands (trade name: Caradol). These polyglycols are prepared by base-catalyzed polyaddition of propylene oxide to a bifunctional or trifunctional alcohol like propylene glycol or glycerol. The polymerization progresses by way of a stepwise mechanism [23] without termination and thus it presents the same characteristics as the anionic polymerization of vinyl polymers described before. Therefore, the polyglycols also have a very narrow molecular weight distribution.

The poly(vinyl acetates) were prepared by conventional radical polymerization of about 40% vinyl acetate solutions

in benzene at 70° C, using azobisisobutyronitrile as initiator. Triethyl amine was used as a chain transfer agent to adjust the desired molecular weight. Precise data concerning the preparation are given in Table II, together with the limiting viscosity numbers in acetone which were determined by means of an Ubbelohde viscometer. The limiting viscosity number is defined as

$$[\eta] = \lim_{c \to o} \frac{\eta - \eta_o}{\eta_o c} \qquad (4.1)$$

in which η and η_o are the viscosities of the solution (concentration c) and the solvent, respectively.

Table II

Polymer	Concentration initiator (g/l)	Concentration chain transfer agent (ml/l)	$[\eta]$ (dl/g)
PVAc-1	0.4	-	1.080
PVAc-2	1.2	-	0.865
PVAc-3	1.8	2	0.704
PVAc-4	2.0	10	0.515
PVAc-5	2.0	20	0.476
PVAc-6	4.0	40	0.341

In all cases the conversion was kept below 10%. This means that the monomer concentration during the polymerization is practically constant. Polymerization at constant monomer concentration in the presence of a chain transfer agent yields polymers with a Flory-Schulz-type distribution[24]:

$$f(M)\,dM = C \exp(-\beta M)\,dM \qquad (4.2)$$

because termination by combination is suppressed. In this equation C and β are constants. The ratio $\overline{M}_w / \overline{M}_n$ for such a distribution is equal to 2.

4.2. CHARACTERIZATION METHODS.

In order to obtain data concerning the number average molecular weights as well as the molecular weight distributions of the polymers described in Section 4.1, several techniques were used. A summary of all results will be found in Section 4.3.

The low molecular weight polystyrenes and some of the polyglycols were analyzed by means of thermoelectric vapour phase osmometry. This method is described in Section 4.2.1. The number average molecular weights of the poly(oxypropylene)glycols were also determined by functional group analysis. In this method the hydroxyl content is calculated from the amount of acetic anhydride needed for the acetylation of the OH-groups[25]. The calculation was performed under the assumption that all polymer molecules are of the same functionality and that all chains are terminated by hydroxyl groups.

For the determination of higher molecular weights, as in the case of the poly(vinyl acetates), membrane osmometry is the most preferable method (see Section 4.2.2.).

Finally, in view of the permeation phenomena in elasto-osmometry it is important to also know the molecular weight distribution. An excellent method for this purpose is gel permeation chromatography, which is described in Section 4.2.3. Without calibration, however, this method does not yield absolute molecular weights.

4.2.1. *Thermoelectric vapour phase osmometry.*

Although discovered as early as 1930[26] thermoelectric vapour phase osmometry has not found full acceptance as a completely equivalent alternative to cryoscopy and ebullioscopy until recently. This is the more surprising as the method possesses some distinct advantages over the latter methods. In this connection its freedom from temperature limitations, its rapidity and its applicability to minute amounts of sample should be mentioned.

The method is based on a conversion of the vapour pressure difference between a solution of the substance under investigation and a reference solution of known activity, usually the pure solvent, into a temperature difference. To that end both solutions are placed in a closed thermostated system saturated with solvent vapour. Because of the difference in vapour pressure with respect to their surroundings solvent vapour condenses into the two solutions at a rate proportional to their activities. The heat of condensation generated will raise the temperature of the solutions. In due course a steady state is established in which the heat losses by conduction and radiation are just compensated by a continuous amount of condensation.

The steady state temperature difference between both solutions can be shown to be proportional to their difference in activity[2,3] :

$$\Delta T = - K_s (RT^2/H) \ln(a_1/a_2) \qquad (4.3)$$

where H is the molar heat of vaporization of the solvent and K_s an apparatus constant.
This temperature difference can be measured by placing the solutions in the form of tiny drops onto the junctions of a thermocouple[3] or, alternatively, onto the tips of two matched thermistors[27]. The thermal EMF or the change in resistance can then be measured by means of a sensitive galvanometer or a Wheatstone bridge, respectively.

A full description of the apparatus used in our investigation can be found in the literature[28]. Although it is possible to put the method on an absolute basis by a detailed study of the heat and mass transfer in the steady state[3], it is more convenient in practice, and often more reliable, to perform a calibration with substances of known molecular weight.

The number average molecular weights of the low molecular weight polystyrenes and some poly(oxypropylene)glycols were calculated from the vapour pressure lowering of benzene solutions of these substances. In order to eliminate influences of the non-ideality of the solutions by extrapolation to infinite dilution, a series of different concentrations was run in each case. The extrapolated temperature difference between a solution of concentration c and the pure solvent is given by:

$$\lim_{c \to o} (\Delta T/c) = K_s (RT^2 M_1/H\overline{M}_n) \qquad (4.4)$$

The calibration constant K_s was determined by a calibration with pure anthracene.

4.2.2. *Membrane osmometry.*

In membrane or "regular" osmometry the activity of a polymer solution is determined by measuring the hydrostatic pressure necessary to maintain isothermal equilibrium between this solution and the pure solvent, separated by a semi-permeable membrane. Such a membrane permits the passage of solvent while fully retaining the solute molecules. This pressure is called the osmotic pressure, π, of the solution:

$$\pi = - (RT/v_1) \ln a_1 \qquad (4.5)$$

As in elasto-osmometry and in vapour phase osmometry, the number average molecular weight can only be obtained

by measuring a series of concentrations in order to eliminate the concentration dependence of the activity coefficient. At infinite dilution Van 't Hoff's familiar relationship holds:

$$\lim_{c \to o} (\pi/c) = RT \, \rho_1 / \overline{M}_n \qquad (4.6)$$

The determination of number average molecular weights above about 15,000 poses no serious problems in membrane osmometry, as bacterial cellulose membranes are commercially available which combine a good retentivity to low molecular weight solutes with a reasonable solvent permeability. In our experiments membranes of the grade "allerfeinst", obtained from the Membranfilter-Gesellschaft Sartorius Werke A.G., Göttingen, Germany, were used.

The osmotic pressures of the poly(vinyl acetate) solutions in toluene were determined with a Zimm-Myerson osmometer[29]. This osmometer consists of a glass cell with a volume of 5 ml which is equipped with a measuring capillary and an "adjusting" capillary. The hydrostatic head in the measuring capillary can be set at a certain level by manipulating a closely fitting steel rod in the adjusting capillary. The osmometer cell, closed by membranes at two sides, is immersed in a wide tube filled with pure solvent.
The equilibrium hydrostatic head or osmotic pressure was attained in about one day, provided that the level in the measuring capillary is set near the value to be expected.

4.2.3. *Gel permeation chromatography.*

Gel permeation chromatography (GPC) is a relatively new and rapid technique by which a polydisperse polymer is separated according to molecular size. The separation is achieved by eluting the polymer sample with a suitable solvent through columns packed with swollen polystyrene gel particles varying in permeability over many orders of magnitude. As the sample passes through the column, the polymer molecules diffuse into all pores of the gel not mechanically barred to them. This means that molecules larger than the maximum pore size pass through the column in the interstitial volume, while molecules smaller than the maximum pore size permeate into the pores and spend the more time in the column the smaller they are.

The permeability of the polystyrene gels is regulated by polymerizing and crosslinking them in the presence of a diluent which is a good solvent for the monomer but a bad solvent for the polymer[30]. By varying the amount and nature of the diluent it is thus possible to produce rigid gel particles

with any desired permeability over an extremely wide range.

A GPC-instrument based on the principles mentioned above is commercially available from Waters Associates Inc., Framingham (Mass.), U.S.A. In this instrument the concentration in the effluent from the columns is followed by measuring the difference in refractive index between the effluent and pure solvent. In this manner a plot of the differential refractive index (or polymer concentration) versus the elution volume can be obtained.

