Fractionation of Polymers by Liquid-Liquid Distribution

I. Theory

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Equations for the calculation of molecular frequency functions of
polymers from counter current experiments are deduced provided that
ideal conditions prevail.

The method of fractionating polymers by distribution between two immiscible
solvents was first applied by Schulz and Nordt [1]. By shaking a water
solution of polyglycol with mixtures of chloroform and benzene of different
composition they obtained a number of fractions of different molecular
weights. The volume ratio of the two phases was kept very high.

The theory of the process was first treated by Brønsted [2]. On the basis
of the assumption that in chemically similar materials the potential energy
of the molecule is proportional to its magnitude he deduces the formula

$$k = \exp \frac{P \cdot \varepsilon}{RT} \tag{1}$$

where k = partition coefficient, P = degree of polymerisation and ε is a
constant dependent of the composition of the solvent system. By experi-
ments Schulz [3] found that a simple relation exists between the constant ε
and the composition of the solvent system. By applying these laws Schulz
and Nordt [1] could conclude that the efficiency of separation is improved by
increasing the volume ratio of the two phases. The conclusion which was
drawn from these investigations is that fractional precipitation can be con-
sidered more efficient, as in the latter case the volume ratio of the two phases
is much higher than can be attained in practice at distribution between two
solvents.

By the use of statistical thermodynamics several equations have been
derived to account for the activity of polymer solutions. (For a review see
e.g., Ref.[4]). These equations confirm at least qualitatively the results of
Schulz and Nordt [1].

As was pointed out by Almin and Steenberg [5] the liquid-liquid distribution method as carried out by Schulz and Nordt suffers from the same weakness as the solution and precipitation methods, as to the calculation of the molecular frequency function from the experimental data. By keeping the composition of the solvent system constant at all steps of the fractionation and compensating for the decreased fractionation effect by a method of multiplication, data can be obtained, making it possible to carry out the calculations in a theoretically correct way.

The scope of this work is to make use of this by distributing polymers between two immiscible solvents according to the Craig counter current method.

FREQUENCY CURVES WITH RESPECT TO PARTTION COEFFICIENT

When a pure substance is distributed between two solvents in a Craig distribution apparatus according to the fundamental procedure [6], the amount of substance present in the pth tube is

$$w(p) = m_0 \cdot \binom{n}{p} \cdot \frac{k^p}{(k+1)^n} \quad (= 0,1,2, \ldots \ldots n) \tag{2}$$

where m_0 is the total amount of substance added to the apparatus and k is the partition coefficient for the substance between the phase to be transferred and the stationary phase, n being the number of transfers. Equal volumes of the two phases are presupposed. If the substance contains molecules of different partition coefficients and the weight frequency function with respect to partition coefficients is $f(k)$, the amount of those molecules which have a partition coefficient in the range between k and $k + dk$ in the pth tube is

$$\delta w(p) = m_0 \cdot \binom{n}{p} \cdot \frac{k^p}{(k+1)^n} \cdot f(k) \cdot \mathrm{d}k$$

or

$$W_n(p) = \frac{m_0}{w(p)} = \int_0^\infty \binom{n}{p} \cdot \frac{k^p}{(k+1)^n} \cdot f(k) \cdot \mathrm{d}k \tag{3}$$

$W_n(p)$ is the weight fraction of the original substance present in the pth tube.*

The condition precedent for the validity of this formula is that no interaction of molecules of different size occurs and that the partition coefficient is independent of concentration. Of course it is a prerequisite that the presence of the polymer does not cause a change in the composition of the solvents, and that real equilibrium conditions are fulfilled.

As $W(p)$ is known from experiments the integral eqn. (3) can be solved with respect to $f(k)$ according to some approximation method. The author has adopted the following method for the solution of the equation.**

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* When confusion is out of question the index n of $W_n(p)$ will be omitted.
** By access of an electronic computor somewhat different treatment of the problem is conceivable.

It is considered that the frequency function $f(k)$ can be expressed as a sum of several functions $\psi_i(k)$:

$$f(k) = \sum_i \psi_i(k)$$

The functions ψ_i are chosen so that 1) they are bell shaped and $= 0$ for $k = 0$ and ∞, 2) the integral

$$\int_0^\infty \binom{n}{p} \cdot \frac{k^p}{(k+1)^n} \cdot \psi_i(k) \cdot dk$$

can be expressed by elementary functions. These conditions are fulfilled if, e.g.,

$$\psi_i(k) = A_i \cdot k^{r_i} \cdot (k+1)^n \cdot \exp(-a_i \cdot k^{s_i}) \tag{4}$$

where r_i, s_i, A_i and a_i are properly chosen numbers. For the sake of simplicity r_i, s_i and a_i ought to be integers and if possible s_i shall be put equal to 1. For the special case $s_i = 1$ one obtains

$$W(p) = \binom{n}{p} \cdot \sum_i A_i \cdot \frac{(p+r_i)!}{a_i^{p+r_i+1}} \tag{5}$$

By trial and error it is posssible to find values of A_i, a_i and r_i to have the calculated and the experimentally determined $W(p)$ values agree. This can be done in a systematic way.

