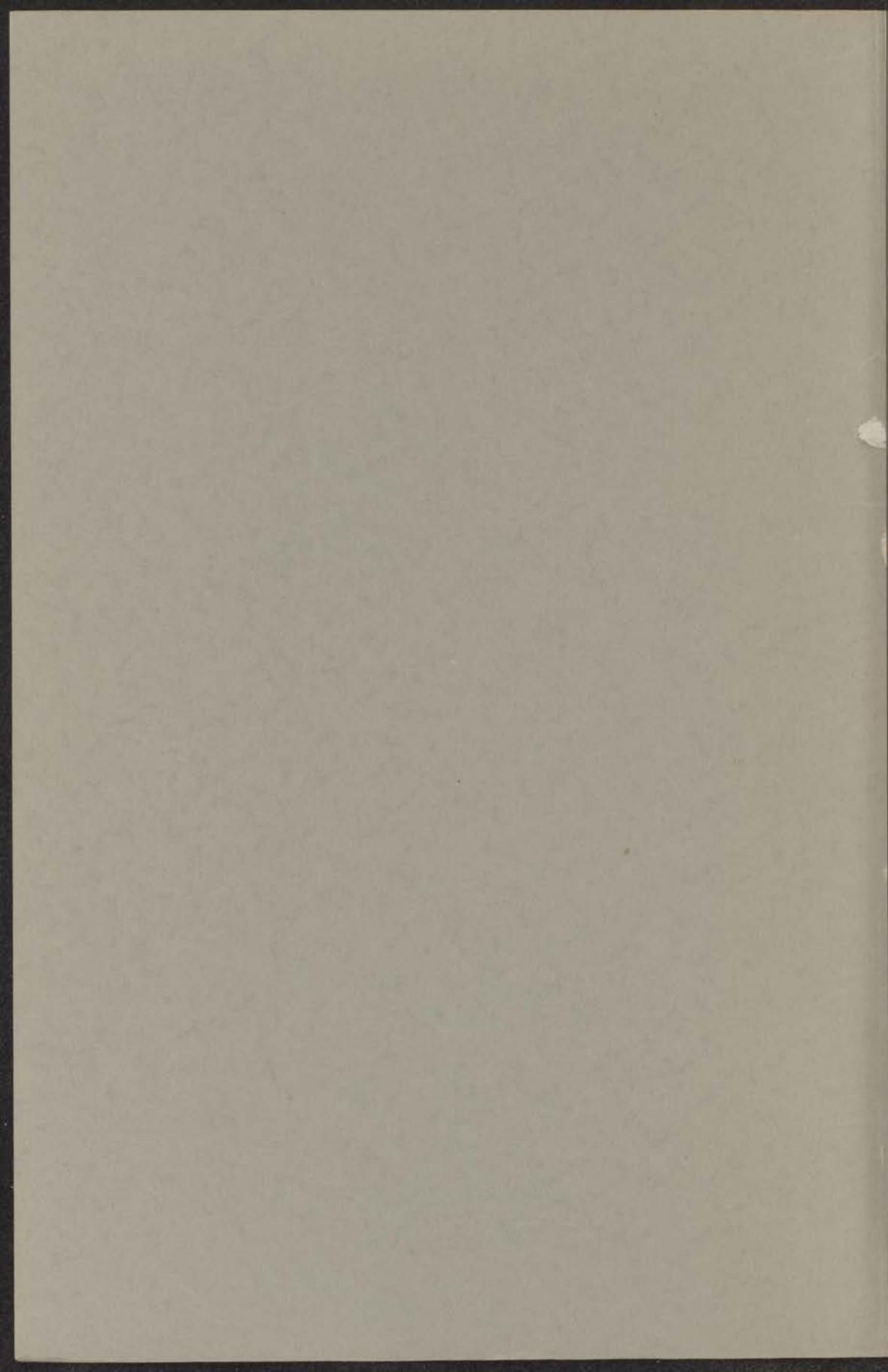


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THERMODYNAMIC AND DIMENSIONAL
PROPERTIES OF POLYMER MOLECULES
IN SOLUTION

A. DIJKSTRA



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IN SOLUTION

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Oan Heit en Mem

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INTRODUCTION

1. *Statement of the problems*

In many respects the physical properties of high polymer solutions are quite different from those of solutions of low molecular weight compounds. For instance the thermodynamic properties are far from ideal, even at low concentrations, and nearly all macromolecular solutions have large viscosities. Various treatments have been developed to explain the properties of macromolecular solutions and have led to a better insight into the problems concerning high polymers and their solutions.

A difficult problem has been the choice of a simple and yet adequate model for high polymer molecules and their solutions. The molecule itself is often too complicated for calculations of the thermodynamic properties by means of statistical thermodynamics. A model that has been quite successful is the quasi-lattice. In this model the polymer chain is divided into segments, which have the same size and shape as the solvent molecules. Even the simple theory of Flory and Huggins gave a rather good explanation of the thermodynamic properties. In later years a number of refinements have been introduced. In some theories the solvent has been treated as a continuum.

The average dimensions of the polymer chain are frequently expressed in terms of statistical chain elements, introduced by Kuhn. It was found by this author that the average square of the end-to-end distance of a polymer chain is proportional to the number of chain elements. The fact, that two chain elements cannot occupy the same volume element at the same time was neglected ("volume-effect"). But during the last years this fact has been taken into account by several authors. This leads to a correction in the root mean square end-to-end distance. It is still an open question whether this correction is a function of molecular weight or not. In any case, however, there exists a connection between the volume-effect and the deviations from ideal thermodynamic behaviour. This connection can be expressed by a relation between a parameter describing the volume effect and the second virial coefficient in the osmotic pressure.

It is the aim of the present work to compare the results of

osmotic pressure determinations with light scattering and viscosity. From osmotic measurements we can derive the number average molecular weight and the second virial coefficient. This second virial coefficient can be derived also from light scattering data which give us, in addition, the weight average molecular weight and the molecular size. We are thus in a position, in principle, to relate both the size and the second virial coefficient to the molecular weight.

The contribution of polymer molecules to the viscosity is a function of size and shape. A discussion of the viscosity data in relation to molecular size and weight will be given.

Before going into a more detailed discussion of existing theories, a brief summary will be given of the fundamentals underlying the three methods used: osmometry, light scattering and viscometry.

2. Osmotic pressure

When a solution is equilibrated with the solvent by means of a semi-permeable membrane, there is a difference in pressure between the solvent and the solution, which is called osmotic pressure. Thermodynamically the osmotic pressure can be easily explained. The chemical potentials of the solvent in the pure solvent and in the solution must be equal at equilibrium, and one can write down the dependence of this potential on pressure and concentration. This leads to the following formula for the osmotic pressure

$$\pi = (RT/v_1) \ln (1-x_2) \quad (I, 1)$$

where π is the osmotic pressure, R the gas constant, T the absolute temperature, v_1 the molar volume of the solvent and x_2 the mole fraction of the solute. This formula is valid for ideal solutions. When the concentrations are small, this formula may be written as

$$\pi = (RT/v_1) x_2 = (RT/M) c \quad (I, 2)$$

Here M is the molecular weight of the solute component and c its weight concentration.

The osmotic pressures of high polymer solutions do not obey van 't Hoff's law, even at low concentrations. According to McMillan and Mayer¹ one can represent the osmotic data by a series expansion:

$$\pi = (RT/M)c + A_2c^2 + A_3c^3 + \dots \quad (\text{I, 3})$$

In most cases the two first terms of the series expansion are sufficient to describe the osmotic behaviour. The coefficients A are the so-called virial coefficients. Molecular weights can be obtained by plotting π/c (the reduced osmotic pressure) against c , and extrapolating to zero concentration.

3. Light scattering

Molecular weights can also be derived from light scattering measurements. When a beam of light is going through a solution, this light is scattered in all directions with an intensity which is proportional to the molecular weight of the solute molecules. This phenomenon can be explained in different ways: one of the theories is based upon the scattering by a single particle; another theory starts from the fact, that fluctuations in concentration and density cause fluctuations in the refractive index. The intensity of the scattered light depends on the magnitude of these fluctuations.

We will give only a short survey of the formulae obtained from the fluctuation theory and its application to solutions of high polymers. In these solutions the effect of density fluctuations is usually negligible compared with that of fluctuations in the composition.

A fluctuation Δc in a volume v requires an osmotic work

$$\Delta G = (v/2c) (d\pi/dc) (\Delta c)^2 \quad (\text{I, 4})$$

The average value of $(\Delta c)^2$ is given by

$$(\Delta c)^2 = \frac{\int_{-\infty}^{+\infty} d(\Delta c) (\Delta c)^2 \exp(-\Delta G/kT)}{\int_{-\infty}^{+\infty} d(\Delta c) \exp(-\Delta G/kT)} = \frac{kT}{v(d\pi/dc)} \quad (\text{I, 5})$$

The fluctuations in the refractive index are given by

$$\Delta n = (\Delta c) \, dn/dc$$

so that

$$(\Delta n)^2 = (dn/dc)^2 \frac{kTc}{v(d\pi/dc)} \quad (\text{I, 6})$$

If the osmotic pressure is given by I,3 one can derive a formula

for the reduced intensity of the light scattered in the 90° direction with the aid of Rayleigh's formula:

$$Kc/R_{90} = 1/M_2 + 2A_2c/RT \quad (I, 7)$$

where

$$K = \frac{2\pi^2 n^2 (dn/dc)^2}{N_A \lambda^4}, \quad (I, 8)$$

R_{90} is the reduced intensity of the scattered light and N_A is Avogadro's number. Formula I,7 is valid, when the solute molecules are not larger than about 1/10 of the wave length and when they are not anisotropic. When the solute molecules are anisotropic there is a depolarisation of the scattered light and we have to correct with the Cabannes factor.