The main difficulty in GPC lies in converting the elution volumes to a molecular weight scale. It is often observed that plotting the logarithms of the molecular weights of chemically identical polymers versus the elution volumes yields straight lines for a particular set of columns. Efforts have been made to obtain a more general calibration curve, also valid for chemically different polymers, by plotting the logarithm of the straight chain length[30] or some other measure for the size of the polymer molecule[31] rather than the molecular weight. However, a general calibration for all kinds of polymers is not available and quite probably, will never be found, because of the existence of specific interactions between the gel and specific polymers.

The polydispersity of our poly(vinyl acetates) and poly(oxypropylene)glycols was determined by passing them through a Waters GPC containing 4 columns in series with maximum pore sizes of 10^6, 3×10^4, 10^3 and 250 Å, respectively*. The instrument was operated at room temperature with tetrahydrofuran as a solvent. The flow rate was kept constant at 1 ml per minute. At this flow rate it takes approximately 4 hours to completely resolve a sample.

4.3. MOLECULAR WEIGHT DATA OF THE POLYMERS.

4.3.1. *Polystyrenes.*

In Table III the molecular weights of the polystyrenes are given. The number average molecular weights of the samples PS-1, PS-2 and PS-3 were determined by vapour phase osmometry. The molecular weights of the other samples are those reported by the manufacturer. The number averages were determined by membrane osmometry, the weight averages by ultracentrifugation in the case of PS-4 and by light scattering in the case of samples PS-5 and PS-6.

* Thanks are due to Mr. A.Bos for performing the GPC measurements.

Table III

Polymer	Supplier	$\overline{M}_n$	$\overline{M}_w$
PS-1	TNO	6480 ± 1.5%	
PS-2	"	8170 ± 1,4%	
PS-3	"	14,000 ± 3.2%	
PS-4	ArRo	10,300 ± 3%	10,300 ± 3%
PS-5	"	19,800 ± 3%	19,800 ± 2%
PS-6	"	51,000 ± 1.2%	51,000 ± 1%
PS-7	"	160,000 ± 3%	

4.3.2. *Poly(oxypropylene)glycols.*

Table IV gives the number average molecular weights of the poly(oxypropylene)glycols. The molecular weights under the heading "OH-number" were calculated from the OH-number as given by the supplier. The molecular weights in the column marked "OH-analysis" were obtained from a functional group analysis as described in Section 4.2.

The values obtained from vapour phase osmometry are consistently lower than those obtained from OH-analysis. This is attributed to the presence of minor quantities of low molecular weight impurities which of course show up very markedly in VPO.

The number average molecular weights obtained from GPC were calculated by using a calibration curve in which the logarithms of the straight chain lengths of a number of monodisperse polystyrenes is plotted versus their elution volumes. In this calculation a correction for longitudinal diffusion is applied. This is necessary because when a sample is being eluted through a GPC column its chromatogram is broadened by two processes, a desirable process leading to separation by permeation and an undesirable process due to mixing in longitudinal direction. As pointed out by Tung[32] the chromatogram resulting from the longitudinal diffusion can be assumed to be Gaussian and consequently a correction for this effect can be calculated.

The molecular weights thus obtained are approximately one half of the values obtained from OH-analysis. This systematic discrepancy is not surprising as pointed out in Section 4.2.3. Indeed it would be highly suspicious if the correct molecular weights were found from the calibration of the elution volume by means of chemically different polymers. Apart from the fact that specific polyglycol-gel interactions may play a role, it is also evident that the extended chain length is by no means the best measure of the

Table IV

Polymer	Supplier	$\bar{M}_n$, obtained from				$(\bar{M}_n)_{GPC}/(\bar{M}_n)_{OH}$	$\bar{M}_w/\bar{M}_n$ from GPC
		OH-number	OH-analysis	VPO	GPC		
P-400	Dow	405	405		145	0.36	1.11
P-1200	"	1180	1205				
P-2000	"	2020	2075	1960	1020	0.49	1.13
P-2700	"	2650	2615	2160	1240	0.47	1.10
P-4000	"	4360	4160		1990	0.48	1.18
P-750	Shell		830	710	330	0.40	1.06
P-5000	"		4920	3500	2020	0.41	1.28

hydrodynamical dimensions. Therefore, a more extensive treatment which includes the measurement of the limiting viscosity number[31], has in some cases given a better agreement. The value of the GPC method so far lies in its "finger printing" ability of the molecular weight distribution. From the pattern the $\overline{M}_w/\overline{M}_n$ ratio's, which are a measure of the width of the distribution, can be reliably calculated because no absolute molecular weights are needed in this case. The uncertainty in the ratio's is estimated at ± 3%. As can be seen from Table IV the polyglycols are to a large extent monodisperse as is also to be expected on the basis of the polymerization kinetics.

4.3.3. *Poly(vinyl acetates).*

The number average molecular weights of the poly(vinyl acetates), as determined by membrane osmometry, can be found in Table V. The accuracy of these molecular weights is 3 to 4%.

Table V

Polymer	$\overline{M}_n$ from membrane osmometry	$\overline{M}_n$ from GPC	$\overline{M}_w/\overline{M}_n$ from GPC
PVAc-1	115,000		
PVAc-2	88,300	69,900	2.12
PVAc-3	70,000	42,800	1,88
PVAc-4	42,000		
PVAc-5	33,600	25,700	1,87
PVAc-6	23,000	17,600	2.03

In this Table the number average molecular weights obtained from GPC which are based on the polystyrene calibration curve, are also given. As in the case of the polyglycols the GPC-values are too low. Here again the useful information to be extracted from the GPC experiment, lies in the $\overline{M}_w/\overline{M}_n$ ratio's, which are quite trustworthy. The correspondence with the value $\overline{M}_w/\overline{M}_n = 2$, predicted from the polymerization kinetics, should be noted.

In Table II, Section 4.1, the limiting viscosity numbers of the poly(vinyl acetates) in acetone are given. This quantity depends on the size and the shape of the polymer molecules in solution and thus it is a measure of the molecular weight within a polymer homologous series. This relationship is normally expressed by the Mark-Houwink-Sakurada equation[33]:

$$[\eta] = K' M^{\alpha} \qquad (4.7)$$

The constants K' and α can be obtained by plotting the logarithms of the limiting viscosity numbers of polymers with a sharp distribution against the logarithms of their molecular weights. In the case of a polydisperse polymer the application of Equation (4.7) yields the so-called viscosity-average molecular weight which gives an intermediate between $\overline{M}_n$ and $\overline{M}_w$, but which is always considerably closer to $\overline{M}_w$ than to $\overline{M}_n$.

Owing to the fact that in the literature [34] values are found varying from 0.67 to 0.74 for α and from 8.6 to 24.5×10^{-5} dl/g for K', an estimate of M from the limiting viscosity numbers is virtually impossible. However, it is possible to use the limiting viscosity numbers in order to check the relative positions of the osmotically determined number average molecular weight values by plotting log $[\eta]$ versus log $\overline{M}_n$. By doing this it is tacitly assumed that the ratio between $\overline{M}_v$ and $\overline{M}_n$ is the same for all polymers. In our case this will not be far beside the truth because the shapes of the distributions of the various poly(vinyl acetates) are very much alike due to the similarity of their polymerization conditions. It is also indicated by the fact that the $\overline{M}_w/\overline{M}_n$ ratio in all samples is about 2, see Table V.