The method will be explained by a fictive experiment. A polymer is assumed to be defined by the frequency function

$$f(k) = 5.784 \times 10^5 \cdot k^4 (k+1)^{19} \cdot \exp(-27 \cdot k^{\frac{1}{2}}) \tag{6}$$

The corresponding curve is drawn in Fig. 1. If this preparation is distributed in a 20-tube countercurrent distribution apparatus ($n = 19$) one obtains in accordance with eqn. (3)

$$W(p) = 1.157 \times 10^6 \cdot \frac{(2p+9)!}{27^{2p+10}} \tag{7}$$

The $W(p)$ values calculated from this formula are listed in Table 1.

Starting from these values $f(k)$ shall be calculated considering that it can be expressed by a sum of functions of the type

$$A \cdot k(k+1)^{19} \cdot \exp(-ak)$$

From the table can be seen that $W(p)$ has its highest value for $p = 11$. A preparation with a frequency function of the type mentioned has its highest $W(p)$ value for $p = 11$ when $a = 9$. The difference

$$\Delta W(p)' = W(p) - A'_1 \cdot \binom{19}{p} \cdot \frac{(p+1)!}{9^{p+2}} \tag{8}$$

Table 1.

p	$W(p)$ (Eqn. 7)	$\Delta W(p)$ (Eqn. 8)	$\Delta W(p)$ (Eqn. 9)
0	0.0020	19×10^{-4}	-1×10^{-4}
1	0.0058	54	3
2	0.0113	100	5
3	0.0184	153	4
4	0.0274	205	0
5	0.0386	247	-3
6	0.0519	267	-4
7	0.0669	253	-1
8	0.0826	202	2
9	0.0972	124	3
10	0.1083	47	2
11	0.1130	0	0
12	0.1091	3	-1
13	0.0959	48	0
14	0.0751	100	0
15	0.0509	123	-2
16	0.0286	104	-4
17	0.0125	61	-4
18	0.0038	23	-1
19	0.0006	4	0
	$\Sigma = 0.9999$		$\Sigma = -2 \times 10^{-4}$

is calculated assuming such a value of A_1 that the difference $= 0$ for $p = 11$ (*i.e.* where $W(p)$ is maximum). As can be seen from the table this difference has its highest values for $p = 6$ and $p = 15$. The new difference

$$\Delta W(p)'' = W(p) - \binom{19}{p} \cdot (p+1)! \cdot \left[\frac{A_1''}{9^{p+2}} + \frac{A_2''}{16^{p+2}} + \frac{A_3''}{5^{p+2}} \right]$$

is calculated assuming such values of the A''-s that $\Delta W(p)'' = 0$ for $p = 6$, 11 and 15. (It shall be borne in mind that the two last terms within the parenthesis have their highest values for $p = 6$ and 15, resp.) When the difference

$$\Delta W(p)''' = W(p) - A_1'' \cdot \binom{19}{p} \cdot \frac{(p+1)!}{9^{p+2}}$$

is now calculated, it is found that its highest values occur when $p = 7$ and 14. This means that the choice of the two last functions was not appropriate. Thus a new attempt is made with functions which give their highest $W(p)$ values for $p = 7$, 11 and 14. This procedure is now repeated until agreement is attained at least in the tubes containing the chief part of the preparation. In this case it is found that this new approach gives good agreement exept for $p = 1$, 2 and 3, but by further subtraction with an expression of the type
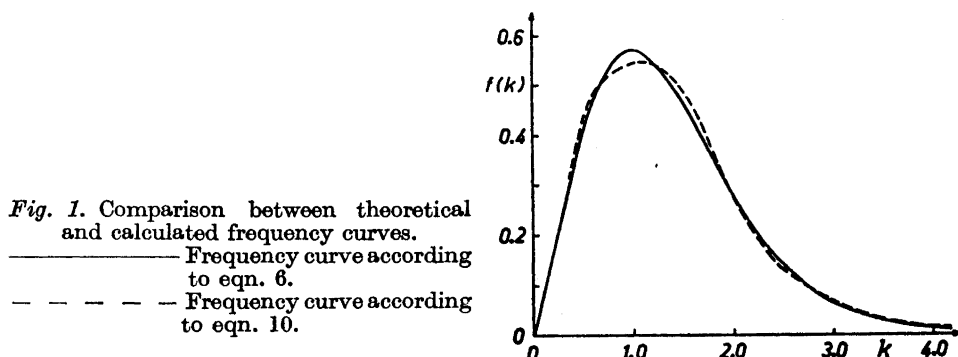
$$A_4 \cdot \binom{19}{p} \cdot \frac{(p+1)!}{25^{p+2}}$$

Fig. 1. Comparison between theoretical and calculated frequency curves.
———————— Frequency curve according to eqn. 6.
— — — — — Frequency curve according to eqn. 10.

