

Fractionation of Polymers by Liquid-Liquid Distribution

IV. Countercurrent Fractionation of Polyglycols

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Three polyglycol preparations have been countercurrent distributed in the solvent system trichloroethylene-alcohol-water. Weights and limiting viscosity numbers of the different fractions have been determined. Curves of weight frequency *vs.* limiting viscosity number have been calculated.

In this paper, experiments will be reported in which polyglycols have been fractionated by means of liquid-liquid countercurrent distribution. The method has been described in earlier papers of this series from both theoretical and practical points of view^{1,2}. Three different preparations, A 6 000, A 4 000 and A 1 500, have been investigated and equal volumes of the two phases obtained by mixing trichloroethylene, alcohol and water (TAW) in the volume ratio 0.414 : 0.43 : 0.156 have been used as solvent system.

In Tables 1-3, the experimental results from experiments with different weights of samples can be seen in columns 2-5. The notations are in agreement with those of Ref.¹. Col. 6 of these tables contains $W(p)$ values at infinite dilution calculated by means of eqn. 4 in Ref.². The method of least squares was applied. The slopes of the lines obtained in this way are given in Fig. 1 (points). In this figure, the $\Delta W(p)$ values calculated from eqn. 5 of Ref.²

$$\Delta W(p) = W(p) \cdot \left(\frac{p}{k_0} - \frac{n}{1+k_0} \right) \cdot \Delta k_0 \quad (1)$$

are also given (curves), suitable values for k_0 and Δk_0 being assumed. The statement in Ref.² that the concentration dependence of the partition coefficient results in an effect which can be compared with an overall change in partition coefficient has thus been experimentally verified. It can further be noted in the case of the preparation A 6 000 that the peak of the $W(p)$ *vs.* p curve moves to higher p values as the sample weight is increased while

Table 1. Countercurrent distribution of polyglycol A 6000. Solvent system: TAW ($v = 0.43$). $w(p)$, $W(p)$ = amount and relative amount, respectively, of polyglycol in fraction no. p . w_0 = initial weight of sample.

| p | $W(p) \times 10^3$ (exptl.) | | | | $W(p) \times 10^3$ (calc.) ($w_0 = 0$) | $\Delta W(p) \times 10^3$ |
|-------------------------|-----------------------------|-------------|-------------|---------------|--|---------------------------|
| | $w_0 = 5$ g | $w_0 = 2$ g | $w_0 = 1$ g | $w_0 = 0.5$ g | | |
| 0 | 0.5 | 1.1 | 1.5 | 3.0 | 2.5 | -0.4 |
| 1 | 0.9 | 1.6 | 1.9 | 3.2 | 2.8 | -0.4 |
| 2 | 2.5 | 2.7 | 3.4 | 4.1 | 3.8 | 0.0 |
| 3 | 7.2 | 6.9 | 7.4 | 8.5 | 7.9 | 0.7 |
| 4 | 17.0 | 16.4 | 15.3 | 16.8 | 16.0 | 0.4 |
| 5 | 34.8 | 32.2 | 31.8 | 32.3 | 31.4 | 0.2 |
| 6 | 61.0 | 54.3 | 53.6 | 56.3 | 53.4 | -0.6 |
| 7 | 89.9 | 85.7 | 82.7 | 83.0 | 81.9 | 0.4 |
| 8 | 116.5 | 108.5 | 106.9 | 106.9 | 104.9 | -2.1 |
| 9 | 128.4 | 129.6 | 128.0 | 124.9 | 126.7 | 3.5 |
| 10 | 133.4 | 128.4 | 126.8 | 126.4 | 125.4 | -1.0 |
| 11 | 121.9 | 119.1 | 118.1 | 115.9 | 116.2 | -0.9 |
| 12 | 94.3 | 101.6 | 100.9 | 99.3 | 101.9 | 1.9 |
| 13 | 74.1 | 78.2 | 79.7 | 76.8 | 79.2 | -0.6 |
| 14 | 50.5 | 56.7 | 57.2 | 57.3 | 58.8 | -0.5 |
| 15 | 32.6 | 36.9 | 39.1 | 38.4 | 39.8 | -0.3 |
| 16 | 18.9 | 21.7 | 23.8 | 24.1 | 24.6 | 0.1 |
| 17 | 9.6 | 11.7 | 12.8 | 13.4 | 13.6 | 0.2 |
| 18 | 4.6 | 4.7 | 6.9 | 7.3 | 7.1 | 0.0 |
| 19 | 1.5 | 2.2 | 2.1 | 1.8 | 2.1 | -0.5 |
| $\sum w(p) - w_0$ mg | -76.2 | -1.2 | -2.4 | 6.4 | | $\sum = 0.1$ |