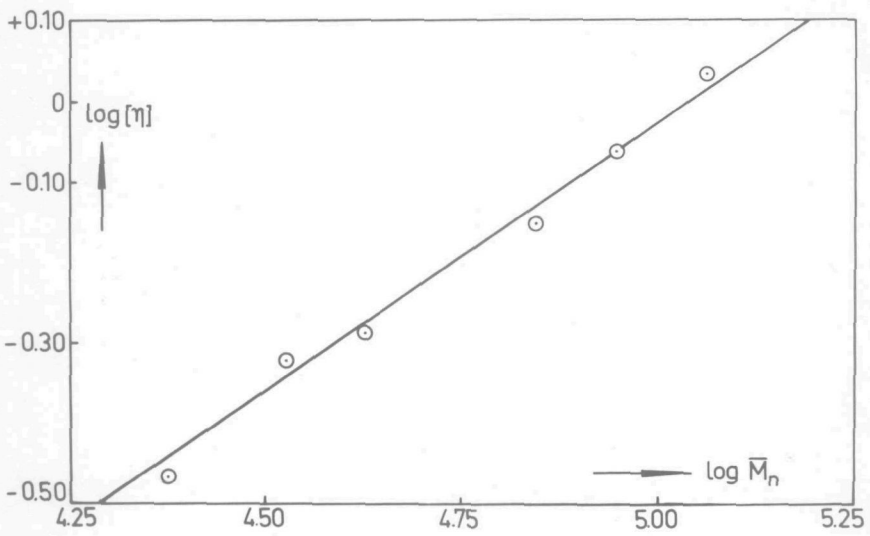

Figure 4. Limiting viscosity number as a function of the number average molecular weight for a series of poly(vinyl acetates) prepared by radical polymerization.

As can be seen from Figure 4 Equation (4.7) is well obeyed by our poly(vinyl acetates). K' and α as calculated from the intercept and the slope of the curve turn out to be 4.0×10^{-4} dl/g and 0.67, respectively. When based on the weight average molecular weight K' is found to be 2.5×10^{-4} dl/g, which is in good accordance with the literature values mentioned above.

CHAPTER 5

DESCRIPTION AND INTERPRETATION OF THE ELASTO-OSMOTIC EXPERIMENTS

5.1. ELASTO-OSMOMETRY BY CALIBRATION

The measurements described in this Section were all performed on strips swollen in toluene. Of course, this solvent was also used for dissolving the polymers of which the molecular weight had to be determined.

After an extraction of the gel sheets (see Section 3.4) in order to remove soluble components, they were cut in the swollen state into rectangular strips with a length of about 4 cm and a width of 5 to 6 mm. The length of these strips when mounted between the clamps was approximately 2 cm.

5.1.1. *Poly(dimethyl siloxane) strips.*

A poly(dimethyl siloxane) strip, with an irradiation dose of 10 megarads, was subjected to deswelling experiments using solutions of anionic polystyrenes of rather low molecular weights. In these experiments all solutions of a given polymer were measured one after another, without returning to the pure solvent in between. In Figure 5 the retractive force difference between the solutions and the pure solvent, Δf, is given as a function of the concentration. In all three cases the plots are linear up to the highest concentration which never exceeds 1 weigth %. This means that the second virial coefficient A_2 (Equation (2.11)) is negligible. In view of the low concentrations employed and the low molecular weights this is not surprising, the more so since the interaction parameter of the solvent-polymer interaction, χ_{1p}, is relatively close to $\frac{1}{2}$ in these systems [35]. According to the Flory-Huggins theory A_2 is proportional to $(\frac{1}{2} - \chi_{1p})$ (see Section 2.1.2.).

The proportionality constant K (Equation (2.11)) can be found by plotting the slopes of the curves at infinite dilution, $(\partial f/\partial c)_{c\to o}$, against the reciprocal number average molecular weights as obtained from vapour phase osmometry (Table III). The resulting plot is shown in Figure 6.

As a consequence of the fact that the relationship between $(\partial f/\partial c)_{c\to o}$ and $1/\overline{M}_n$ is strictly linear, we may conclude

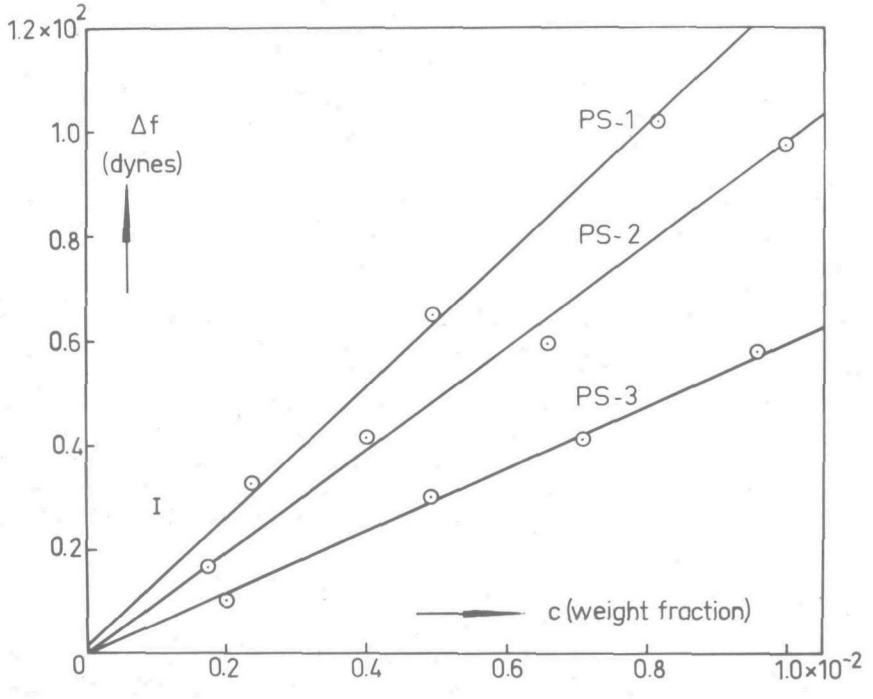

Figure 5. Retractive force of a poly(dimethyl siloxane) strip as a function of the concentration of solutions of three polystyrenes.

that no penetration of polymer solute into the gel strip occurs. It is obvious that in the case of penetration the $(\partial f/\partial c)_{c\to 0}$-values would be too small. From the slope of the line we obtain a K-value equal to 3.28×10^{-3} g/cm.

Because of rupture of the gel strip used for the polystyrene measurements, another strip of the same material was used for measuring the effects for two poly(vinyl acetates), PVAc-3 and PVAc-4 (see Figure 7).
As in all experiments the measurement was started by replacing the pure solvent by the polymer solution of lowest concentration. As a result a normal deswelling took place. However, replacing this dilute solution by a solution of higher concentration did not lead to a further increase of the force, roughly proportional to the concentration. Instead there was almost no change in force: in one hour an in-

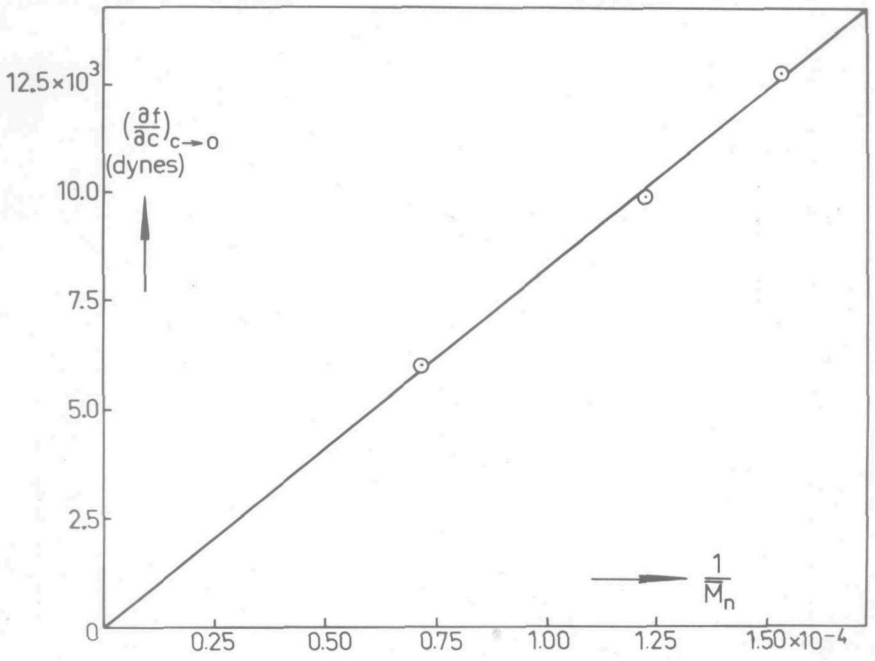

Figure 6. Elasto-osmotic effect of some polystyrenes as a function of the reciprocal number average molecular weight as determined by vapour phase osmometry.

crease of 5% of the expected change was observed, in two hours about 7%.
This difficulty can be circumvented by conditioning the gel strip again in pure solvent and by not bringing the solution of higher concentration into the cell until the swelling equilibrium is complete. This swelling equilibrium is attained in about one hour and introduction of the new solution then yields a normal deswelling in a reasonable time.