When the particles are large, the interference between the rays, scattered by different parts of the molecule, must be taken into account. It is then found that the intensity is larger in forward directions than in backward directions. The ratio $R_{45^\circ}/R_{135^\circ}$ is called dissymmetry; it is a measure of the mean dimensions of the solute molecules. Formula I,7 must now be replaced by

$$\frac{Kc}{R_{90}f(\rho)} = \frac{1}{MP_{90}} + \frac{2A_2}{RT} c \quad (I, 9)$$

where $f(\rho)$ is the Cabannes factor and P_{90} is a function of the dissymmetry and thus of the dimensions of the molecules. Formulae for P_{90} have been derived for long chain molecules, rods and spheres ^{2,3}. Numerical data can be found in the work of Doty and Steiner ⁴.

4. Viscosity

A polymer sample in a given solvent is often characterised by its limiting viscosity number. This quantity is given by:

$$[\eta] = \lim_{c \rightarrow 0} (\eta - \eta_0)/\eta_0 c \quad (I, 10)$$

where η and η_0 are the viscosities of the solvent and the solution respectively.

A well-known empirical relation between this limiting viscosity number and the molecular weight is

$$[\eta] = kM^a \quad (I, 11)$$

proposed by several authors (Kuhn, Mark, Houwing). We shall in the following refer to it as Mark's equation. Theoretical considerations ^{5,6,7,8,9,10,11} on the viscosities of high polymer solutions show a dependence of K and a on the size and shape of the molecules. Strictly speaking the exponent a is also dependent on the molecular weight. In section II,4 a discussion of these theories will be given. A log-log plot of $[\eta]$ and M should give a straight line, when the molecular weight range is not too large.

According to Peterlin ⁸ one will obtain a straight line for the whole molecular weight range, when $M/[\eta]$ is plotted against M^a in accordance with the relation

$$[\eta] = k_1 M / (1 + k_2 M^a) \quad (I, 12)$$

II

REVIEW OF CURRENT THEORIES

1. *The second virial coefficient*

Calculations of the thermodynamic properties can be carried out by means of statistical thermodynamics. The free energy of a system is related to the partition function Z :

$$F = -kT \ln Z ,$$

where

$$Z = \sum_i g_i \exp(-E_i/kT)$$

The main problem is the calculation of the total number of distinct configurations g_i with energy E_i . When the translational and internal degrees of freedom of the molecules are independent of the composition of the mixture, the partition function may be written as

$$Z = f_1^{N_1} f_2^{N_2} \sum_j g_j(N_1, N_2) \exp(-E_j/kT) ,$$

where f_1 and f_2 are those parts of the partition function which are due to the internal degrees of freedom of the molecules of the species 1 and 2 respectively; N_1 and N_2 are the numbers of these molecules, $g_j(N_1, N_2)$ is the number of ways in which the N_1 and N_2 molecules can be arranged such that E_j is the total potential energy of the molecules. Since we are interested only in the free energy of mixing, the factor $f_1^{N_1} f_2^{N_2}$ may be ignored.

Let us first consider zero heat of mixing. This means that the interactions between all kinds of molecules in the system are the same and all possible configurations have the same energy. In this case the free energy of mixing is $-T$ times the entropy of mixing. This entropy is then related to g by means of Boltzmann's formula

$$S = k \ln g(N_1, N_2)$$

and

$$\Delta S_{\text{mix}} = S_{N_1, N_2} - S_{N_1, 0} - S_{0, N_2}$$

An exact solution of the problem is impossible and a simplified model of the solution has to be introduced. Such a model is

the quasi-crystalline lattice. The polymer chains are assumed to be composed of segments, which have the size and shape of a solvent molecule. Each solvent molecule and polymer segment occupy a site of the lattice. It is clear that the partial molar volumes v_1 and v_2 in the solution are equal to the specific molar volumes.

The model of the quasi lattice has been used by several authors. Flory¹² and Huggins¹³ calculated the combination factor g for solutions without heat of mixing. The method used is often called the filling up method and consists of placing first the solute molecules on the lattice sites (one at a time) and afterwards the solvent molecules and counting the number of ways, in which the N_1 solvent molecules and the N_2 polymer molecules can be arranged. This treatment leads to a rather simple expression for the second virial coefficient:

$$A_2 = RTv_1/2M_0^2 \quad (\text{II}, 1)$$

where M_0 is the "molecular weight" of a segment. This result shows an independence on molecular weight.

A slight refinement was introduced by Miller¹⁴, Guggenheim¹⁵ and Huggins¹⁶. The probability, that two neighbouring sites are occupied by a solvent molecule is somewhat larger than the product of the over-all probabilities. The expression for the second virial coefficient becomes

$$A_2 = (RTv_1/2M_0^2)(1-2/z) \quad (\text{II}, 2)$$

where z is the coordination number of the lattice.

The method used by Miller and Guggenheim is different from the filling up method. They calculated the probability that a sequence of P neighbouring sites is occupied by a polymer chain and the probability, that these sites are occupied by P solvent molecules. The authors obtained a differential equation, whose solution leads to the combination factor.

The result of Munster¹⁷ is somewhat more complicated. This author tried to account for the flexibility of the polymer chain and found that the virial coefficient is dependent on molecular weight and flexibility. When the polymer molecules are completely flexible, the second virial coefficient may be written as

$$A_2 = \frac{1}{2} \frac{RTv_1}{MM_0} \left[1 + \frac{z-2}{z} (x-1) \right] \quad (\text{II}, 3)$$

This result was obtained by the introduction of the so-called virtual molecules. These are sequences of sites, which have the

same size and shape as the polymer molecules. When the number of virtual molecules is Λ , the combination factor is

$$g(N_1, N_2) = \frac{(N_1 + \Lambda)!}{N! \Lambda!}$$

When there is a small heat of mixing the theories of athermal solutions are extended to thermal solutions in the following way: the free energy of mixing consists of an entropy term and a heat term. It is assumed that the entropy of mixing is the same as in the absence of heat effects¹⁸, so that the free energy of mixing is

$$\Delta G = \Delta G(\text{ath}) + \Delta H \quad (\text{II}, 4)$$

When the heat of mixing is expressed according to Van Laar¹⁹, the partial molar heat of mixing of the solvent (heat of dilution) becomes:

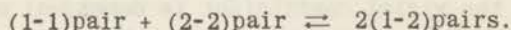
$$\Delta h_1 = \beta \varphi^2 \quad (\text{II}, 5)$$

where β is a constant and φ the volume fraction of the solute. The second virial coefficient is usually written as

$$A_2 = (RTv_1/M_0^2)(\frac{1}{2} - \mu) \quad (\text{II}, 6)$$

where μ is a parameter depending on the heat of mixing. In practice, μ plays the role of an empirical parameter which accounts not only for the heat of mixing but also for several shortcomings in the entropy calculation. So its exact physical meaning is not at all clear. In a recent paper, however, Huggins²⁰ has given a revised discussion of his theory, and the basis of the parameter μ is somewhat clarified.

Orr²¹ and Guggenheim²² also derived a result for mixtures with a finite heat of mixing. Guggenheim applied the method of the quasi chemical equilibrium to polymer solutions. When the mixture consists of two components, there are three different kinds of neighbours. The equilibrium is written as



The reaction constant is easily obtained in terms of the number of neighbours, also when there is a heat of mixing. A calculation of the partition function is then possible. Orr used a mathematically identical method and derived the same result.

According to McMillan and Mayer² the second virial coefficient can be expressed in terms of the molecular distribution functions.

$$A_2 = \frac{RTN_A}{2VM_2^2} \int [F_2(x_{12}) - F_1(x_1) \cdot F_1(x_2)] dx \quad (\text{II}, 7)$$

$F_1(x_1)$ is the probability that particle 1 has the coordinates x_1 and $F_2(x_{12})$ the probability that 1 and 2 have the coordinates x_1 and x_2 respectively. V is the volume of the system considered. So the second virial coefficient is closely related to the molecular interactions in the liquid. Zimm²³ evaluated the integral for a pair of chain molecules. The interaction between these molecules is due to interaction between pairs of segments and in this way a result is obtained for A_2 , which is the same as the result of Flory and Huggins. This result is only approximate, since the interactions between the segments of a single chain are neglected. Zimm gave a discussion of this problem and came qualitatively to the conclusion that there should be a dependence on M and on the stiffness of the chain.

The work of Flory and Krigbaum²⁴ and of Grimley²⁵ on the second virial coefficient is closely related to their work on the volume effect. Their starting point is the evaluation of the function $F_2(x_{12})$. According to Grimley, this function may be written in terms of configurational partition functions. Since the distribution functions F_1 are equal to unity for liquid systems, it is possible to evaluate the integral II,7 when the interactions between three and more segments are neglected and the solvent is treated as a continuous medium. The final result for the second virial coefficient is rather complicated, but for a limited range of molecular weights can be written as

$$A_2 = cM^\epsilon \quad (\text{II}, 8)$$

where c and ϵ are constants. In the second and third section of this chapter we will revert to Grimley's theory.

The theory developed by Flory and Krigbaum shows also a dependence of A_2 on M . Their result is obtained in the following way: Inside the chain which has the shape of a sphere with a Gaussian density distribution, the solution is treated as a lattice. Outside the sphere the solvent is treated as a continuum. The polymer chains can penetrate into each other to some extent. The free energy required for this interpenetration is identified with a macroscopic free energy of mixing. Thus, when a

polymer segment is approached by another arbitrary segment, there is a decrease in entropy, which may be expressed in terms of the original Flory-Huggins theory. The heat of "mixing" too is accounted for in a manner analogous to Huggins' treatment for solutions. Integration over all segments and over the whole volume gives an expression for the change of the free energy when two molecules approach and interpenetrate each other. When the distribution function F_2 is given by $c^2 \exp(-w_2/kT)$, where w_2 is equal to the free energy calculated and c is a normalization constant, a result is obtained for the second virial coefficient which indicates that A_2 decreases with increasing molecular weight.

Prigogine ^{26,27} and coworkers applied the cell model to polymer solutions. The quasi lattice approximation is used and the molecules or molecule segments are considered to be point centers, interacting with each other according to the Lennard-Jones interaction law. When a polymer is mixed with a solvent, the mean field changes somewhat and when this fact is taken into account, excess functions for volume, heat and entropy can be derived. In this manner the lattice model can be extended to cases in which there is a volume change.