Table 2. Countercurrent distribution of polyglycol A 4000. Solvent system: TAW ($v = 0.43$). For symbols see Table 1.

| p | $W(p) \times 10^3$ (exptl.) | | | | $W(p) \times 10^3$ (calc.) ($w_0 = 0$) | $\Delta W(p) \times 10^3$ |
|-------------------------|-----------------------------|-------------|-------------|---------------|--|---------------------------|
| | $w_0 = 5$ g | $w_0 = 2$ g | $w_0 = 1$ g | $w_0 = 0.5$ g | | |
| 0 | 0.7 | 1.2 | 1.6 | 2.3 | 2.1 | 1.1 |
| 1 | 4.0 | 6.0 | 7.2 | 8.3 | 8.3 | 0.6 |
| 2 | 18.1 | 22.5 | 24.2 | 27.9 | 27.2 | -1.1 |
| 3 | 43.7 | 57.4 | 58.6 | 66.5 | 66.2 | -2.2 |
| 4 | 88.0 | 107.0 | 112.3 | 117.1 | 119.5 | -0.9 |
| 5 | 128.7 | 152.8 | 159.5 | 161.4 | 166.4 | 2.3 |
| 6 | 168.8 | 174.0 | 176.0 | 179.5 | 179.1 | -0.1 |
| 7 | 169.3 | 172.0 | 165.6 | 167.8 | 167.6 | 7.4 |
| 8 | 151.1 | 134.1 | 123.8 | 122.0 | 118.8 | 0.0 |
| 9 | 111.0 | 87.9 | 76.6 | 72.7 | 68.9 | -4.9 |
| 10 | 64.5 | 46.9 | 39.8 | 37.7 | 34.4 | -4.6 |
| 11 | 30.6 | 21.7 | 22.0 | 17.4 | 17.3 | -0.6 |
| 12 | 12.6 | 8.8 | 13.5 | 7.6 | 9.3 | 1.4 |
| 13 | 4.9 | 3.8 | 8.5 | 3.6 | 5.5 | 1.1 |
| 14 | 2.1 | 1.7 | 4.7 | 2.5 | 3.4 | 0.2 |
| 15 | 0.9 | 0.8 | 2.6 | 1.7 | 2.1 | -0.4 |
| 16 | 0.4 | 0.4 | 1.3 | 1.5 | 1.4 | -0.3 |
| 17 | 0.2 | 0.7 | 0.9 | 1.1 | 1.1 | 0.2 |
| 18 | 0.2 | 0.2 | 0.9 | 1.3 | 1.1 | 0.8 |
| 19 | 0.1 | 0.1 | 0.3 | 0.3 | 0.3 | 0.2 |
| $\sum w(p) - w_0$ mg | -88.0 | -36.4 | 6.1 | 2.0 | | $\sum = 0.2$ |

Table 3. Countercurrent distribution of polyglycol A 1500. Solvent system: TAW ($v = 0.43$). For symbols see Table 1.