The probable explanation of this effect is that the gel does not respond to the higher concentration because of clogging of its surface due to adsorbed polymer molecules. As a result diffusion of solvent molecules out of the strip is strongly hindered. The reason that clogging of the surface does not occur when the solvent is replaced by a polymer solution most probably is that the solvent flow out of the strip is so large that the solvent molecules do not get a chance to adsorb onto the surface before the deswelling is

centration of 2%. This is somewhat surprising since we do not expect that these high polymer solutions behave ideally in this concentration range. Probably, in spite of the precautions indicated above, some influence of the clogging effect is perceptible.

In actual practice an elasto-osmotic determination of the number average molecular weight of an unknown sample will usually be based on a calibration of the apparatus with only one substance of exactly known molecular weight. If we apply this procedure to the poly(vinyl acetates) of Figure 7 we can calculate a K-value of 3.60×10^{-3} g/cm by using PVAc-4 as the calibration sample. The molecular weight of PVAc-3, based on this calibration, turns out to be 69,000 which is in good accordance with the membrane osmotic value of 70,000.

Finally, the agreement of the latter K-value with the one determined before should be noticed, although they were determined for different strips of, most probably, not exactly the same dimensions.

5.1.2. *Poly(cis-isoprene) strips.*

As pointed out in Section 5.1.1 the use of a non-polar strip might offer a possibility for avoiding the time-consuming technique of returning to the pure solvent after each measurement of a solution of a polar polymer. Indeed, using a strip of the non-polar poly(cis-isoprene), the normal procedure of successive measuring of the various concentrations could be followed without any difficulty. The results of these measurements for a series of five poly(vinyl acetates), using a strip crosslinked with a dose of 30 megarads, are shown in Figure 8.

These solutions exhibited distinct deviation from the ideal behaviour. Therefore $\Delta f/c$, instead of Δf, was plotted as a function of the concentration. In Figure 9 the intercepts are plotted against $1/\overline{M}_n$. For $\overline{M}_n$ the osmotically determined values were employed (see Table V).

Here also a linear relationship is obtained, indicating that penetration does not occur to any noticeable extent.

The proportionality constant K as calculated from the slope of the curve, is found to be equal to 4.49×10^{-3} g/cm.

From the deviations of the individual points from the straight line the standard deviation of the intercepts can be calculated. It varies between 1.2 and 3.0% going from the lowest to the highest molecular weight. For a good comparison of the results obtained from membrane osmometry and those obtained from elasto-osmometry it is re-

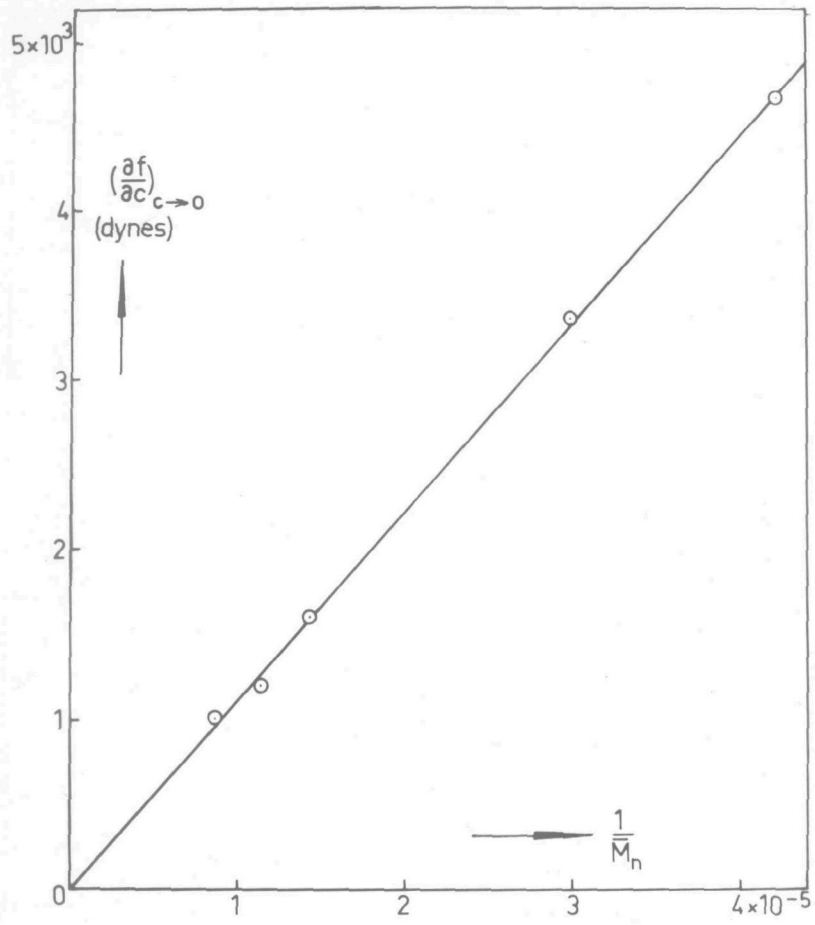

Figure 9. Reduced retractive force change at infinite dilution as a function of the reciprocal number average molecular weight as obtained from membrane osmometry, for five poly(vinyl acetates).

commendable to calculate the number average molecular weights from the $(\Delta f/c)_{c\to 0}$ values, using the average value of K. The results of this calculation can be found in Table VI.

The deviations between the two sets of values are very small. Of course, if the calibration of the elasto-osmometer is based on one sample, the error will, generally speaking, become larger, probably in the order of 3 to 8%, depending on the magnitude of the molecular weight.

It should be noted that elasto-osmometry may also yield

Table VI

Polymer	$\bar{M}_n$ from membrane osmometry	$\bar{M}_n$ from elasto-osmometry	Difference $(\bar{M}_n)_{el}-(\bar{M}_n)_{membr}$
PVAc-1	115,000	110,600	-3.0 %
PVAc-2	88,300	92,800	+5.1 %
PVAc-3	70,000	69,800	-0.3 %
PVAc-5	33,600	33,200	-1.2 %
PVAc-6	23,700	23,800	+0.4 %

valuable data concerning the deviation from non-ideality of the polymer solutions. The second virial coefficient A_2 (Equation 2.11)) can readily be calculated from the slopes of the curves in Figure 8. In this case A_2 varies between 3.89×10^{-2} for the highest molecular weight and 4.88×10^{-2} for the lowest molecular weight. These A_2-values carry an error of about 10%.

If we assume that the Flory-Huggins approach is valid for the poly(vinyl acetate) solutions, we are able to obtain χ_{1p} from the A_2-values because then $A_2 = (\frac{1}{2} - \chi_{1p})(\rho_1/\rho_2)^2$. For the highest molecular weight χ_{1p} is equal to 0.43, for the lowest molecular weight to 0.44, both with an error of about 3%. Unfortunately no literature data are known for the system poly(vinyl acetate)/toluene, but the χ-values appear to be quite reasonable. Also, the tendency of A_2 to decrease with increasing molecular weight is often found for other systems[36].

In order to check whether an increase in crosslinking density would have much influence on the efficiency of the poly(cis-isoprene) strips, two measurements were carried out with a strip irradiated to 42 megarads, rather than 30 megarads. The results of these measurements are given in Figure 10.

Evaluation of K from the slopes of these two curves yields an average of $(4.76\pm0.06)\times10^{-3}$ g/cm. As we see, the difference with the more lightly crosslinked strip is only 6%.

5.1.3. *Poly(butadiene-co-styrene) strips.*

A poly(butadiene-co-styrene) strip was calibrated by means of two polymers, PS-5 and PVAc-3 (see Figure 11).

The K-value calculated from the intercept of PS-5 is 8.48×10^{-3} g/cm, that from the intercept of PVAc-3 is 7.87×10^{-3} g/cm. The average value is $(8.15\pm0.28)\times10^{-3}$ g/cm.