2. Volume effect

The mean size and shape of unbranched polymer chains depends on several factors. The length of a monomer unit, the valence angle and restricted free rotation affect the mean end-to-end distance of a polymer chain. Calculations of this end-to-end distance have been performed by various authors. Among these W.Kuhn ²⁸ introduced the statistical chain element and treated the problem as a random flight one. The polymer chain is replaced by a chain consisting of N statistical chain elements with a mean length A in such a way, that the orientation of one of the chain elements is independent of the orientation of any other element. The calculation leads to a proportionality between the mean square end-to-end distance of the chain and the number of chain elements.

The length of a statistical chain element depends on the valence angle, the hindered rotation and the bond length. Calculations, which account for these parameters were carried out by Eyring ²⁹, Debye ³⁰, Taylor ³¹ and Benoit ³². Beside these interferences between successive elements along the chain there exist

interferences between elements which, along the chain, are further apart. The fact that two chain elements cannot occupy the same volume element at the same time is well-known under the name of the volume effect. In this section we will give a survey of the theories dealing with the volume effect. These theories have led to three types of results for large molecular weights:

- a. the volume effect is negligible.
- b. the mean square end-to-end distance $\langle h^2 \rangle_{av}$ is proportional to the molecular weight; one can say, that the length of a statistical chain element increases somewhat.
- c. the ratio $\langle h^2 \rangle_{av}/N$ depends on the molecular weight.

It can be shown that result (a) is incorrect. This has been discussed, among others, by Hermans, Klamkin and Ullman³³. In the first treatment of Hermans³⁴, the theory of Hadwiger³⁵ and that of Grimley²⁵, the fact that the elements are connected to form a chain is ignored and a result of type (a) is obtained. At the present time it is hardly possible to say which of the results (b) or (c) is correct. With respect to this question the treatment of Rubin³⁶ is of interest. He treated a polymer chain in m -dimensional space. For $m=2$ the average square of the end-to-end distance diverges for large molecular weights. A convergence was found for four dimensions. Rubin could not make a decision for real polymer chains, but he proposed a formula of the following type:

$$\langle h^2 \rangle_{av} = NA^2 \cdot f(N^a) \quad (\text{II}, 9)$$

where a has a value between 0 and 0.5.

Some authors have looked for a solution of the Fokker-Planck equation for the problem considered. Here the chain is represented by a string of beads (numbered 0, 1 ... N). When the center of the first bead is at the origin, the location of the other beads can be represented by the vectors $\mathbf{r}_1, \mathbf{r}_2$, etc. In the absence of a volume effect, the vectors $(\mathbf{r}_i - \mathbf{r}_j)$ can have any value, but when real polymer chains are considered not every value is possible. One can write

$$f(\mathbf{r}, t+1) = \int ds f(\mathbf{r} - \mathbf{s}, t) \psi(\mathbf{r}, \mathbf{r} - \mathbf{s}) \quad (\text{II}, 10)$$

This means, that the probability of finding the $(t+1)^{\text{th}}$ element at \mathbf{r} is equal to the integral of the probability of finding the t^{th} element at $(\mathbf{r} - \mathbf{s})$ multiplied by the transition probability ψ . The function $\psi(\mathbf{r}, \mathbf{r} - \mathbf{s})$ denotes the probability that the link

between the elements t and $t+1$ has a vector displacement \mathbf{s} . The assumption is made that

$$\psi(\mathbf{r}, \mathbf{r}-\mathbf{s}) = \lambda [1 + \nu F(\mathbf{r})]$$

where ν is the volume forbidden by the presence of a bead and $F(\mathbf{r})$ is the probability that any of the other beads has a position \mathbf{r} with respect to the origin; λ is a normalising constant. Hermans, Klamkin and Ullman³³ (HKU) considered only the first order perturbation which means that F may be replaced by F_0 , the probability of finding a bead at \mathbf{r} when there is no volume effect. Solution of the Fokker-Planck equation derived from (II,10) led to the following expression (type b) for large molecular weights:

$$\langle h^2 \rangle_{av} = NA^2 [1 + c\nu] \quad (\text{II, 11})$$

The constant c depends on the shape of the beads. Wall³⁷ derived the same result for a cubic lattice. In James' theory³⁸ the chain elements are impenetrable spheres with a constant diameter, but the distance between adjacent spheres is not constant the probability function for this distance is Gaussian. The volume effect was treated in a way similar to the KHU method, but the result is somewhat different, since other approximations are involved. At the limit of very large N the result is

$$\langle h^2 \rangle_{av} \sim \nu^2 N^2 \quad (\text{II, 12})$$

However, it would appear to be inconsistent in this theory to retain a term of order ν^2 , so that the physical significance of the result II,12 is doubtful.

Grimley³⁹ has remarked that the function ψ can be related to the pair distribution function for the two elements. With a number of approximations he came to a result which shows an increasing effect with increasing molecular weight:

$$\langle h^2 \rangle_{av} = NA^2 [1 + cN^{1/2}] \quad (\text{II, 13})$$

This result differs appreciably from one obtained earlier by Grimley²⁵. In this former treatment the chain molecule was considered as a gas with Gaussian density distribution around the centre, which means that the chain-character is neglected. In the absence of a volume effect the chain behaves like an ideal gas; the real chain is treated as an imperfect gas. Grimley calculated

the configurational partition function, neglecting ternary and higher order interactions. The result obtained is

$$\langle h^2 \rangle_{av} = NA^2 [1 - 0.143 (\beta_1/A^3) N^{-1/2}] \quad (\text{II}, 14)$$

Here $-\beta_1$ is the volume excluded for a segment by the presence of another one. For large molecular weights the volume effect can be neglected.

Flory¹⁰ made the following assumptions: (a) the density distribution of the chain elements remains Gaussian in the presence of a volume effect; (b) the connection between the chain elements can be neglected. The molecule is then divided into shells around the center of gravity; the density of the elements in each shell is constant. Flory stated that the mean dimensions of the molecule can be corrected with a factor α and it was the purpose of this theory to derive an equation for this parameter. When the lattice model is used, the number of ways of arranging a certain number of elements in a shell can be calculated. Summation over the shells gives the number of ways, in which the molecule can be built up. It turns out that α is dependent on the molecular weight in the following way

$$\alpha^5 - \alpha^3 = CN^{1/2} \quad (\text{II}, 15)$$

So the correction as a result of the volume effect increases slightly with increasing molecular weight. This result is confirmed by the calculations of Bueche⁴⁰. His model is nearly the same as that of James. Flory's α is found to be given by

$$\alpha^2 = (1 + 2\varepsilon N^{1/2}/kT) \quad (\text{II}, 16)$$

where ε is an interaction parameter.

Zimm, Stockmayer and Fixman⁴¹ (ZSF) calculated the excluded volume by means of the molecular distribution functions, already mentioned in the first section of this chapter. Their starting point is an equation similar to equation II, 10

$$f_N(p, t+1) = \int f_N(p, t) \Phi(p, t, t+1) d(t) \quad (\text{II}, 17)$$

Here the f_N are pair distribution functions for two elements of a chain of N elements; Φ plays the role of a transition probability. The first step in the ZSF treatment is the derivation of the distribution functions f_N and the function Φ . Their basic distribution function is $F_{NN}^{(N)}$, i.e. the distribution function of a

molecule consisting of N elements with specified coordinates $\{N\}$. It is assumed that this function is given by

$$F_{NN}\{N\} = Q_N^{-1} \prod_{i=1}^{N-1} \psi(i, i+1) \prod_{1 \leq i < j \leq N} \varphi(i, j) \quad (\text{II, 18})$$

Here Q_N is a normalising factor, ψ is a bond probability and φ is a measure for the interactions between the chain elements. The function $\Phi(p, t, t+1)$ is given by

$$\Phi(p, t, t+1) = j(p, t) \psi(t, t+1) \{1 + (J_N(p, t, t+1))\} / f_t(p, t) \quad (\text{II, 19})$$

where j is another normalising constant and J_N a function accounting for the interactions between the elements of the chain. It is also a measure for the deviation from random behaviour. An explicit expression for the mean molecular dimensions on the basis of this theory could not be obtained. However, it is common to all theories thus far advanced, that there is a straightforward relation between the volume effect and the second virial coefficient. In the ZSF treatment this appears from the fact that the second virial coefficient can be expressed in terms of the function J_N .

Even so, the ZSF equations are too implicit to lead to an explicit relation between volume effect and second virial coefficient unless drastic approximations are made. The only case worked out so far is the very first approximation, in which the assumption is made that the only configurations to be considered are those in which the chain does not bend back on itself more than once. The authors express the hope that the relation found between volume effect and second virial coefficient may be applied also to cases in which more than one segmental contact occur, even though the expressions obtained for the volume effect and the second virial coefficient separately would be valueless for these cases. The result derived is

$$\langle h^2 \rangle_{av} = \langle h_0^2 \rangle_{av} + KA_2 M^2 / N_A h_0 \quad (\text{II, 20})$$

where h_0 is the root mean square end-to-end distance in the absence of volume effect, A_2 the second virial coefficient, M the molecular weight, N_A Avogadro's number and K a numerical constant. The procedure of relating volume effect to second virial coefficient has the advantage, that unknown parameters can be eliminated. ZSF hesitate to make a decision of the asymptotic behaviour for large molecular weights.

Recently Wall, Hiller, Wheeler and Atchison^{42, 43} and Rosen-

bluth and Rosenbluth ⁴⁴ have made calculations with the aid of electronic computers. These calculations have not yet led to a result for large molecular weights.

3. Volume effect and second virial coefficient

It has been mentioned in the preceding sections that a relation exists between the volume effect and the second virial coefficient. Physically this is quite clear since both phenomena are due to interactions between segments of polymer molecules. In the paper of Zimm, Stockmayer and Fixman the relation between the mean square end-to-end distance of the chain and the second virial coefficient is very clear (II, 20). In principle every theory of the volume effect can lead to an expression of this kind. These expressions have the great advantage that some unknown parameters can be eliminated.