| p | $W(p) \times 10^3$ (exptl.) | | | | $W(p) \times 10^3$ (calc.) ($w_0 = 0$) | $\Delta W(p) \times 10^3$ |
|-------------------------|-----------------------------|-------------|-------------|---------------|--|---------------------------|
| | $w_0 = 5$ g | $w_0 = 2$ g | $w_0 = 1$ g | $w_0 = 0.5$ g | | |
| 0 | 3.6 | 5.2 | 7.9 | 9.4 | 9.1 | 0.6 |
| 1 | 34.3 | 35.8 | 43.8 | 48.4 | 46.5 | 0.3 |
| 2 | 83.6 | 100.1 | 104.1 | 120.2 | 116.7 | -1.8 |
| 3 | 155.2 | 164.0 | 185.9 | 184.3 | 186.8 | -4.5 |
| 4 | 201.4 | 208.4 | 210.3 | 209.6 | 211.6 | -6.5 |
| 5 | 199.9 | 196.3 | 188.7 | 179.7 | 183.1 | -3.4 |
| 6 | 157.2 | 143.5 | 125.7 | 121.3 | 120.3 | -3.7 |
| 7 | 93.3 | 82.3 | 72.0 | 64.6 | 65.5 | -0.1 |
| 8 | 42.4 | 37.7 | 32.6 | 30.0 | 30.1 | 2.0 |
| 9 | 17.2 | 15.4 | 13.4 | 12.3 | 12.4 | 2.6 |
| 10 | 6.3 | 5.8 | 4.3 | 5.7 | 5.0 | 2.2 |
| 11 | 2.4 | 2.3 | 2.7 | 2.8 | 2.7 | 2.0 |
| 12 | 1.1 | 1.3 | 2.1 | 1.8 | 2.0 | 1.9 |
| 13 | 0.6 | 0.5 | 1.0 | 1.7 | 1.3 | 1.3 |
| 14 | 0.3 | 0.3 | 0.8 | 1.6 | 1.2 | 1.2 |
| 15 | 0.3 | 0.3 | 0.9 | 1.4 | 1.2 | 1.2 |
| 16 | 0.2 | 0.2 | 0.9 | 1.5 | 1.2 | 1.2 |
| 17 | 0.2 | 0.2 | 0.9 | 1.3 | 1.1 | 1.1 |
| 18 | 0.2 | 0.3 | 1.0 | 1.6 | 1.3 | 1.3 |
| 19 | 0.2 | 0.1 | 0.8 | 0.6 | 0.7 | 0.7 |
| $\sum w(p) - w_0$ mg | 5.8 | -16.8 | 7.8 | 5.3 | | $\sum = -0.4$ |

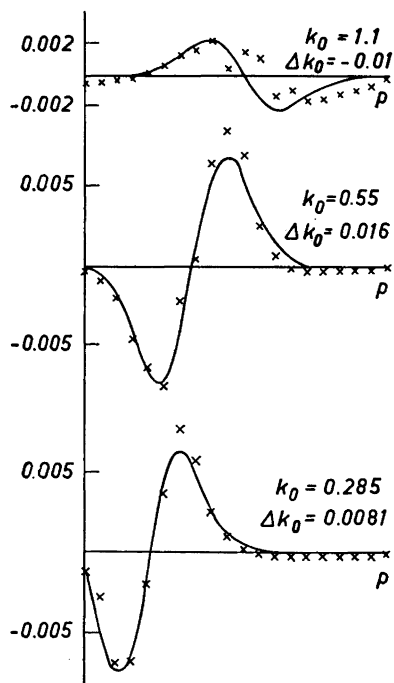


Fig. 1. Changes in the $W(p)$ values due to the concentration dependence of the partition coefficient (*cf.* text).

Table 4. Parameters of the formulas giving the mathematical expressions for the frequency functions of polyglycols A 6 000 and A 4 000. (Cf. eqn. 2).

| Sample | i | A_i | r_i | a_i | s_i |
|---------|-----|------------------------|-------|-------|-------|
| A 6 000 | 1 | 4.08 | 1 | 38 | 1 |
| | 2 | 7.684×10^{-4} | 1 | 5.9 | 2 |
| | 3 | 9.53×10^{-5} | 1 | 7 | 1 |
| | 4 | 1.9×10^{-15} | 1 | 2 | 1 |
| A 4 000 | 1 | 9.84×10^{-1} | 12 | 40 | 2 |
| | 2 | 1.6×10^{-2} | 1 | 6 | 1 |

the opposite is the case for the two other preparations. This is in accordance with the signs of the slopes of the lines in Fig. 4 of Ref.²

The calculations of the frequency functions of the partition coefficient have been based on the calculated $W(p)$ values at infinite dilution. In accordance with Ref.¹, it is assumed that the frequency functions of the preparations A 6 000 and A 4 000 can be expressed as a sum of functions of the type

$$A_i \cdot k^{r_i} \cdot (1+k)^{19} \cdot \exp(-a_i \cdot k^{s_i}) \quad (2)$$

The results of these calculations are given in Table 4. The differences between the $W(p)$ values in col. 6 of Tables 1 and 2 and the $W(p)$ values calculated from the calculated frequency functions can be seen in col. 7 of Tables 1 and 2. These differences are small considering the experimental errors and hence the calculated frequency functions must be regarded as satisfactory. The frequency curve of preparation A 6 000 shows a small peak at low k values.