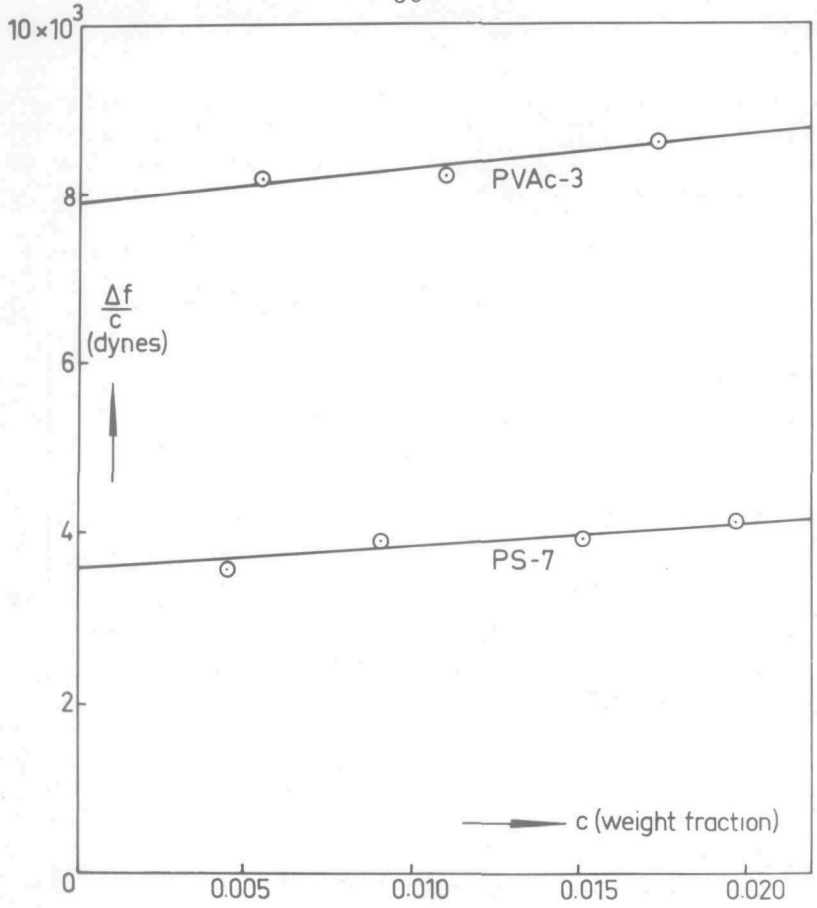

Figure 12. Reduced retractive force change plotted against the concentration of solutions of a poly(vinyl acetate) and a polystyrene sample, measured on a poly(butadiene-co-acrylonitrile) strip.

effect did not occur with measurements on the polystyrene sample.

The K-value which can be evaluated from the intercepts, is much higher than that obtained for any other strip so far. The measurement on PVAc-3 gives 2.23×10^{-2} g/cm, that on PS-7 2.31×10^{-2} g/cm, so that the most probable value can be estimated at $(2.27\pm0.04)\times10^{-2}$ g/cm.

5.1.5. *Poly(cis-butadiene) strips.*

A poly(cis-butadiene) strip was used in order to investigate the effect of penetration on the retractive force. To this end the low molecular weight poly(oxypropylene)glycols

we may consider all polyglycol solutions of concentrations below 1% to be ideal since the relative influence of the second virial coefficient on the measured force decreases the lower the molecular weight is. For this reason, only one concentration was measured of each polyglycol and the retractive force divided by the concentration was assumed to be equal to $(\Delta f/c)_{c\to 0}$.
In Figure 14 these $(\Delta f/c)_{c\to 0}$ values, together with those of the calibration samples, are given as a function of the reciprocal molecular weights.

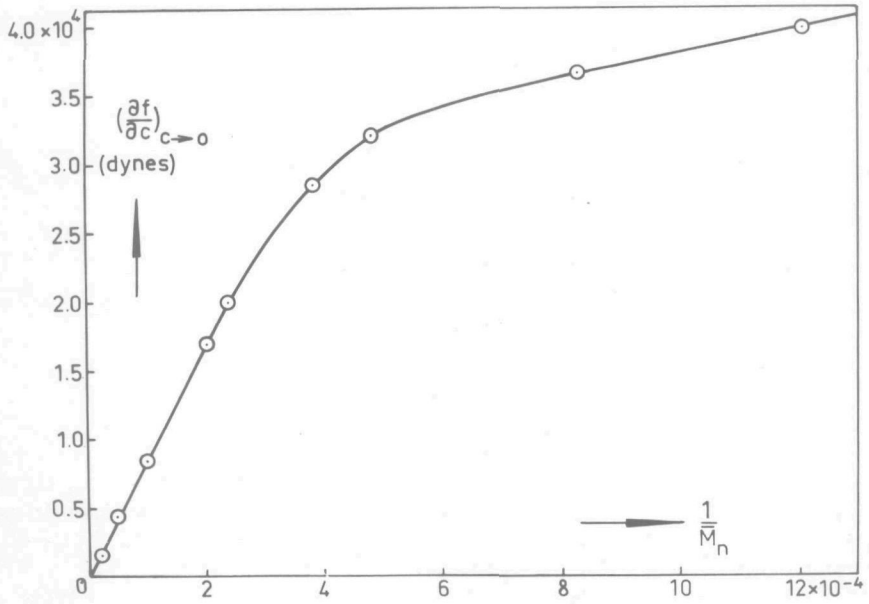

Figure 14. Reduced retractive force change at infinite dilution as a function of the reciprocal number average molecular weight for three polystyrenes and a number of low molecular weight poly(oxypropylene)glycols.

This Figure demonstrates clearly that the penetration begins to play a role at a molecular weight of about 4000 to 5000. The interpretation of these penetration data is treated in more detail in Section 5.3. The proportionality constant K follows from the slope of the curve in the region of molecular weight above 5000, where the curve is linear. For this poly(cis-butadiene) strip K is equal to 3.42×10^{-3} g/cm.

is at least equivalent to membrane osmometry. A membrane osmotic determination of molecular weights around 500,000 requires a very sensitive osmometer and considerably more experience and carefulness than the elasto-osmotic determination.

5.2. ABSOLUTE ELASTO-OSMOMETRY

In Chapter II an equation (Equation (2.11)) is derived which describes the elasto-osmotic effect of an ideal elastomer. The question arises whether the behaviour of the strips used in our experiments, can be sufficiently accurately predicted by means of this expression. If so, elasto-osmometry could be put on an absolute basis, although we have to keep in mind that the evaluation of the proportionality constant K requires the measurement of various characteristic quantities of the gel strip. Apart from the fact that the theory may not be applicable to the particular gel and the fact that not all quantities occurring in K can be obtained with sufficient accuracy, it remains to be seen if a calibration with a substance of known molecular weight will not be more convenient than the time-consuming gel strip characterization.

First of all we discuss the methods for obtaining the network parameters, viz. q, q_o, p_e, σ_o and χ_{1g}. These methods are based on the elasticity theory, as described in Section 2.1.1.

The degree of swelling, q, can easily be obtained by measuring the dimensions of the strip before and after swelling. In principle we thus obtain q_1, the degree of swelling in the unstrained, swollen state, but in view of the fact that in all deswelling experiments the change of q is less than about 5%, the error introduced by this approximation is negligibly small.

The average chain length between crosslinks, p_e, can be obtained by measuring the stress-strain curve of the dry elastomer. Since the crosslinking has been performed in the dry state, the conformations of the chains in the dry, unstrained network should be close to those in the non-crosslinked material. We further assume that the volume of the strip does not change upon stretching. Then the relative deformations in the expression for the conformational free energy (Equation (2.3)) are given by

$$\lambda_x = L/L_d \quad \text{and} \quad \lambda_y^2 = \lambda_z^2 = L_d/L,$$

An evaluation of K was carried out for all gel strips. The values of p_e, q_o, χ_{1g} and the values of K, calculated using these network parameters, are tabulated in Table VIII.