Grimley described both the volume effect and the second virial coefficient by means of the molecular distribution functions. With certain approximations he obtained formulae with a parameter β_1 . When this excluded volume parameter is eliminated a rather complicated expression can be derived.

In the same way Flory's α can be eliminated and a formula quite analogous to expr. II, 20 is obtained. The constant has an other numerical value.

For comparison we write down the result which can be calculated from the Hermans, Klamkin and Ullman treatment:

$$\langle h^2 \rangle = \langle h^2 \rangle_{Av} + K' A_2 M^2 / N_A h_0 N^{1/2} \quad (\text{II, 21})$$

The formulae obtained have in common that the volume effect disappears when the second virial coefficient is zero. The asymptotic behaviour for large molecular weight is not at all clear, since A_2 also depends on the molecular weight. At this point we may ask how the second virial coefficient depends on the molecular weight. With respect to this we can only say that the second virial coefficient decreases with increasing molecular weight. The theory of Munster leads to a linear relation between A_2 and M^{-1} . The formula proposed by Grimley will hardly be distinguishable from this result unless the molecular weight range is very large.

4. Viscosity

In this section on viscosity theories we will restrict our-

selves to those theories, which take into account the hydrodynamic interactions between the segments of a single chain. The earlier work on free drained coils (Huggins, Kuhn, Kramers, Hermans) will not be considered here.

Kirkwood and Riseman ⁷, and also Peterlin ⁸, used the model of the polymer chain. In the theory of Kirkwood and Riseman this polymer chain consists of monomer units with an effective bond length b ; Peterlin used the concept of the statistical chain element. Debye and Bueche ⁵ and, independently, Brinkman ⁶ introduced a porous sphere with an effective radius R . Sadron ⁹ and also Flory ^{10,11} worked with the equivalent particle concept. According to this concept a polymer chain may be represented by an impenetrable particle which has the same shape as the average chain. This equivalent particle is a sphere when the molecular weight is large and more rod-like when the molecular weight is small.

Obviously the model of Kirkwood and Riseman is the most realistic one. The presence of the monomer units causes a disturbance of the flow at any arbitrary point in the liquid. Using the method of Oseen as adapted by Burgers, and averaging over all possible configurations of the chain, the following result is obtained:

$$[\eta] = (N_A \zeta b^2 P / 36 \eta_0 M) P.F. (\lambda_0 P^{1/2}) \quad (\text{II, 22})$$

where ζ is the frictional constant for a monomer unit and η_0 the viscosity of the solvent; λ_0 is a parameter which contains ζ , η_0 and b . Formula II, 22 may be written as

$$[\eta] = (0.38 N_A \langle h^2 \rangle_{av}^{3/2} / M) x F(x) \quad (\text{II, 23})$$

where $x = \lambda_0 P^{1/2}$.

A similar result was obtained by Debye and Bueche and by Brinkman. The effective radius R of their porous sphere is defined by

$$R^2 = (5/3 P) \sum_{j=1}^P \langle r_j^2 \rangle_{av} \quad (\text{II, 24})$$

where r_j is the distance of the r -th segment from the center of gravity. The radius is found to be $0.53 \langle h^2 \rangle_{av}^{1/2}$. Outside the sphere the flow is the same as it would be if the molecule were a compact sphere. Inside the sphere a friction between the monomeric groups and the solvent appears. Stresses and velocities have to be continuous at the surface of the sphere. When possible defor-

mations (and thus the influence of the gradient) are neglected, the following formula can be derived:

$$[\eta] = (4\pi N_A R^3/3M) \Phi(\sigma) \quad (\text{II, 25})$$

where $\Phi(\sigma)$ is a function of the parameter defined as follows:

$$\sigma^2 = 3 P \zeta / (4\pi R \eta_0).$$

We see that the expressions II,22 and II,25 have the same form. The numerical constants are somewhat different. The frictional constant ζ can be given a value which will make the $[\eta]$ - M -relation coincide practically with the appropriate Mark equation. This can be shown by plotting $\ln[\eta]$ against $\ln M$. Tables of the exponent a in Mark's equation and the corresponding values of the functions F and Φ are given in the papers of Kirkwood-Riseman and Debye-Bueche. It is therefore possible to calculate $[\eta]$, when we know also the mean end-to-end distance and thus the effective radius of the polymer coils. The result of Brinkman is essentially the same as the result of Debye-Bueche. The limits of the exponent a of Mark's equation for large and small molecular weights are 0,5 and 1 respectively. However, the theories are valid only for large molecular weights. Peterlin derived a result with the same limits for large and small molecular weights. In terms of the Kirkwood-Riseman parameters his result may be written as

$$[\eta] = (N_A \zeta b^2 P / 24 \eta_0 M) P (1 + 1,2 \lambda_0 P^{1/2})^{-1} \quad (\text{II, 26})$$

According to Sadron the viscosity of high polymer solutions can be described by the viscosity of solutions of impenetrable particles. The shape of the particles depends on their molecular weight. At high molecular weights, for instance, Einstein's law may be applied, and the exponent a of Mark's equation is found to be 0.5.

Flory's model also is an impenetrable sphere, but the dimensions of this sphere are not given by the formulae of Kuhn. According to Flory's theory of the volume effect the mean dimensions of the polymer chain have to be multiplied by a factor α . Since in good solvents this factor is proportional to $M^{0.1}$ and in poor solvents nearly independent of M , Mark's exponent a is expected to vary from 0.5 to 0.8. The formula is usually written as

$$[\eta] = k' M^{1/2} \alpha^3 \quad (\text{II, 27})$$

III

EXPERIMENTAL PART

1. *Techniques used*

When one wants to measure the physical properties of high polymers as a function of molecular weight, the polymer sample has to be divided into fractions with a narrow molecular weight range. The fractionation can be performed on the basis of the solubility which is in general a function of the molecular weight⁴⁵. The extraction method has the advantage that the fractions with a high molecular weight contain a relatively small amount of low molecular weight components compared with the fractions obtained when the precipitation method is used. This last method has the advantage that the equilibrium between the two phases is reached more rapidly. Overbeek and Staverman⁴⁶ suggested therefore a method which would have the advantages of both methods. According to this method the polymer sample is dissolved and a large part is precipitated by means of a precipitant, so that the lowest fraction remains in solution. The precipitate is dissolved again and the procedure of precipitating is repeated. The polystyrene fractions numbered with arabic figures were obtained by Benninga⁴⁷ using this method; the polyvinylacetate was fractionated by van Beek⁴⁸ in the same way. A discussion of the problems concerned with this fractionation method was given by Benninga. The polystyrene fractions A, B, etc. were obtained by us using the precipitation method.

The limiting viscosity number can be easily derived from viscosity measurements with solutions of different concentrations. The flow time of a polymer solution in a capillary viscometer is proportional to the viscosity of that solution if the correction for kinetic energy may be ignored and the flow is Newtonian. Then the quantity $(\eta - \eta_0)/\eta_0 c$ can be replaced by $(t - t_0)/t_0 c$ where t and t_0 are the flow times of the solution and pure solvent respectively. Plotting $(t - t_0)/t_0 c$ against c and extrapolating to zero concentration leads to the limiting viscosity number. According to Huggins⁴⁹ the slope of the straight line is equal to $k[\eta]^2$ where k is independent of the molecular weight and for many polymers of the order of 0.5. Our viscosities were determined with an Ubbelohde viscometer. Solutions of different concen-

trations could be prepared in the viscometer by adding a certain amount of a stock solution to a known volume of the solvent. In this way a series of viscosities was determined very rapidly.

Osmotic pressures and turbidities are not so easily obtained. The first of these properties can be measured by means of an osmometer in different ways. One can apply the dynamic method, the static method and the compensation method. We always used the static method. After filling the osmometer with a solution we waited until equilibrium was reached. The measurements were performed by means of a modified Zimm-Meyerson osmometer described by Benninga ⁴⁷. We placed the membranes between two copper plates in the same way as described by Stabin and Immergut ⁵⁰. In this way equilibrium was reached sooner than when the membrane was supported only by one copper plate. The difference in height between the levels in the two capillaries was read by means of a telescope. The accuracy of the reading was about 0.05 mm. The difference in height multiplied by the density of the solution is equal to the osmotic pressure of the solution when a few assumptions have been made. In the first place the surface tension of the solvent and the solution have to be equal. Solutions of polystyrene in organic solvents have nearly the same surface tension as the pure liquid; so the influence of a difference in capillary effects may be neglected. Further the concentration does not remain the same during the experiment since the level in one of the capillaries changes somewhat after filling. We used capillaries with a small diameter and thus the influence of the change in the concentration on the osmotic pressure may be neglected. An uncertain point is the „asymmetry” of the membrane. When the osmometer is filled with pure liquid there remains always a small “osmotic pressure”. We always used membranes with an asymmetry less than 0.3 mm. So the influence on the osmotic pressures can never be very large and when the osmotic pressures are not too small this asymmetry may be neglected. Since the densities of the solution and the solvent are not the same, one must in principle apply a “density correction”. In our case, however, the influence of the density was very small. We assumed that the density of solution and solvent were the same, an approximation which is valid for dilute solutions of the samples investigated in the type of osmometers used by us.

In contrast to the molecular weight determinations with the aid of osmotic pressure measurements which leads to the number average molecular weight M_n , the determination of the molecular weight by light scattering gives us the weight average M_w . From this fact it is also clear that the presence of dust has a large influence on the molecular weight derived from the turbidity.

Preparation of completely dust-free solutions is difficult and is the critical point in the technique of measuring turbidities. Two methods can be applied for preparing dust-free liquids: filtering and centrifuging. Dust-free solvents can be prepared best by filtering through a glass filter, solutions of high polymers are better centrifuged (the density of the solvent has to be lower than that of the dust particles; it was therefore necessary to filter the ethylene chloride solutions).

The solutions which were measured in Leiden were centrifuged and brought into a dust-free rectangular cuvette by means of a dust-free pipette. The cuvettes and pipettes were cleaned by means of condensed acetone vapour in the usual way ⁵¹. In Delft we prepared the solutions starting from a filtered solvent and a centrifuged stock solution. The solutions were prepared in a cuvette which had the shape of a half octagon.