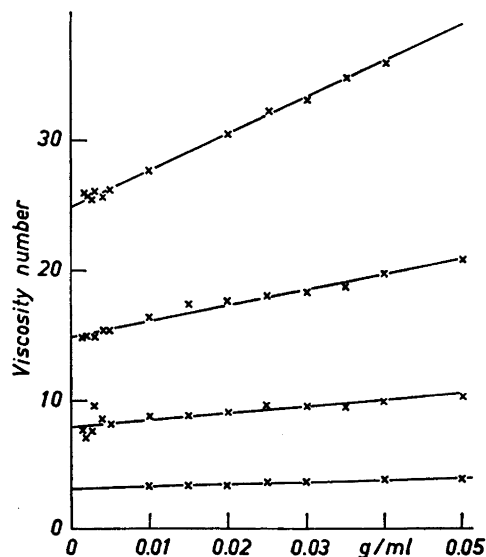


Fig. 2. Viscosity number of the polyglycol samples as a function of concentration. Solvent: chloroform.

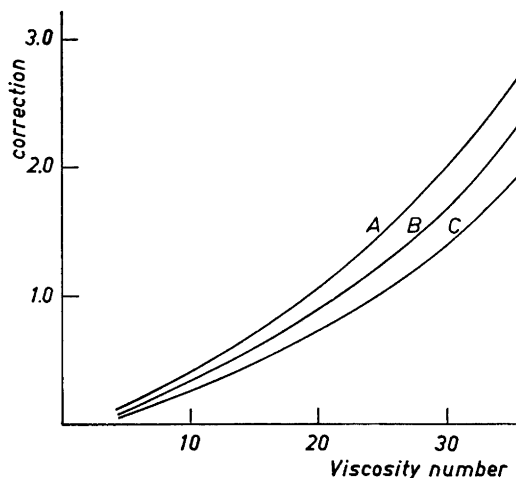


Fig. 3. Curves giving the correction to be subtracted from an experimentally determined viscosity number for polyglycol in chloroform in order to obtain the limiting viscosity number. A = 0.006 g/ml; B = 0.005 g/ml; C = 0.004 g/ml.

This peak must be a consequence of slight errors in the experimental and numerical methods.

No attempts were made to calculate a frequency curve for preparation A 1500. The reason for this was that the $W(p)$ vs. p curve for this preparation agreed so closely with the corresponding curve for a preparation containing molecules of only one size. The differences between the $W(p)$ values in col. 6 of Table 3 and the $W(p)$ values expected for a substance with $k = 0.285$ can be seen in col. 7 of Table 3. These differences are only slightly greater than the experimental errors. They show, however, a pronounced trend, thus indicating that molecules of different sizes are present. The frequency curve must therefore have been very narrow. The resolving power was thus too low in these experiments to permit a determination of the shape of the frequency curve. One of the reasons for this is the disadvantageous volume ratio of the phases in the experiment. It can be calculated that a volume ratio of about 1 : 0.285 for the two phases would increase the resolving power by about 45%. Such an increase cannot, however, be regarded as sufficient. Thus, some other solvent system must be used. The results of the distribution experiment with polyglycol A 1 500 can therefore only serve as an aid in determining the relation between partition coefficient and molecular weight.

In order to determine the frequency functions of the limiting viscosity number, the latter quantity was calculated from the viscosities of chloroform solutions, for each of the fractions containing more than about 25 mg polyglycol. The calculations of the limiting viscosity numbers were carried out under the assumption that the slope of the line giving the relation between viscosity number and concentration is a function solely of the limiting viscosity number of the preparation. These slopes were determined from the relation

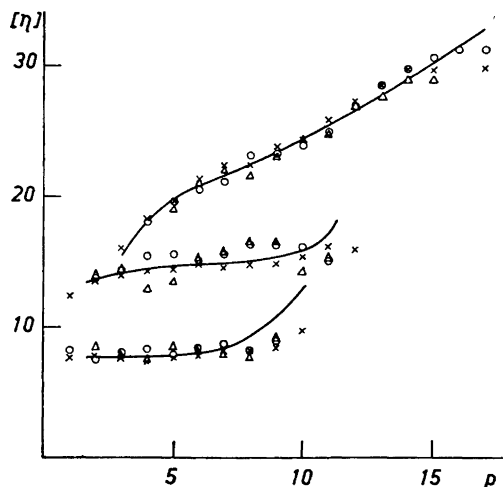


Fig. 4. Comparison between experimentally determined (points) and calculated (curves) limiting viscosity numbers for the polyglycol fractions obtained from polyglycols A 6 000, A 4 000 and A 1 500. \times 5 g, \circ 2 g and \triangle 1 g experiments.