Table VIII

	Pe	q_o	χ_{1g}	K_{calc} (g/cm)	K_{exp}/K_{calc}
poly(dimethyl siloxane)	240	1.86	0.55	6.1×10^{-3}	0.54
poly(cis-butadiene)	28	1.17	0.54	5.1×10^{-3}	0.68
poly(cis-isoprene) (30 megarads)	110		0.47	7.7×10^{-3}	0.59
poly(cis-isoprene) (42 megarads)	100		0.51	6.3×10^{-3}	0.76
poly(butadiene-co-styrene)	59		0.48	10.2×10^{-3}	0.80
poly(butadiene-co-acrylonitrile)	29		0.61	6.2×10^{-3}	3.64

The average chain length between crosslinks, expressed by the dimensionless parameter p_e, was calculated under the assumption that A equals $\frac{1}{2}$. It should be mentioned that the absolute values of the factors A and B (Equation (2.3)) have no influence on the values of q_o, χ_{1g} and K_{calc}, provided that they are equal to one another (see page 13). For the strips where no information about the dry modulus is available, q_o was assumed to be unity. The calculation of K_{calc} is subject to large errors, because not all network parameters can be obtained with sufficient accuracy. This is particularly true for χ_{1g} which is found by subtracting large terms of about equal magnitude and consequently carries an error of $\pm$ 0.05. As a result the uncertainty of the calculated K-values can be estimated at at least 50%. In view of these large errors the agreement between the calculated and experimental values is quite reasonable. As can be seen from the data the calculated values have a tendency to be somewhat lower than the experimental values with one very notable exception, viz. the poly(butadiene-co-acrylonitrile) strip. This strip exhibits an efficiency which is many times larger than the one to be expected from the theoretical calculation. It seems likely that in this case the usual network

although very crude estimate of the efficiencies of the various strips based on their Young moduli, can only be obtained by comparing the Young moduli with the values of $K/\sigma q^2$. For our strips this is done in Table IX.
In order to obtain a better survey these data are also plotted in Figure 15.

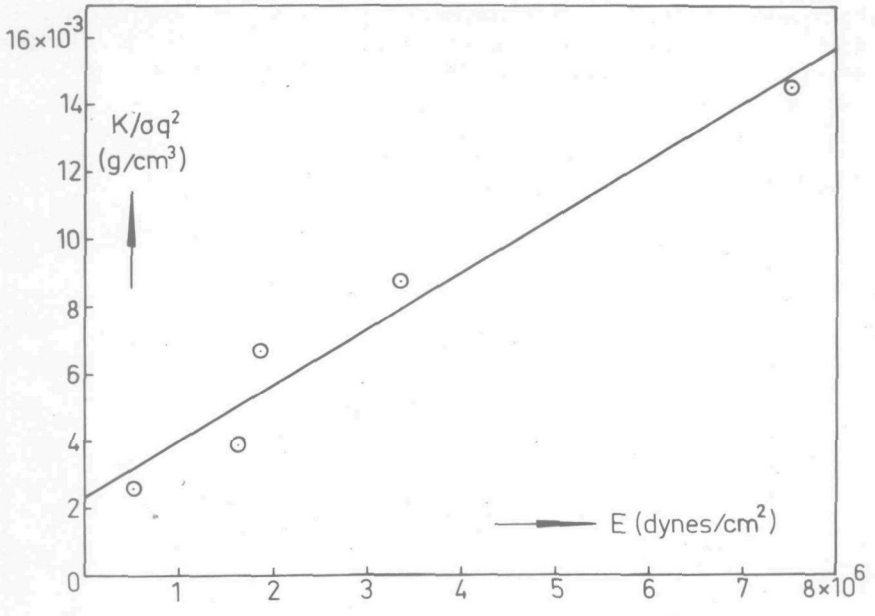

Figure 15. The elasto-osmotic efficiencies of the gel strips as a function of their Young moduli.

Within the limits of experimental error the proportionality is fully satisfied, again with the exception of the poly(butadiene-co-acrylonitrile) strip. The high efficiency of this latter elastomer as compared to those of the other materials indicates that an extension of elasto-osmometry to still higher molecular weights should not be sought in relatively highly swollen elastomers which behave according to the ideal elasticity theory. A higher sensitivity is to be expected from strips with a low degree of swelling which do not obey the ideal network theory. In such strips intermolecular effects usually play an important role.

A very good linear relationship is obtained for molecular weights of 4000 and lower. This means that the series expansion in Equation (2.33) may be broken off after the second term. Equation (2.33) also indicates that ϵ, which is a measure of the distribution of the solutes over the two phases, can be calculated from both the intercept and the slope of the straight line. This calculation yields values of ϵ of 0.95 and 0.96, respectively.

As can be seen from Equation (2.33) for a polydisperse sample the weight average molecular weight should be used in this expression rather than the number average molecular weight. This is proved by an experiment with a polydisperse poly(oxypropylene)glycol sample made up by mixing approximately equal quantities of P-400, P-750, P-1200, P-2000 and P-2700. This sample had a number average molecular weight of 1000 and a weight average molecular weight of 1530. Indeed the weight average molecular weight of the polydisperse sample (marked by a square) lies almost exactly on the straight line obtained for the monodisperse samples. The number average molecular weight (triangle), on the contrary, clearly deviates from the straight line. The linear relationship breaks down at a molecular weight of about 4500, indicating that penetration no longer occurs above this value, as is also demonstrated in Figure 14. This means that for a polydisperse sample with $\overline{M}_n > 5000$ only the low molecular weight tail of the distribution can penetrate. It is of considerable interest to know to what extent such a partial penetration influences the number average molecular weight to be determined.

In Section 2.2.2 this problem has been considered. A condition for the calculation of the correction to be applied is that the approximate shape of the molecular weight distribution must be known. In the following we perform this calculation for some polymers of molecular weights ranging between 10,000 and 100,000 and with the same type of molecular weight distribution as our poly(vinyl acetates) which have a Flory or most probable distribution with $\overline{M}_w/\overline{M}_n = 2$ (see Equation (4.2), Section 4.1 and Table V, Section 4.3.3). According to Equation (2.36) we need ψ, the volume fraction of penetrating polymer (Equation (2.37)), and the number and weight average molecular weights of the penetrating part of the sample, $(\overline{M}_n)_c$ and $(\overline{M}_w)_c$ (Equation (2.38)). These are found by means of partial differentiation:

Table X

Correct molecular weight $(\overline{M}_n)_{corr}$	ψ	$(\overline{M}_n)_c$	$(\overline{M}_w)_c$	Experimentally obtained molecular weight, $(\overline{M}_n)_{exp}$	Error: $\frac{(\overline{M}_n)_{exp}-(\overline{M}_n)_{corr}}{(\overline{M}_n)_{corr}}$
100,000	0.0012	2480	3390	104,000	4.0 %
50,000	0.0047	2460	3315	53,900	7.8 %
20,000	0.0265	2395	3260	24,000	20 %
10,000	0.0902	2295	3190	14,400	44 %

Already at very small times in the order of 20 seconds the linear relationship breaks down, indicating that the approximation mentioned above is not warranted. Due to the mathematical complexity of Equations (2.40) and (2.41) an alternate treatment of the problem is virtually impossible.

5.4. CONCLUSIONS

The measurements described in this Chapter clearly demonstrate the usefulness of elasto-osmometry as a completely equivalent alternative to membrane osmometry. The elasto-osmotic technique is at least comparable to this latter method with regard to rapidity, ease of operation and sensitivity since it is capable of delivering correct number average molecular weights up to about 500,000. Whereas the limits of membrane osmometry cannot be pushed further because of limitations in the sensitivity with which small hydrostatic pressures can be measured, the elasto-osmometry still offers a possibility of extension to higher molecular weights since gel strips may be found which show large retractive force changes due to small changes in the activity of the solvent.

For rather highly swollen gels which behave in good approximation according to the ideal rubber elasticity theory a prediction of their efficiency in elasto-osmometry is possible. However, this type of strips opens no prospects of increasing the sensitivity to a very large extent. More can be expected from lightly swollen elastomers which show specific interactions between the network chains. This is proved by the high efficiency of the poly(butadiene-co-acrylonitrile) strip. With strips of this type often difficulties are encountered due to adsorption of solute molecules onto the surface of the gel. However, at the cost of an almost twofold increase in measuring time these difficulties can easily be circumvented by cleaning the strip in pure solvent after the measurement of each polymer solution in a concentration series.