The apparatus for measuring turbidities used in Leiden is described in the thesis of Trap ⁵² and that of Prins ⁵³. The light-source was a high pressure mercury arc and the intensity of the scattered light was measured in the usual way by means of a photomultiplier. Fluctuations in the intensity of the light-source could only be observed by measuring the intensity of the light scattered by a standard solvent. We used benzene, and our calculations were based upon the values of the reduced intensity obtained by Carr and Zimm ⁵⁴. The apparatus at the Central Laboratory T.N.O. in Delft had the advantage that the fluctuations of the light-source were not important. The intensity of the primary beam is compared directly with the intensity of the scattered light in such a way that the electric currents given by the photomultiplier (scattered light) and the photocell (a part of the light of the light-source) are compared with each other. The values obtained were also compared with a benzene standard.

The values of the increment of the refractive index were obtained by using a Zeiss interferometer.

An important question is the question of the accuracy of the measurements. Rather accurate are the measurements of the viscosity. Since we used viscometers with a flow time for the pure solvent of the order of 100 seconds and since the accuracy of our time estimations was about 0.2 sec., it is easily seen that the errors in the limiting viscosity number are rather small. And they become completely unimportant when they are compared with the molecular weight determinations of the polymer. We have already discussed the corrections which have to be applied to the osmotic data, but which are negligible. And since we always used

an accurate temperature bath (0.02 °C) and thus thermometer effects could not play an important role, we might expect that osmotic pressures could be determined with a rather large accuracy. In practice, however, the osmotic pressure measurements are far from accurate for reasons which are not yet quite clear. The membrane processes are not well known and the reason for the small accuracy can perhaps be found in the membrane itself, for instance absorption of polymer on the membrane. Since the accuracy of our osmotic data is as a rule not better than 5 - 10%, it makes no sense to take into account a possible effect of the third virial coefficient, so that the extrapolation to zero concentration can be performed with the aid of the formula:

$$\pi/c = (RT/M) + A_2c \quad (\text{III}, 1)$$

It has already been said in the foregoing part that the presence of dust in a solution strongly affects the turbidity of that solution. The presence of dust can be detected by measuring the dissymmetry of the scattered light. When the molecular weights are small a correction can be applied. But when the molecules cause a dissymmetry this point becomes very uncertain. The accuracy of the molecular weight (and the second virial coefficient) is furthermore affected by the accuracy of the dn/dc determinations. An error of one percent of this quantity causes an error of two percent in the molecular weight. We conclude that the molecular weights obtained from the light scattering measurements can be given with an accuracy of about 5 - 10%.

At this point we wish to acknowledge the help and assistance given by Dr. Pals and Mr. Huldy of the Central Laboratory T.N.O. in Delft. Further we are much indebted to Messrs. H. van Niekerk, J. Hermans, H. Zweegman and H. Wiesenbahn for doing part of the measurements.

2. Results

In this section we will give the results obtained from osmometry, viscometry and light scattering. Since one part of the light scattering was performed in Leiden and another part in Delft, we will denote these results in the tables by L and D respectively. In table I we have collected the values of the refractive index n and the increment dn/dc . The values of n are the values published by Outer, Carr and Zimm⁵⁵. The dn/dc values

Table I
Values of refractive index n and increment dn/dc
for various polymer solvent systems.

	n	dn/dc cm ³ /g
polystyrene-butanone	1.378	0.224
polystyrene-toluene	1.496	0.112
polystyrene-ethylene chloride	1.444	0.165
polyvinylacetate-butanone	1.378	0.095

are measured at a wave length of 5460 Å. Tables II, III, IV and V contain the results of the systems polystyrene-butanone, polystyrene-toluene, polystyrene-ethylene chloride and polyvinylacetate-butanone respectively. In table V, also, some osmotic data of the system polyvinylacetate-toluene are given.

Table II
Molecular weights M , root mean square end-to-end distances h , limiting viscosity numbers $[\eta]$ and second virial coefficients A_2 for various polystyrene fractions in butanone.

fraction	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$A_2 \cdot 10^{-7}$ (dyne cm ⁴ g ⁻²)			h (Å)		$[\eta]$ (cm ³ /g)	
			osm.	light scattering L	D	L	D		
A	415	760	520	0.25	0.36	0.35	990	515	76
B	275	470	-	0.22	0.36	-	655	-	62
C	-	390	330	-	0.36	0.50	550	445	59.5
D	-	205	-	-	0.47	-	-	-	43.5
E	-	145	155	-	0.50	0.57	-	-	32
F	-	120	95	-	0.59	0.80	-	-	24
3	-	125	105	-	0.53	0.79	-	-	30
6	305	385	375	0.22	0.36	0.45	525	405	68

It is clear from the theoretical considerations given in the chapters I and II, that in c.g.s. units the dimensions of our virial coefficients become dyne cm⁴g⁻². The slope of the line obtained by plotting π/c against c leads directly to this virial coefficient. The lines obtained by plotting Kc/R_{90} against c have a slope which has to be multiplied by $RT/2$. The limiting viscosity number and the refractive index increment are expressed in

Table III

Molecular weights M , root mean square end-to-end distances h , limiting viscosity numbers $[\eta]$ and second virial coefficients A_2 for various polystyrene fractions in toluene.

fraction	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	$A_2 \cdot 10^{-7}$ (dyne cm ⁴ g ⁻²)			h (Å)		$[\eta]$ (cm ³ /g)	
			osm.	light scattering		L	D		
				L	D				
A	-	-	505	-	-	0.84	-	475	156
B	-	-	350	-	-	0.97	-	365	108.5
C	-	-	340	-	-	0.97	-	375	102
E	-	-	160	-	-	1.21	-	-	61
F	-	-	-	-	-	-	-	-	35
3	50	-	-	1.68	-	-	-	-	38
4	90	140	-	1.56	1.30	-	-	-	54
5	135	200	-	1.31	1.25	-	355	-	67
6	330	445	345	1.09	1.30	0.97	600	310	123
7	545	765	-	1.14	0.99	-	770	-	174
2'	17.5	-	-	7.5	-	-	-	-	15.5
3'	-	-	125	-	-	2.01	-	-	49

Table IV

Molecular weights, root mean square end-to-end distances, limiting viscosity numbers and second virial coefficients for some polystyrene fractions in ethylene chloride.

fraction	$M_w \cdot 10^{-3}$ D	$A_2 \cdot 10^{-7}$ D	h (Å) D	$[\eta]$ (cm ³ /g)
A	490	1.41	720	120
B	-	-	-	97
C	330	1.14	640	86.5
D	-	-	-	65.5
E	145	1.36	-	-
F	85	1.86	-	37.5
6	335	1.14	640	99

cm³g⁻¹. The average end-to-end distance of the chain is given in Ångstroms.

All our measurements were carried out at a temperature of

Table V

Molecular weights, intrinsic viscosities, mean square end-to-end distances and second virial coefficients of some polyvinylacetate fractions in different solvents.

fraction	Toluene		Butanone								
	$M_n \cdot 10^{-3}$	$A_2 \cdot 10^{-7}$	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$		osm.	$A_2 \cdot 10^{-7}$		h (Å)		[η]
				L	D		L	D	L	D	
I	220	0.38	205	290	240	245	0.70	1.25	665	665	80
II	650	0.29	-	740	805	-	0.97	1.24	725	920	170
III	775	0.23	-	-	1200	-	-	0.79	-	1445	220
IV	-	-	-	1650	2450	-	0.51	0.30	1340	2080	360

25 °C except the light scattering measurements at Delft which were done at room temperature. The errors due to a small temperature difference are negligible and therefore we have collected all our results in the same tables. The M_w values and the values of A_2 in table III obtained in Leiden are the averages of the measurements carried out at wave lengths of 4360 Å and 5460 Å. The concentrations used in Leiden were of the order $0,1-0,5 \times 10^{-4}$ g/cm³; in Delft we measured turbidities of solutions which had in general a concentration less than $0,1 \times 10^{-4}$ g/cm³.

Part of the osmotic measurements of polystyrene in toluene has already been presented in the thesis of Benninga⁴⁷. We have done some more experiments and have obtained results which are a little different. Although in some cases it seemed that the third virial coefficient had to be taken into account, the straight lines are within the experimental errors. Therefore we have calculated all our values with formula III,1.

DISCUSSION

1. General remarks

A measure of the efficiency of a fractionation is the difference between the molecular weights obtained from osmometry and light scattering. When the fraction is homogeneous the M_w and M_n values are equal and when the heterogeneity is large the difference between the two molecular weights of the fraction is also large. According to Flory⁵⁶ the ratio M_w/M_n is equal to 2 when the polymer sample is unfractionated. When we compare our number averages with the weight averages given in tables II, III and V we can conclude that in general the fractions were not sharp. Furthermore it is obvious that the fractionation method applied by Benninga has no great advantage compared with the precipitation method since there is still a rather large difference between the two average molecular weights. It appears, however, that the difference in molecular weights of two successive fractions is in general somewhat larger in the first case. This conclusions are strongly dependent on the calculation of the M_w values which were performed on the basis of the R_{90} -values of benzene, obtained and discussed by Carr and Zimm⁵⁴. ($R_{90} = 16.3 \cdot 10^{-6} \text{cm}^{-1}$, $\lambda = 5460 \text{ \AA}$).

It is worth while to give the R_{90} -values of butanone, toluene and ethylene chloride, which were measured by us. When we take again the value $16.3 \cdot 10^{-6} \text{cm}^{-1}$ for the reduced intensity of benzene, the reduced intensities for butanone, toluene and ethylene chloride become $5.0 \cdot 10^{-6}$, $18.5 \cdot 10^{-6}$ and $8.0 \cdot 10^{-6} \text{cm}^{-1}$ respectively.