(this expression has its highest value for $p = 2$) good agreement is obtained. In column No. 4 of Table 1 the difference

$$\varDelta W(p)'''' = W(p) - \binom{19}{p} \cdot (p+1)! \cdot \left[\frac{4.441 \times 10^{-6}}{6^{p+2}} + \frac{5.934 \times 10^{-3}}{9^{p+2}} + \frac{3.550 \times 10^{-1}}{14^{p+2}} + \frac{1.4 \times 10^{-2}}{25^{p+2}} \right] \tag{9}$$

is calculated. As can be seen, the differences can be regarded as small in comparison to experimental errors in a real experiment. If the amount of original substance had been 1 g, no error exceeds 0.5 mg. These calculations thus lead to the conclusion that the frequency curve can be expressed by

$$f_1(k) = k \cdot (k+1)^{19} \cdot [4.441 \times 10^{-6} \cdot \exp(-6k) + 5.934 + 10^{-3} \cdot \exp(-9k) + 3.550 \times 10^{-1} \cdot \exp(-14k) + 1.4 \times 10^{-2} \cdot \exp(-25k)] \tag{10}$$

The corresponding curve is drawn in Fig. 1. The agreement with the theoretical curve must be regarded as good.

In this connection it seems justified to mention that the moments of the frequency functions can easily be obtained from the data of experiments of this type. According to definition the νth moment about the origin is

$$\mu_\nu = \int_0^\infty k^\nu \cdot f(k) \cdot \mathrm{d}k = \int_0^\infty \frac{k^\nu \cdot (k+1)^n}{(k+1)^n} \cdot f(k) \cdot \mathrm{d}k = \sum_{p=0}^n \binom{n}{p} \int_0^\infty \frac{k^{p+\nu}}{(k+1)^n} \cdot f(k) \cdot \mathrm{d}k =$$

$$= \sum_{p=0}^n \frac{\binom{n}{p}}{\binom{n}{p+\nu}} \cdot W(p+\nu) = \mu_\nu' + \varDelta\mu_\nu \tag{11}$$

where $\quad \mu_\nu' = \sum_{p=0}^{n-\nu} \frac{\binom{n}{p}}{\binom{n}{p+\nu}} \cdot W(p+\nu) \tag{12 a}$

$$\text{and} \quad \Delta\mu_\nu = \sum_{p=n-\nu+1}^{n} \frac{\binom{n}{p}}{\binom{n}{p+\nu}} \cdot W(p+\nu) \tag{12 b}$$

Although μ_ν' can be calculated from the experimental $W(p)$ values, $\Delta\mu_\nu$ cannot because all terms in this expression are of the indefinite form $0/0$. Thus the calculation of the moments cannot be done completely and it can only be regarded as justified if $\Delta\mu_\nu$ is a small number in comparison to μ_ν'. In any case calculation of moments of high order cannot be done with any accuracy. In Table 2 the first three moments are calculated for the curve given in eqn. (6) and compared to those calculated from the $W(p)$ values given in Table 1. As can be seen from the table the accuracy diminishes as the order of the moment increases.

Table 2.

Order of moment	Theoretical moment	Moment calc. from eqn. 12 a
1	1.366	1.364
2	2.450	2.40$_9$
3	5.369	4.90$_5$

The fitting of the frequency curve by the method of moments as for instance developed by Pearsom (see, *e.g.*, Ref.[7]) can of course be done, but this method presupposes a frequency function of only one mode. If the frequency curve contains more than one peak this method will fail. With the first one given, however, more details can be detected.

As far as the author knows no mathematical analytical method exists to determine (calculate) the accuracy of the frequency curve. It is quite evident that a very sharp peak in the curve cannot be detected only by mathematical means. This can only be done by changing the experimental conditions so that the resolving power of the distribution apparatus is increased, *e.g.* by increasing the number of fractions or choosing another solvent system.

The result is no doubt dependent on the mathematical method chosen for the calculations. In the method adopted by the author it is considered that the frequency function can be represented by a sum of a limited number of functions of a special type. It is of course not certain that this approach is correct, but as long as it is not unreasonable it must be considered justified. The only possibility to check the results is to vary the experimental conditions and to test whether the same result is obtained when the resulting frequency curve in respect to distribution coefficient is converted into a molecular frequency curve. Negative $\Delta W(p)$ values should of course be avoided at early stages of the calculations.