The measurements on the low molecular weight poly(oxypropylene)glycols show the feasibility of determining the molecular weight of fully or partially penetrating samples. For fully penetrating samples the weight average molecular weight is obtained. For partially penetrating samples, the correct number average molecular weight can be obtained if the shape of the molecular weight distribution is known. It turns out that even for moderately high molecular weights of 50,000 to 100,000 a correction of several percents will

APPENDIX I

SOLUTION OF THE DIFFUSION EQUATIONS FOR A STRIP IN AN INFINITE MEDIUM

According to Section 2.3 the diffusion equations must be solved with the following initial and boundary conditions (see also Figure 18):

$$t = 0, \quad |x| < d: \quad \varphi_{1g} = (\varphi_{1g})_o , \quad \varphi_{ig} = 0$$

$$|x| > d: \quad \varphi_{1s} = (\varphi_{1s})_o , \quad \varphi_{is} = (\varphi_{is})_o \qquad (A.1)$$

$$x = \pm d, \quad t \geqslant 0 : \quad \varphi_{1g}/\varphi_{1s} = \alpha_1 , \quad \varphi_{ig}/\varphi_{is} = \alpha_i \qquad (A.2)$$

$$D_{1g}(\partial\varphi_{1g}/\partial x)_{x=\pm d} = D_{1s}(\partial\varphi_{1s}/\partial x)_{x=\pm d}$$

$$D_{ig}(\partial\varphi_{ig}/\partial x)_{x=\pm d} = D_{is}(\partial\varphi_{is}/\partial x)_{x=\pm d} \qquad (A.3)$$

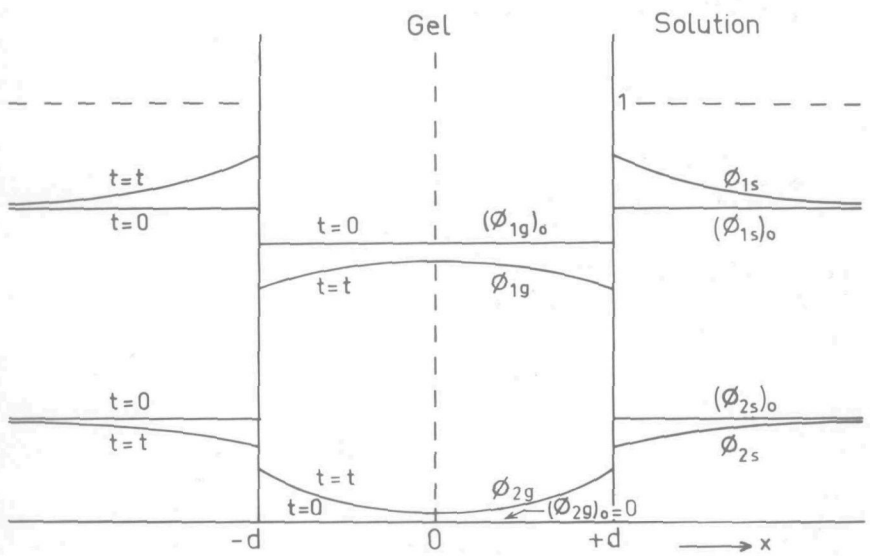

Figure 18. Distribution curves of the solvent (1) and a solute component (2) in the case of diffusion out of a plate into an infinite medium and vice versa.

ary between the gel and the solution. Although the ratio between the volume fractions inside and outside the gel at the boundary is a constant throughout, this will in general not be true for the volume fractions themselves.
Proceeding in the same way for the solution phase, we get

$$\mathcal{L}\left[\phi_{1s} - (\phi_{1s})_o\right] = \left[\frac{1}{\alpha_1}\mathcal{L}(\phi_{1g})_{x=\pm d} - \frac{1}{p}(\phi_{1s})_o\right] \exp\left\{-(x-d)\sqrt{p/D_{1s}}\right\} \tag{A.10}$$

$\mathcal{L}(\phi_{1g})_{x=\pm d}$ can be found from the boundary condition formulated in Equation (A.3):

$$D_{1g}\left[\frac{\partial}{\partial x}\mathcal{L}(\phi_{1g})\right]_{x=\pm d} = D_{1s}\left[\frac{\partial}{\partial x}\mathcal{L}(\phi_{1s})\right]_{x=\pm d} \tag{A.11}$$

After performing the differentiations indicated in Equation (A.11) and introducing $x = \pm d$, $\mathcal{L}(\phi_{1g})_{x=\pm d}$ can be solved. This yields:

$$\mathcal{L}(\phi_{1g})_{x=\pm d} = \frac{\alpha_1\left[(\phi_{1g})_o\sqrt{D_{1g}}\sinh d\sqrt{p/D_{1g}} + \right.}{p(\alpha_1\sqrt{D_{1g}}\sinh d\sqrt{p/D_{1g}} + \left. + (\phi_{1s})_o\sqrt{D_{1s}}\cosh d\sqrt{p/D_{1s}}\right.} \\ \frac{}{\left. + \sqrt{D_{1s}}\cosh d\sqrt{p/D_{1s}}\right)} \tag{A.12}$$

Substituting Equation (A.12) into Equation (A.9), we obtain:

$$\mathcal{L}(\phi_{1g}) = \frac{1}{p}(\phi_{1g})_o\left[1 + \right. \\ \left. - \frac{\sqrt{D_{1s}}\left\{1 - \alpha_1(\phi_{1s})_o/(\phi_{1g})_o\right\}\cosh x\sqrt{p/D_{1g}}}{\alpha_1\sqrt{D_{1g}}\sinh d\sqrt{p/D_{1g}} + \sqrt{D_{1s}}\cosh d\sqrt{p/D_{1g}}}\right] \tag{A.13}$$

This expression is too complicated to be transformed directly to the function ϕ_{1g}. However, a solution in terms of a series of error functions can be obtained by recasting $\mathcal{L}(\phi_{1g})$ in the following form:

$$\mathcal{L}(\phi_{1g}) = \frac{1}{p}(\phi_{1g})_o\left[1 - \frac{\sqrt{D_{1s}}\left\{1-\alpha_1(\phi_{1s})_o/(\phi_{1g})_o\right\}}{\alpha_1\sqrt{D_{1g}} + \sqrt{D_{1s}}} \times \right. \\ \left. \times \frac{\exp\left\{-(d+x)\sqrt{p/D_{1g}}\right\} + \exp\left\{-(d-x)\sqrt{p/D_{1g}}\right\}}{1 - \left\{(\alpha_1\sqrt{D_{1g}} - \sqrt{D_{1s}})/(\alpha_1\sqrt{D_{1g}} + \sqrt{D_{1s}})\right\}\exp(-2d\sqrt{p/D_{1g}})}\right] \tag{A.14}$$

APPENDIX II

LIST OF IMPORTANT SYMBOLS

a_i activity of species i
c concentration in weight of solute per unit weight of solution
d thickness of the gel strip
f retractive force
n_i number of molecules of species i
p pressure
p_i chain length of species i, as expressed by the molar volume divided by the molar volume of the solvent
p_e effective chain length between crosslinks, expressed in number of solvent lattice sites
q degree of swelling
q_o degree of swelling in the reference state
q_1 degree of swelling in the unstretched swollen state
t time
v_1 molar volume of the solvent
A, B dimensionless network parameters
A_2 second virial coefficient
D diffusion coefficient
E Young's modulus
F free energy
ΔF_m free energy of mixing
ΔF_c conformational free energy
H molar heat of vaporization
K proportionality constant in elasto-osmometry
L length of the gel strip
L_d length of the gel strip in the dry state
L_o length of the gel strip in the reference state
L_1 length of the gel strip in the unstretched swollen state
M molecular weight
M_1 molecular weight of the solvent
$\overline{M}_n$ number average molecular weight
$\overline{M}_w$ weight average molecular weight
N_i number of moles of species i
R universal gas constant
S entropy
T absolute temperature
U energy
V volume
V_d volume of network material

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SUMMARY

Elasto-osmometry is a recent method for the determination of number average molecular weights, largely developed at Delft. The method is based on the phenomenon that the degree of swelling of a swollen, crosslinked network or gel is dependent on the activity of the solvent in the solution around the gel. This activity can be influenced by adding a solute to the swelling agent. In the elasto-osmometer the change in retractive force at constant length of a gel strip, as a result of the change in degree of swelling is measured, rather than the degree of swelling itself.