In general the dissymmetries of the light scattered by the polystyrene solutions were small. It was therefore impossible to make accurate determinations of the mean end-to-end distances of the chain molecules. We have ignored the dissymmetries of the fractions with the lowest molecular weights. The dissymmetries of the fractions with higher molecular weights were taken into account but we do not believe that they are very accurate since they are still rather small and easily affected by the presence of a small amount of dust. So it is not possible to give a definite answer to the question of the volume effect from direct measurements of the dimensions of the chain molecules. In section

3 of this chapter we will try to answer this question using the viscosity data and the molecular weights.

The measurements on the polyvinylacetate fractions which showed a much larger dissymmetry gave us some information about the relation between the mean end-to-end distance and the molecular weight. These measurements, too, are discussed in the next sections.

2. Thermodynamic properties

The Flory-Huggins formula for athermal solutions predicts the independence of the second virial coefficient A_2 on the molecular weight M . From the later theories based upon the lattice approximation and which introduced a number of refinements, only the theory of Munster led to a (linear) relation between A_2 and $1/M$. When this theory is extended to thermal solutions, as was applied by Huggins, there still exists a linear relation between A_2 and $1/M$. In contrast with this the theories of Grimley and Flory-Krigbaum show a dependence of A_2 on M which is not linear. It is not easily seen from the Flory-Krigbaum treatment what the explicit relation is, for there are two parameters which are characteristic of the system. These parameters are related to the critical temperature of the solution. But even when we know the magnitude of these parameters there is still the uncertainty of Flory's parameter α of the volume effect, which has also an influence on the second virial coefficient. It is therefore impossible to check the Flory-Krigbaum theory with our data.

Grimley's expression for A_2 , which can be approximated by formula II,8, shows a linear relation between $\log A_2$ and $\log M$ for a limited molecular weight range. Besides the plot of A_2 against M in fig. 1 we have also given a log-log plot of these quantities (fig. 2). The second virial coefficients are not very accurate, and taking this fact into account we cannot make a definite conclusion about the relationship between A_2 and M . From the figures, however, it is clear that the $\log A_2$ - $\log M$ relation may well be linear. In that case the second virial coefficients of the systems polystyrene-butanone, polystyrene-toluene and polystyrene-ethylene chloride can be represented by $A_2 = 2.9 \cdot 10^8 M^{-0.30}$, $A_2 = 7.1 \cdot 10^8 M^{-0.30}$ and $A_2 = 7.8 \cdot 10^8 M^{-0.28}$ respectively. In principle it is possible to calculate the ratio of Grimley's excluded volume parameter β_1 to the cube of the length of a statistical chain element from the values of A_2 and M . But we then have to know the exact relation between M and A_2 since

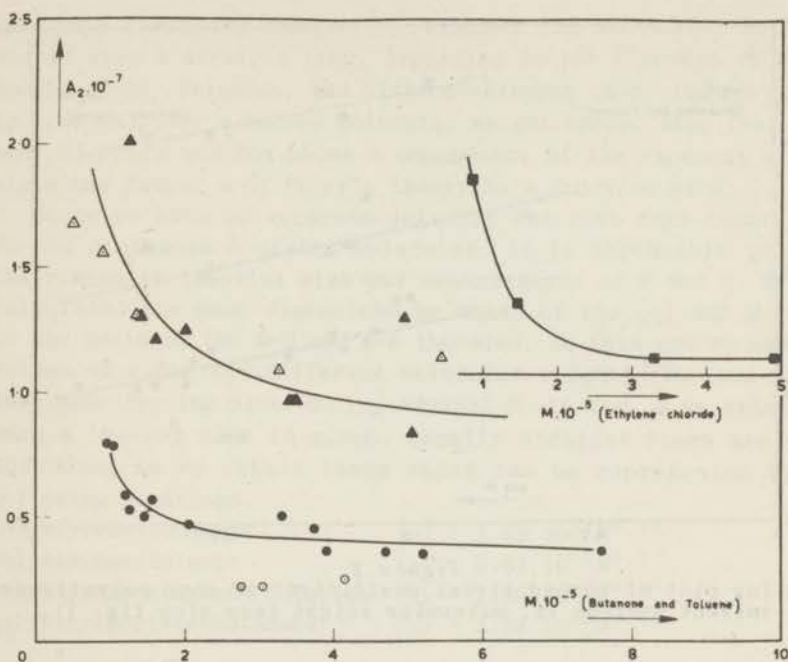


Figure 1
Second virial coefficient of some polystyrene-solvent systems vs. molecular weight.

- butanone (light scattering) ⊙ butanone (osmometry)
- ▲ toluene (light scattering) △ toluene (osmometry)
- ethylene chloride (light scattering)

the exponent ϵ is strictly speaking a function of M . We have tried to fit our data to a theoretical curve but it was not possible to make any accurate determinations of the parameters we wanted to know. Qualitatively we can say that the excluded volume parameter is larger in toluene and ethylene chloride than in butanone, since the constant c of formula II,8 is much larger for the toluene and ethylene chloride solutions. In that case, however, the exponent ϵ must be different although the dependence of ϵ on β_1 is a logarithmic one and thus the influence of the solvent on ϵ is much smaller.

In table VI we have collected some μ -values for various polystyrene-solvent systems. The molecular weights of polystyrene are the averages of the different weight averages measured in Delft. The calculation of μ can be performed with equation II,6 which can be transformed into

$$A_2 = (RTd_1/M_1d_2^2) (\frac{1}{2} - \mu) \quad (\text{IV}, 1)$$

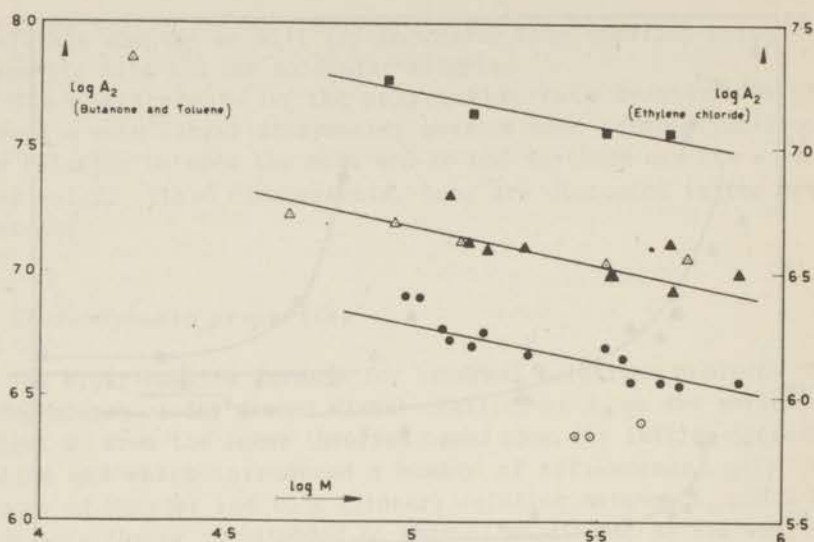


Figure 2
log-log plot of second virial coefficient of some polystyrene-solvent systems vs. molecular weight (see also fig. 1).

Table VI
Some μ -values for different
polystyrene-solvent systems

$M_w \cdot 10^{-3}$	μ Butanone	μ Toluene	μ Ethylene chloride
505	0.486	0.459	0.459
350	0.481	0.453	0.459
330	0.479	0.453	0.459
150	0.477	0.442	0.451
115	0.468		
90	0.467		0.433

where d_1 and d_2 are the densities of the solvent and polymer respectively and M_1 is the molecular weight of the solvent component. For d_2 the value of 1.06 is inserted. (H. Staudinger, "Die Hochmolekularen Organischen Verbindungen", Berlin 1932).

3. Viscosities and dimensions of the polymer molecules

According to Mark's equation (I,11) a log-log plot of the

limiting viscosity number $[\eta]$ against the molecular weight M should give a straight line. According to the theories of Debye-Bueche (D-B), Brinkman, and Kirkwood-Riseman (K-R) this is strictly true only for a narrow molecular weight range. Also the treatment of Flory and Fox shows a dependence of the exponent a on M , since the factor α of Flory's theory is a function of M .

Since we have no accurate data for the root mean square end-to-end distances h of the molecules, it is impossible to check the viscosity theories with our measurements of M and h . We have calculated the mean dimensions by means of the $[\eta]$ and M -values on the basis of the D-B and K-R theories. To this end we need the values of a for the different molecular weights. We have therefore made log-log plots of $[\eta]$ against M . In fig. 3 an example of such a log-log plot is given. Usually straight lines are drawn and doing so we obtain lines which can be represented by the following equations.

polystyrene-butanone	$[\eta] = 1.69 \cdot 10^{-2} M^{0.64}$
polystyrene-toluene	$[\eta] = 0.61 \cdot 10^{-2} M^{0.77}$
polystyrene-ethylene chloride	$[\eta] = 1.80 \cdot 10^{-2} M^{0.67}$
polyvinylacetate-butanone	$[\eta] = 2.38 \cdot 10^{-2} M^{0.65}$

The molecular weights M are the weight averages. It is better to plot this quantity against $[\eta]$ than the number average since the viscosity average differs less from M_w than from M_n .

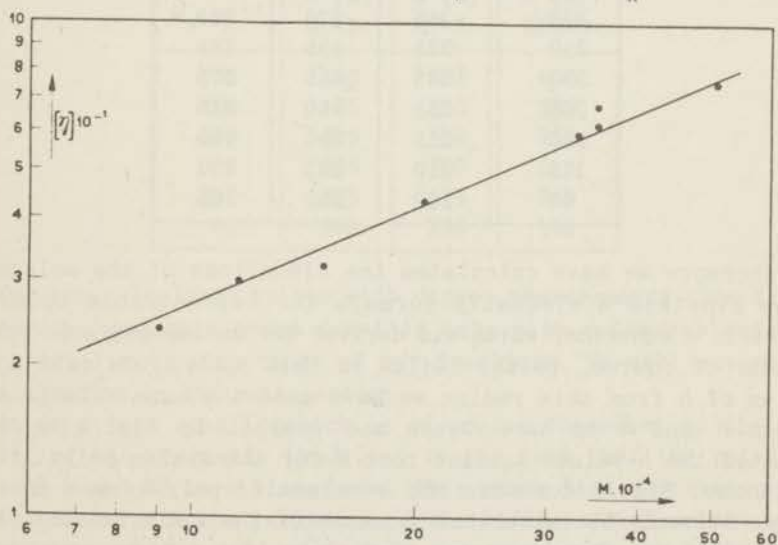


Figure 3
log-log plot of limiting viscosity number vs. molecular weight
for some polystyrene fractions in butanone.