RELATION BETWEEN MOLECULAR WEIGHT AND PARTITION COEFFICIENT

When the frequency function with respect to the partition coefficient in a certain solvent system is known, it remains to determine the relation between the partition coefficient and the molecular weight before the molecular frequency function can be determined. The fractionation method suggested in this paper is not selective and thus the procedure will depend upon the way and method of measuring molecular weights. As was pointed out by Almin· and Steenberg [5] the average molecular weight $\overline{M(p)}$ in fraction No. p can be written

$$\overline{M(p)}^{a} = \frac{1}{W(p)} \cdot \binom{n}{p} \cdot \int_0^\infty \frac{k^p}{(k+1)^n} \cdot f(k) \cdot M^a \cdot dk \tag{13}$$

where M is the molecular weight of molecules with the partition coefficient k, and a is a parameter fixed by the conditions of the method of molecular weight determination. This formula is valid in cases when number averages ($a = -1$), weight averages ($a = 1$) or viscosity averages ($0.5· < a < 1$) of the molecular weight are measured.

Eqn. (13) can be solved with respect to $f(k) \cdot M^a$ according to a method quite analogous to the one suggested for eqn. (3). By dividing the solution of eqn. (13) with the solution of eqn. (3) one obtains M^a as a function of k. By applying such a method serious errors can be expected because errors from the two approximate solutions are introduced. For this reason other methods to calculate M^a as a function of k ought to be tried. By introducing a model for the relation between M^a and k as below a solution is obtained which is independent of the solution of eqn. (3):

$$M^a = B \cdot \ln k + \sum_i C_i \cdot k^i \tag{14}$$

where it is considered that i can only adopt small negative or positive values (including 0).

From eqns. (13) and (14) one obtains

$$S(p) \cdot \overline{M(p)}^{a} = B \cdot \int_0^\infty \frac{k^p}{(k+1)^n} \cdot f(k) \cdot \ln k \cdot dk + \sum_i C_i \int_0^\infty \frac{k^{p+i}}{(k+1)^n} \cdot f(k) \cdot dk$$

$$= B \cdot \frac{dS(p)}{dp} + \sum_i C_i \cdot S(p+i) \tag{15}$$

where

$$S(p) = \frac{W_p}{\binom{n}{p}} \tag{16}$$

By dividing with $S(p)$ one obtains

$$\overline{M(p)}^{a} = B \cdot \frac{d\ln S(p)}{dp} + \sum_i C_i \cdot \frac{S(p+i)}{S(p)} \tag{17}$$

As $\overline{M(p)}$ and $S(p)$ are known from the experiments and $\dfrac{d\ln S(p)}{dp}$ can be obtain-

ed graphically it is possible to calculate B and C_i for instance by the method of least squares. If a good correlation between observed and calculated values is not obtained when only a few terms of the sigma of eqn. (17) are made use of, this method is not to be recommended. Then another model must be tried or the first mentioned method must be used. The expression in eqn. (14) is, however, not chosen only because it gives a rather simple solution (eqn. 17), but also for theoretical reasons. According to the Brønsted formula (eqn. 1) ln k is proportional to the degree of polymerisation. The real relation between these quantities is certainly more complex and therefore the author has chosen a modified approach. The formula can be considered especially convenient in cases when $\alpha = 1$ or close to one, as for instance in viscometric measurements.

The range of validity of the relation obtained between the molecular weight and the partition coefficient is difficult to estimate from one experiment only. Especially at high and low molecular weights appreciable errors can be expected. By investigating several samples of different mean molecular weights of the same polymer at the same experimental conditions it would be possible to obtain a curve which covers an appreciable molecular weight range.

MOLECULAR FREQUENCY CURVES

The final problem is to convert the frequency functions of partition coefficient to molecular weight frequency functions. This can be achieved by applying the formula

$$g(M) = f(k) \cdot \frac{\mathrm{d}k}{\mathrm{d}M} \qquad (18)$$

where $g(M)$ is the molecular weight frequency function. The derivative $\dfrac{\mathrm{d}k}{\mathrm{d}M}$ is obtained from the relation between partition coefficient and the molecular weight by graphical or other means.

DISCUSSION

The mathematical methods for treating the experimental data from counter current fractionations are based on the assumptions that the quantities involved can be represented by models. These models are chosen so that a rather simple numerical treatment is possible.

The basic assumptions which are made are discussed by Almin and Steenberg [5]. It is, however, very probable that the laws which are used to deduce eqns. (3) and (13) do not hold in practice. The relation between the molecular weight and the partition coefficient affords a special problem. The experimental conditions ought to be chosen so that this relation is a monotonous one. These problems will be discussed in the experimental parts of this series.

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