In this thesis a new type elasto-osmometer is described in which the gel strip is connected to one arm of a balance, the other arm of which is attached to an inductive transducer. Such an arrangement with a transducer has the advantage of yielding directly the change in force, while at the same time only a very small change in length of the gel strip occurs.

Application of the commonly used theories for ideal networks and polymer solutions shows that the retractive force change as a result of replacement of the pure swelling agent by a polymer solution is at low concentrations inversely proportional to the number average molecular weight of the dissolved polymer. The proportionality constant is a function of the network parameters. It appears from a calibration of various strips by means of polymers of known molecular weight that in most cases the theory affords a satisfactory description. However, the experimental errors involved in the determination of the network parameters are of such an order of magnitude that in actual practice an accurate determination of the molecular weight of an unknown sample is only possible by a calibration of the strip by means of substances of known molecular weight.

To this end some poly(vinyl acetate) samples were prepared; use was also made of a number of poly(oxypropylene) glycols and some anionically polymerized polystyrenes. The molecular weights and molecular weight distributions of these calibration substances were obtained from vapour phase osmometry, membrane osmometry and gel permeation chromatography.

The sensitivity to changes in activity of the surrounding polymer solution is not very different for relatively highly swollen gel strips. A much greater sensitivity is achieved by using strips with a low degree of swelling, in which in-

SAMENVATTING

Met de naam elasto-osmometrie wordt een recente, hoofdzakelijk in Delft ontwikkelde methode ter bepaling van aantal-gemiddelde molecuulgewichten aangeduid. De methode is gebaseerd op het feit dat de zwelgraad van een gezwollen, verknoopt netwerk, een z.g. gel, afhankelijk is van de activiteit van het oplosmiddel in de oplossing waarin het gel zich bevindt. Deze activiteit wordt gevariëerd door in het zwelmiddel rondom het gel een hoeveelheid van het te onderzoeken polymeer op te lossen. In de elasto-osmometer wordt niet direct de zwelgraad bepaald, maar de verandering in rekkracht, die gepaard gaat met de verandering in zwelgraad, van een op constante lengte gehouden gel strip.

In dit proefschrift wordt een nieuw type elasto-osmometer beschreven waarin de gel strip bevestigd is aan een arm van een balans, waarvan de andere arm verbonden is met een inductieve krachtmeter. Een dergelijke opstelling heeft het voordeel dat direct de krachtsverandering gemeten kan worden met slechts een minieme lengteverandering van de strip.

Door toepassing van de gangbare theorieën voor ideale netwerken en polymeeroplossingen wordt afgeleid, dat de krachtsveranderingen t.g.v. het vervangen van het zuivere oplosmiddel door een polymeeroplossing bij voldoend lage concentratie omgekeerd evenredig is met het aantal-gemiddelde molecuulgewicht van het opgeloste polymeer. De evenredigheidsconstante is een functie van de netwerkparameters. Uit een ijking van verschillende strips met polymeren met bekend molecuulgewicht blijkt, dat in de meeste gevallen in goede benadering aan de theorie wordt voldaan. De experimentele fouten in de bepaling van de netwerkparameters zijn echter van een dusdanige grootte, dat voor een nauwkeurige molecuulgewichtsbepaling een ijking van de strips met ijkstoffen met bekend molecuulgewicht de aangewezen weg is.

Als ijkstoffen werden gebruikt radicaal gepolymeriseerde poly(vinylacetaten), poly(oxypropyleen)glycolen en anionisch gepolymeriseerde polystyrenen. Gegevens omtrent de molecuulgewichten en molecuulgewichtsverdelingen van deze stoffen werden verkregen met behulp van dampfase-osmometrie, membraan-osmometrie en gel permeatie chromatografie.

De gevoeligheid voor activiteitsveranderingen loopt voor tamelijk hoog gezwollen strips niet ver uiteen. Een veel grotere gevoeligheid wordt bereikt met strips met een lage

Op verzoek van de Senaat van de Technische Hogeschool volgt hier een korte levensbeschrijving van de schrijver.

Jacob van Dam werd op 17 maart 1938 te Klundert geboren. Van 1950 tot 1953 bezocht hij de Christelijke M.U.L.O.-school te Zevenbergen. Na het behalen van het M.U.L.O.-B diploma bezocht hij het Christelijk Lyceum te Dordrecht, waar hij in 1955 het diploma H.B.S.-B behaalde.
In hetzelfde jaar werd hij ingeschreven als scheikundig student aan de Technische Hogeschool Delft, waar hij het propaedeutisch examen aflegde in 1958, het kandidaatsexamen met lof in 1962 en het ingenieursexamen in 1963.
Van 1961 tot 1963 was hij als assistent en vanaf 1963 tot heden als wetenschappelijk medewerker verbonden aan de afdeling Fysische Chemie van de Technische Hogeschool Delft. Gedurende deze laatste periode werd hem de gelegenheid geboden het in dit proefschrift beschreven onderzoek te verrichten, onder leiding van Prof.Dr.W.Prins.

STELLINGEN

I

Bij de berekening van het aantal vertakkingen, ontstaan door ketenoverdracht, in radicaal-gepolymeriseerde vinylpolymeren uit de snelheid waarmee deze vertakkingen gevormd worden, houdt Flory ten onrechte geen rekening met het aantal vertakkingen dat reeds gevormd is. Ditzelfde bezwaar geldt ook voor zijn berekening van de crosslinkdichtheid.

P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press, New York (1953), p. 384.

II

De aanname van Kopeček, Jokl en Lím, dat in hun gelen de zwelgraad in de referentietoestand gelijk aan één gesteld kan worden, is in strijd met alle gangbare netwerktheorieën en ook op logische gronden niet verdedigbaar.

J. Kopeček, J. Jokl en D. Lím, Proceedings of the International Symposium on Macromolecular Chemistry, Praag (1965), J. Polymer Sci. C (1967).

III

Als maat voor de concentratie van oplossingen, gebruikt voor de bepaling van colligatieve eigenschappen, verdient de gewichtsfractie opgeloste stof verreweg de voorkeur boven de meer gebruikelijke maat van gewicht per volume-eenheid.

IV

Bij het corrigeren van osmotische druk-metingen voor de capillaire opstijging wordt vaak ten onrechte geen rekening gehouden met de concentratie-afhankelijkheid van de oppervlaktespanning.

V

De veronderstelling van Klots en Johnsen en ook van Falconer en Burton, dat bij de door aangeslagen kwikatomen gesensitiveerde omzetting van verzadigde koolwaterstoffen olefinevorming alleen door disproportionering plaatsvindt, is onjuist.

C.E. Klots en R.H. Johnsen, Can. J. Chem., 41 (1963) 2702.
J.W. Falconer en M. Burton, J. Phys. Chem., 67 (1963) 1743.

VI

In haar beschouwingen over de diëlectrische eigenschappen van copolymeren gaat Shima uit van een onjuiste berekening van de samenstelling van deze copolymeren.

M.Shima, J. Polymer Sci., 56 (1962) 213.

VII

De berekening van de relaxatietijden, die optreden bij viscoëlastische metingen aan onverdunde polymeren, door Tobolsky c.s. is gebaseerd op een ongeoorloofd doortrekken van de analogie tussen het model van Maxwell-Wiechert en dat van Rouse.

A.V.Tobolsky en K.Murakami, J. Polymer Sci., 40 (1959) 443.

VIII

In hun berekening van het transport van oplosmiddeldamp door een gaslaag zien Tomlinson c.s. voorbij aan het feit, dat dit transport beïnvloed wordt door de beweging van de gasmoleculen in een richting tegengesteld aan de richting van het eerstgenoemde transport.

C.Tomlinson, Ch.Chylewski en W.Simon, Tetrahedron, 19 (1963) 949.

IX

De beschouwingen van Hoffmann en Unbehend over de diffusie door gezwollen membranen getuigen van weinig inzicht in de elementaire diffusiewetten.

M.Hoffmann en M.Unbehend, Makromol.Chem., 88 (1965) 256.

X

De in Nederland geldende posttarieven getuigen van weinig werkelijkheidszin.