As mentioned above, the straight lines are not theoretical ones. According to the theories the slopes of the lines have the limits of 1 and 0.5 for small and large molecular weights respectively. We have therefore assumed that the estimated value of a belongs to the molecular weight of 330 000 (polystyrene).

Since we are able to calculate the values of the parameters σ (D-B) and x (K-R) from the values of a and since we know the relationship of these parameters to M , it is possible to derive the values of $\Phi(\sigma)$ (D-B, from II, 25) and $xF(x)$ (K-R, from II, 23) for each molecular weight. Inserting the values of these functions and M and $[\eta]$ into equations II, 25 and II, 23 leads to the mean end-to-end distances of the chain molecules. The results of these calculations are given in the tables VII, VIII and IX.

Table VII

Mean end-to-end distances of some polystyrene fractions in butanone calculated from $[\eta]$ according to Debye-Bueche, Kirkwood-Riseman and Einstein.

$M_w \cdot 10^{-3}$	h (Å) D.-B.	h (Å) K.-R.	h (Å) Einst.
505	400	545	345
350	345	470	295
350	335	455	285
330	325	445	275
205	255	350	215
150	215	290	190
115	210	285	170
90	170	230	135

Furthermore we have calculated the dimensions of the molecules from Einstein's viscosity formula for impenetrable spheres. Einstein's equation, which was derived for an impenetrable sphere leads, of course, to the radius of this sphere. To derive the value of h from this radius we have used the same relation between R and h as have Debye and Bueche. In fig. 4 we have plotted the h -values against root M for the system polystyrene-butanone. Fig. 5 contains the h -values of polystyrene in the three solvents as calculated by means of the K-R treatment. From the tables and figures we see that there is a difference of about 25% between the values of h calculated by means of D-B and K-R. A conclusion about the correct values can be obtained only by com-

Table VIII

Mean end-to-end distances of some polystyrene fractions in toluene calculated from $[\eta]$ according to Debye-Bueche, Kirkwood-Riseman and Einstein.

$M_w \cdot 10^{-3}$	h (Å)	h (Å)	h (Å)
	D.-B.	K.-R.	Einst.
505	595	805	440
350	505	695	360
350	480	665	345
330	465	640	330
150	325	440	215
115	285	385	185
90	240	330	150

Table IX

Mean end-to-end distances of some polystyrene fractions in ethylene chloride calculated from $[\eta]$ according to Debye-Bueche, Kirkwood-Riseman and Einstein.

$M_w \cdot 10^{-3}$	h (Å)	h (Å)	h (Å)
	D.-B.	K.-R.	Einst.
505	480	655	405
350	405	550	335
350	405	550	335
330	385	520	315
205	305	415	245
90	205	280	145

paring the calculated values with direct measurements from light scattering and this seems feasible only with molecular weights which are larger than those of our fractions. We will revert to this question in the next section.

An important result (which is of course dependent on the validity of the viscosity theories) is the fact that the relation between h and $M^{\frac{1}{2}}$ is a linear one. This means that for rather low molecular weights the influence of the volume effect on the mean dimensions of the molecules does not depend on the molecular weight. However, we have to take into account a certain inaccuracy

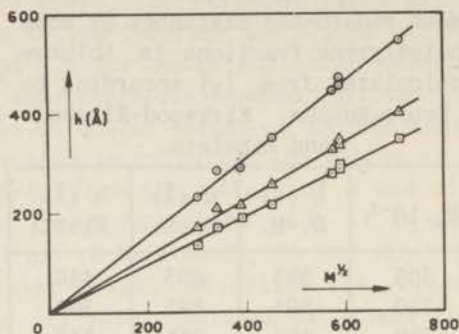


Figure 4
 Root mean square end-to-end distance vs. square root of molecular weight for some polystyrene fractions in butanone.

- △ Debye-Bueche
- Kirkwood-Riseman
- Einstein

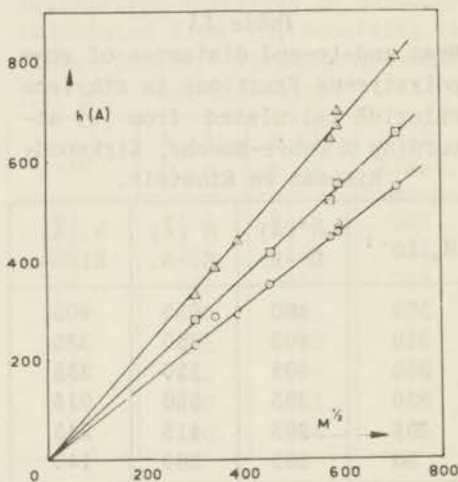


Figure 5
 Root mean square end-to-end distance calculated by the Kirkwood-Riseman theory vs. square root of molecular weight for some polystyrene fractions in butanone (○), toluene (△) and ethylene chloride (□)

cy and perhaps a possible effect of M would be within the experimental errors.

The ratio of the frictional constant for a monomer unit to the viscosity of the solvent in the viscosity theories is much lower than expected from Stokes' law. Even if we take into account the fact that Stokes' law cannot be applied to the segments of the chain molecule, a value of about 10% of that according to

Stokes is unreasonably small. This discrepancy is not new; it had been observed by many authors in previous work.

A check of the theory of Flory and Fox on the relationship between M and $[\eta]$ (form. II, 27) would be possible by plotting $[\eta]^{2/3} M^{-1/3}$ against $M/[\eta]$. At low molecular weights the factor α becomes equal to unity and from the intercept the constant K could be calculated. To apply this method, great accuracy is necessary. Our polystyrene data plotted in this manner did not give an accurate value of the constant.

According to the relationships between $[\eta]$ and M and to formula (II, 27) the factor would be proportional to $M^{0.05}$. Deviations from the linear relation between h and M^{α} would therefore be small and frequently within the experimental errors. Appreciable values of α would be obtained only at much higher molecular weights. In fact, if Flory's relation is correct, the linear dependence of $[\eta]$ on $M^{0.65}$ would mean that for two molecular weights which are in the ratio 2:1, the h -values would be in the ratio $1.034 \sqrt{2}$ to 1.

The theory of Kirkwood-Riseman applied to the polyvinyl acetate data of table V in the same manner as described in the foregoing part, leads to the following average dimensions: fraction I: 495 Å; II: 875 Å; III: 1065 Å and IV: 1545 Å. Comparison with the h -values obtained from light scattering shows a large difference. A better agreement between the observed and calculated values would be possible if the function $\alpha F(x)$ were smaller than that calculated from the exponent α of Mark's equation. This would mean that the frictional constant would also become much smaller. The ratio of this frictional constant to that calculated from Stokes' law would then be about 10^{-2} .

Since we have too few data, a plot of the calculated and observed h -values against the root of M does not lead to a definite conclusion about the relationship between h and M^{α} . Again, however, a linear relation is compatible with the experimental results (fig. 6).

4. Second virial coefficient and dimensions

Much data about various polystyrene-solvent systems can be found in the literature. In general the molecular weight-viscosity relations are not in very good agreement with each other. This is mainly due to the inaccuracy of the molecular weight determinations by means of light scattering and osmometry. With respect to this the surveys of Frank and Mark^{57,58} about investigations

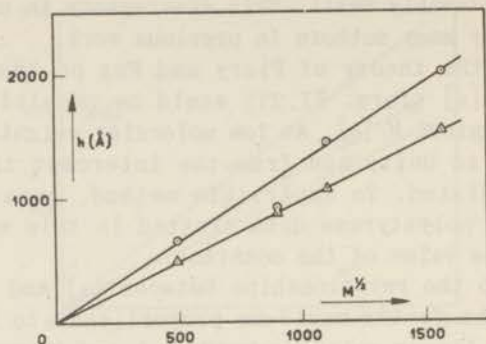


Figure 6
Relation between end-to-end distance of polyvinylacetate
in butanone and square root of molecular weight
 Δ h according to the Kirkwood-Riseman theory
 \circ h from dissymmetry.

on a polystyrene sample are very interesting. There exists a large scatter in the data obtained. Only a few publications about the estimation of the mean end-to-end distances of polystyrene molecules exist. An extensive investigation was published by Outer, Carr and Zimm⁵⁵, who measured the dimensions of large molecular weight polystyrene molecules in various solvents, namely butanone, toluene, ethylene chloride, cyclohexane and some mixtures of solvents. Kunst⁵⁹ reported a number of measurements of polystyrene in benzene, and recently Notley and Debye⁶⁰ published an investigation of polystyrene in cyclohexane and toluene. Comparing our calculated dimensions of the polystyrene molecules with the measurements of the end-to-end distances from light scattering mentioned above, it seems that the Kirkwood-Riseman theory leads to results which are in good agreement with those measurements. The molecular weights of our samples were much lower than those of Outer, Carr and Zimm and Notley and Debye. but a comparison of the h -values of polystyrene at about the same temperature can be made by comparing h^2/M (fig. 7). In this manner the h -values obtained by applying the Kirkwood-Riseman theory were found to be in better agreement with the light scattering data than the values calculated by means of the Debye-Bueche theory. However, for the system polystyrene-toluene this does not seem to apply, but here the light scattering data are small in number and are considerably scattered.