giving the viscosity number as a function of the concentration for the preparations A 6 000, A 4 000, A 1 500 and A 300. These relations can be seen in Fig. 2. The difference between the viscosity number and the limiting viscosity number was then plotted as a function of the viscosity number at different concentrations (Fig. 3). Using this figure, it is possible to find the correction which must be subtracted from a certain viscosity number determined at a known concentration in order to obtain the limiting viscosity number.

In Fig. 4, the limiting viscosity numbers of the different fractions obtained from the 5 g, 2 g and 1 g distribution experiments are plotted as a function of the tube number. No systematic differences between results obtained from countercurrent experiments with different sample weights can be detected. The author has therefore regarded all the experimental points as being of

Table 5. Comparison between limiting viscosity numbers calculated from the fractions in the countercurrent experiments and the limiting viscosity numbers obtained from Fig. 2.

| w_0 | A 6 000 | A 4 000 | A 1 500 |
|----------------------|-------------------|-------------------|------------------|
| 5 g | 25.0 | 14.8 | 7.8 |
| 2 g | 24.9 | 15.7 | 8.3 |
| 1 g | 24.7 | 15.6 | 8.1 |
| $[\eta]$ from Fig. 2 | 24.8 _s | 14.8 _s | 7.9 _o |

equal statistical weight and equal to the values which would have been obtained in a fictitious countercurrent experiment carried out at infinite dilution.

In Table 5, limiting viscosity numbers for the three fractionated samples, calculated from the limiting viscosity numbers and the corresponding fraction weights according to Philippoff³, are compared with the directly determined limiting viscosity numbers of the original polyglycol preparations. Considering the accuracy of the viscosity determinations, the agreement must be regarded as satisfactory.

The relation between the limiting viscosity number and the partition coefficient was determined according to the method described in Ref.¹ The experimentally determined values for the limiting viscosity numbers of the fractions, $[\eta]_p$, and the corresponding $S(p)$ values calculated from the $W(p)$ values at infinite dilution were used. The values of $\frac{d \ln S(p)}{dp}$ were obtained by an interpolation method. The i values chosen were $-2, -1, 0, 1$ and 2 . In this way, a set of equations was obtained from which the constants of the relation

$$[\eta] = B \cdot \ln k + \sum_i C_i \cdot k^i \quad (i = -2, -1, 0, 1, 2) \quad (3)$$

were obtained using the method of least squares. Because of the large number of equations and variables, an electronic computer (BESK) was used for the calculations. The results of these calculations can be seen in Table 6. The

Table 6. Numerical values of the constants of eqn. 3.

| | | |
|-----------------------------|---------|------------------|
| B | 5.38 | (± 6.05) |
| C_{-2} | 0.2821 | (± 0.1501) |
| C_{-1} | -4.519 | (± 2.420) |
| C_0 | 26.52 | (± 2.45) |
| C_1 | 1.608 | (± 4.377) |
| C_2 | -0.2649 | (± 0.3456) |
| Standard deviation (eqn. 4) | 1.02 | |

errors in the constants B and C_i are considerable. The reason for these large errors is that $\ln k$ can be expressed as a series of the type $\sum C_i k^i$ in a limited range of k and this makes it difficult for the numerical method to «decide» which term in the author's formula shall predominate. This difficulty can be overcome by decreasing the number of terms in eqn. 1, but then the solution would not be free from assumptions that may be biased. The reliability of the final relation between the limiting viscosity number and the partition coefficient should be judged from the standard deviation, σ , calculated from the formula

$$\sigma^2 = \frac{1}{m-n} \cdot \sum ([\eta]_{p, \text{ obs}} - [\eta]_{p, \text{ calc}})^2 \quad (4)$$