The molecular dimensions found from light scattering for polyvinylacetate in butanone were larger than those obtained by Shultz⁶¹ for the same system and those of Chinai, Scherer and Levi⁶² for polyvinylacetate in acetone. It is possible that this

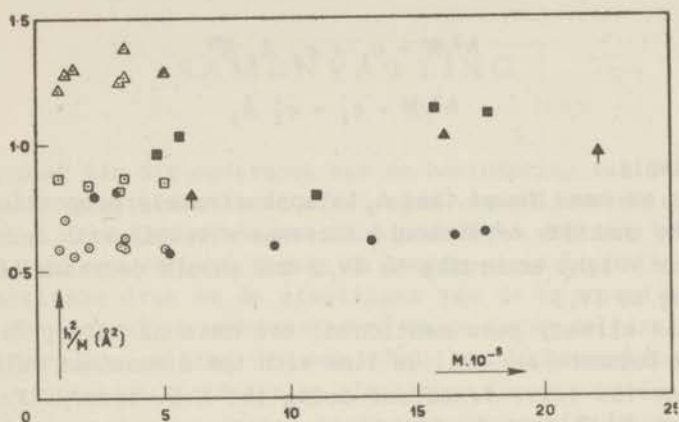


Figure 7

Mean square end-to-end distances divided by the molecular weight vs. molecular weight for polystyrene in some solvents.
 Toluene: \blacktriangle Notley and Debye, \triangle Outer, Carr and Zimm, \triangle calculated from $[\eta]$ (K.-R.).
 Butanone: \bullet Outer, Carr and Zimm, \circ calculated from $[\eta]$ (K.-R.).
 Ethylene chloride: \blacksquare Outer, Carr and Zimm, \square calculated from $[\eta]$ (K.-R.).

must be attributed to different degrees of branching in the samples. In fact, it has been suggested by several authors that polyvinylacetate is often branched appreciably.

It has been established as an empirical rule that for a given polymer with a certain molecular weight the second virial coefficient increases with increasing limiting viscosity number. This fact can be explained by theoretical considerations: the limiting viscosity number increases with the root mean square end-to-end distance and when the second virial coefficient increases the mean end-to-end distance becomes larger too. In general our data confirm this rule but when we assume that the viscosity measurements are correct, the second virial coefficients of the system polystyrene-ethylene chloride are too large. Perhaps the influence of dust on the turbidities of ethylene chloride solutions was somewhat different since we filtered the stock solutions of this solvent and centrifuged all the other solutions. But an influence of this kind is not very probable and the thermodynamic behaviour of the ethylene chloride solutions is not clear.

An explicit relation between h^2 and A_2 is given by the formulae of Zimm, Stockmayer and Fixman (II,20) and that of Hermans, Klamkin and Ullman (II,21). These equations can be transformed into

$$h^2/M = c_1 + c_2 A_2 M^{0.3} \quad (\text{IV}, 2)$$

and

$$h^2/M = c_1 + c_2' A_2 \quad (\text{IV}, 3)$$

respectively.

Since we have found that A_2 is approximately proportional to $M^{-0.3}$ the quantity h^2/M should increase slightly with increasing molecular weight according to IV,2 and should decrease slightly according to IV,3.

As has already been mentioned, the data of Outer, Carr and Zimm for butanone are well in line with the dimensions calculated by us for the lower fractions using the K.R. theory. From the fact that h^2/M appears to increase with increasing molecular weight whereas at the same time the second virial coefficient decreases, we may conclude that eq IV,3 cannot represent the data. The formula IV,2 can be made to agree with experiment and as has been shown by Zimm, Stockmayer and Fixman, the constant c_2 in this formula has the value expected from their theory.

Acknowledgement. The author is much indebted to Mr. R.Longworth for reading the manuscript and improving the English.

SAMENVATTING

Het doel van dit onderzoek was de bestudering van de thermodynamische grootheden en de afmetingen van polymeermoleculen in oplossing. Door het meten van deze grootheden zou het tevens mogelijk zijn een verband tussen de tweede viriaalcoëfficiënt van de osmotische druk en de afmetingen van de macromoleculen te geven. Een dergelijk onderzoek werd enige jaren geleden verricht door Outer, Carr en Zimm, die met behulp van lichtverstrooiing een aantal viriaalcoëfficiënten en afmetingen in verscheidene oplosmiddelen bepaalden voor een serie polystyreenfracties met een groot molecuulgewicht. Een onderzoek voor kleinere molecuulgewichten zou ons een inzicht kunnen geven in het gedrag over een breed molecuulgewichtsgebied.

Ons onderzoek werd uitgevoerd met behulp van viscosimetrie, osmometrie en lichtverstrooiing. De molecuulgewichten en de viriaalcoëfficiënten kunnen berekend worden uit de osmotische en lichtverstrooiingsmetingen, terwijl de dissymmetrie van het verstrooide licht inlichting kan geven over de afmetingen van de moleculen in oplossing. Ook het viscositeitsgetal is een maat voor de afmeting van de moleculen.

De thermodynamica en de theorieën over de afmetingen van de kluwenmoleculen werden besproken in hoofdstuk II. Uit deze theorieën is gebleken, dat de tweede viriaalcoëfficiënt kleiner zal worden met stijgend molecuulgewicht.

De afmetingen van de ketenmoleculen zijn in eerste benadering evenredig met de wortel uit het molecuulgewicht. Gedurende de laatste jaren is een aantal publicaties verschenen waarin het zgn. volumeëffect in rekening wordt gebracht. Een exacte oplossing van dit probleem is nog niet gevonden, zodat een aantal benaderingen ingevoerd moesten worden. Deze benaderingen zijn veelal van dezelfde aard als de benaderingen, die toegepast moeten worden bij de berekening van de tweede viriaalcoëfficiënt. Er zijn dan ook pogingen gedaan om de afmetingen van de kluwenmoleculen te beschrijven door middel van formules, waarin de tweede viriaalcoëfficiënt voorkomt.

De resultaten zijn besproken in hoofdstuk IV. Aangezien de dissymmetrieën van het verstrooide licht klein en niet zeer nauwkeurig waren, was een bepaling van de molecuulafmetingen alleen mogelijk door berekening uit de viscositeit. Door vergelijking van deze berekeningen met waarnemingen van andere onderzoekers

voor grotere molecuulgewichten, kwamen we tot de conclusie, dat de viscositeitstheorie van Kirkwood-Riseman tot betere resultaten leidt dan die van Debye-Bueche.

In het door ons gemeten molecuulgewichtsgebied wordt de tweede viriaalcoëfficiënt aanmerkelijk kleiner met toenemend molecuulgewicht. In dit molecuulgewichtsgebied is tevens het kwadraat van de afstand tussen begin en eindpunt van het molecuul evenredig met het molecuulgewicht, aangenomen dat de theorie van Kirkwood-Riseman tot goede resultaten leidt. De metingen van Outer, Carr en Zimm, voor grotere molecuulgewichten in butanon vertonen een afwijking van deze lineariteit, waardoor de theorie van Zimm, Stockmayer en Fixman bevestigd schijnt te worden. Het effect is echter zeer klein en in ons molecuulgewichtsgebied zouden de afwijkingen van de eenvoudige betrekking tussen de deeltjesgrootte en het molecuulgewicht waarschijnlijk binnen de foutengrenzen vallen.

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STILLING

The first part of the report deals with the general situation of the country and the progress of the work during the year.

The second part of the report deals with the results of the work done during the year and the progress of the various projects.

The third part of the report deals with the financial situation of the institution and the progress of the various projects.

The fourth part of the report deals with the administrative work done during the year and the progress of the various projects.

The fifth part of the report deals with the general situation of the country and the progress of the work during the year.

REPORT ON THE WORK OF THE INSTITUTION DURING THE YEAR 1911

The sixth part of the report deals with the general situation of the country and the progress of the work during the year.

The seventh part of the report deals with the general situation of the country and the progress of the work during the year.

REPORT ON THE WORK OF THE INSTITUTION DURING THE YEAR 1911

STELLINGEN

1

Berekeningen van de derde viriaalcoëfficiënt uit osmotische drukmetingen hebben wegens de onnauwkeurigheid der metingen geen zin.

2

De extrapolatiemethode voor de osmotische drukken, voorgesteld door Guggenheim en McGlashan, heeft zowel praktische als theoretische nadelen.

E.A.Guggenheim en M.L.McGlashan, *Trans.Faraday Soc.* **48**, 206 (1952)

3

Het is didactisch niet juist, in leerboeken in het hoofdstuk over de molecuulgewichtsbepalingen van polymeren ook de viscositeit op te nemen.

4

De berekeningen van de ketenlengte van vloeibare seleen door Krebs en Morsch zijn onjuist.

H.Krebs en W.Morsch, *Z.Anorg.Chem.* **263**, 305 (1950)
H.Krebs, *Z.Anorg.Chem.* **265**, 156 (1951)

5

Het bestaan van macromoleculaire ringen, opgebouwd uit zwavel- of seleenatomen, is niet waarschijnlijk.

b.v. H.Krebs, *Z.Anorg.Chem.* **265**, 156 (1950)
H.Krebs en E.Weber, *Z.Anorg.Chem.* **272**, 288 (1953)
P.W.Schenk, *Z.Anorg.Chem.* **280**, 1 (1955)

6

Het is mogelijk, dat een deel van de discrepantie tussen de uit de experimenten berekende en de theoretisch verwachte waarden van de wrijvingsparameter in de viscositeitstheorieën toegeschreven moet worden aan een foutieve bepaling van het grensviscositeitsgetal.

7

Het door Blatt voorgestelde mechanisme voor de isomerisatie van de niet gebonden en gebonden oximen van de ortho-hydroxy-benzophenonen is niet waarschijnlijk.

A.H.Blatt, *J.Org.Chem.* **20**, 591 (1955)

8

De door Müller voorgestelde methode voor het bepalen van thermodynamische grootheden van mengsels langs diëlectrische weg levert voor polymeeroplossingen geen nieuwe gezichtspunten.

F.H.Müller, Kolloid Z. 121, 79 (1951)

9

Als de door Bohm voorgestelde interpretatie van de quantummechanica juist is, dan dient bij het onderricht ook de aandacht op deze interpretatie gevestigd te worden.

D.Bohm, Phys.Rev. 85, 166 (1952)

10

Het is wenselijk, dat de kennis der verkeersregels als verplicht leervak in het lagere schoolprogramma wordt opgenomen.