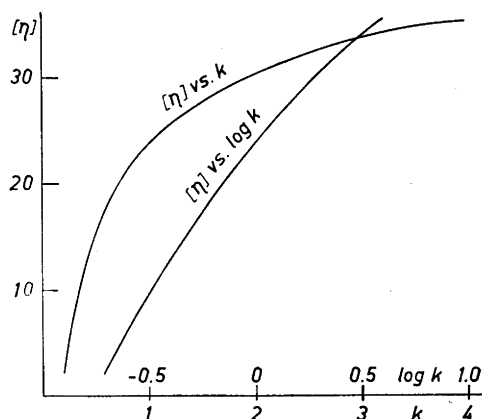


Fig. 5. Relation between the limiting viscosity number of polyglycol in chloroform and the partition coefficient of polyglycol in the solvent system TAW ($v = 0.43$).

where $m =$ number of equations and $n =$ number of coefficients. The value of σ (Table 6) must be considered consistent with the spread of the experimental $[\eta]_p$ values. It should be pointed out that the final relation and its derivative are monotonic. The corresponding curve is shown in Fig. 5. The $[\eta] \text{ vs. } \log k$ curve is almost a straight line but it does not pass through the origin. This indicates that Brønsted's exponential formula for the partition coefficient of polymers⁴ has to be multiplied by a constant if it is to represent approximately the experimental results of this investigation. This circumstance must also be responsible for some of the discrepancies given by the partition coefficient formula of Schulz⁵.

The $[\eta]_p$ values calculated using the constants in Table 6 and the $W(p)$ values at infinite dilution are plotted in Fig. 4 (curves). The agreement between

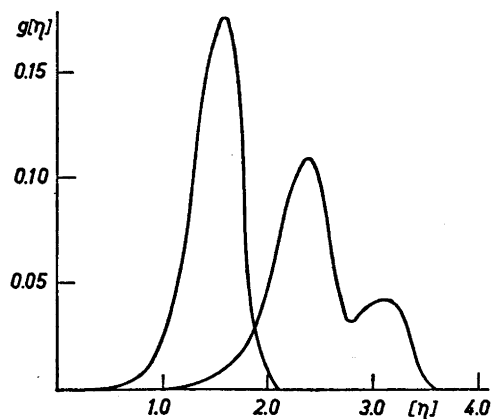


Fig. 6. Curves of weight frequency vs. limiting viscosity number in chloroform solutions for the polyglycol samples A 4 000 and A 6 000.

the experimental points and the calculated curves must be regarded as good, especially considering the appreciable molecular weight range of the substances investigated.

The derivative $\frac{d[\eta]}{dk}$ can now be calculated from the constants of eqn. 3.

The curves of frequency *vs.* the limiting viscosity number in chloroform can thus be calculated using the method given in Ref.¹ The results of these calculations are given in Fig. 6 for the samples A 4 000 and A 6 000.

The accuracy of the frequency curves obtained will not be discussed completely in this paper because, as earlier reported¹, the results can only be checked by comparing them with results obtained under different experimental conditions. However, a few remarks can be made. The double peak in the frequency curve for polyglycol A 6 000 must be considered to be rather well established. This double peak can also be seen in the curve of frequency *vs.* partition coefficient and it has not been possible for the author to make the $W(p)$ values obtained consistent with an unimodal frequency curve. According to Flory⁶, polymers prepared using a type of reaction which involves the successive addition of the monomer to a functional group and which can be characterized by a single rate constant have unimodal frequency curves. Polyglycol belongs to such a group of polymers. From this point of view, the double peak in the frequency curve for sample A 6 000 is suspect. However, the manufacturer of the samples used has informed the author that A 6 000 was produced by adding ethylene oxide to a mixture of two different polyglycol preparations of lower molecular weights and thus a double peak should appear. For the preparations A 4 000 and A 1 500, on the other hand, unimodal frequency curves should, according to the manufacturer, be expected.

In the case of sample A 4 000 the frequency curve is, as can be expected from the theory of Flory⁶, rather narrow. It should, however, be pointed out that if the relation between limiting viscosity number and partition coefficient is calculated from only the experimental data obtained for preparation A 4 000, then a $[\eta]$ *versus* k relation with a smaller slope and thus a somewhat more sharply peaked curve is obtained. Such a treatment of the problem cannot be considered justified even if, as will be shown in a later paper, a sharper peaked curve is probably more correct.

EXPERIMENTAL

For experimental details: see Experimental of Refs.^{2,7}.

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Received May 13, 1959.