

# Fractionation of Polymers by Liquid-Liquid Distribution

## III. The Interaction Problem

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Fractionated polyglycols have been countercurrent distributed both separately and in mixtures. From the experimental data the conclusion has been drawn that no interfering interaction occurs between molecules of different sizes.

In polymer countercurrent distribution experiments, association phenomena between molecules of different sizes can be expected to influence the results<sup>1</sup>. It was suggested that such phenomena should result in effects closely related to the coprecipitation occurring during the precipitation fractionation of polymers.

This paper consists of a report on a theoretical and experimental investigation performed by the authors on this association effect. Because polymer specimens are always inhomogeneous with respect to molecular weight, the effect must be studied on samples containing molecules of different sizes.

We consider two polymer samples of the same monomer with frequency functions,  $f_1(k)$  and  $f_2(k)$ , with respect to the partition coefficient and, in addition, a sample made up by mixing equal parts of these samples. These three preparations are then fractionated in a Craig apparatus. If ideal conditions prevail, the relative amount of polymer in each fraction of the three experimental series can be written<sup>2</sup>.

$$W(p)^{(1)} = \int_0^{\infty} F(k,p) \cdot f_1(k) \, dk \quad (1)$$

$$W(p)^{(2)} = \int_0^{\infty} F(k,p) \cdot f_2(k) \, dk \quad (2)$$

$$W(p)^{(3)} = \int_0^{\infty} F(k,p) \cdot \frac{f_1(k) + f_2(k)}{2} \, dk \quad (3)$$

where  $F(k,p) = \binom{n}{p} \frac{k^p}{(1+k)^n}$ .

It is easily deduced that  $W(p)^{(3)}$  is equal to the arithmetical mean of  $W(p)^{(1)}$  and  $W(p)^{(2)}$ . If interaction occurs, then the eqns. 1–3 become more complicated. The function  $F(k,p)$  cannot then be identical for the three cases. This means that  $W(p)^{(3)}$  must differ from the arithmetical mean of the two other  $W(p)$  values.

The same type of discussion can be applied to the mean molecular weight of the fractions, using eqn. 13 of Ref.<sup>2</sup>:

$$\overline{M(p)}^{\alpha} = \frac{1}{W(p)} \cdot \binom{n}{p} \cdot \int_0^{\infty} \frac{k^p}{(1+k)^n} \cdot f(k) \cdot M^{\alpha} \cdot dk \quad (4)$$

as a basis for the discussion. Such a discussion leads to essentially the same result, *viz.* that the product of the measured property, which is proportional

to  $\overline{M(p)}^{\alpha}$ , and  $W(p)$  in the third series should be equal to the arithmetical mean of the corresponding quantities in the other two series provided that no interaction occurs, but should differ from the mean if interaction occurs.

It is important that not only the relative weights of the different fractions in the three experimental series are compared but also the quantities closely related to the mean molecular weight of the fractions. From eqns. 1 and 4, it can be seen that the expression within the integral contains the molecular weight in the second case but not in the first. This indicates that, if the arithmetical mean law is valid by mere accident in one case, then it must be practically impossible for this law to be valid in the other case if interaction occurs.

In order to make any possible interaction effect easy to observe, polymer specimens with greatly different mean molecular weights and rather narrow molecular frequency functions should be used. The polymer used in this investigation was polyglycol. The solvent system was prepared by mixing trichloroethylene, alcohol (95 %) and water in the volume ratio 2 : 2 : 1. The viscosity numbers were used as a measure of the molecular weight.

Two preparations with relatively sharp-peaked frequency curves were obtained as fractions in a large-scale countercurrent fractionation of two polyglycol preparations with number-average molecular weights of about 1 500 and 6 000 (called A 1 500 and A 6 000). These two fractions were then countercurrent fractionated according to the fundamental Craig procedure ( $n = 19$ ) both separately and using a mixture of equal parts. The weights of the fractions obtained were then determined, *cf.* Figs. 1 and 2. The curve in Fig. 2 was obtained as the arithmetical mean of the two curves in Fig. 1. The viscosity numbers of those fractions in which sufficient polymer was present were also measured. The results are given in Figs. 3 and 4. In Fig. 4, there is also shown a curve which was calculated from the curves (not the points) in Fig. 3 assuming that the viscosity numbers are additive with respect to weight. The experimental  $W(p)$  values were used for the calculations.

The experimental points in Figs. 2 and 4 agree, within the experimental accuracy, with the corresponding calculated curves. The conclusion must be drawn that no interfering interaction occurs between molecules of different sizes apart from the concentration-dependent interaction discussed in Ref.<sup>1</sup> This means that intermolecular association, which results in irreversible

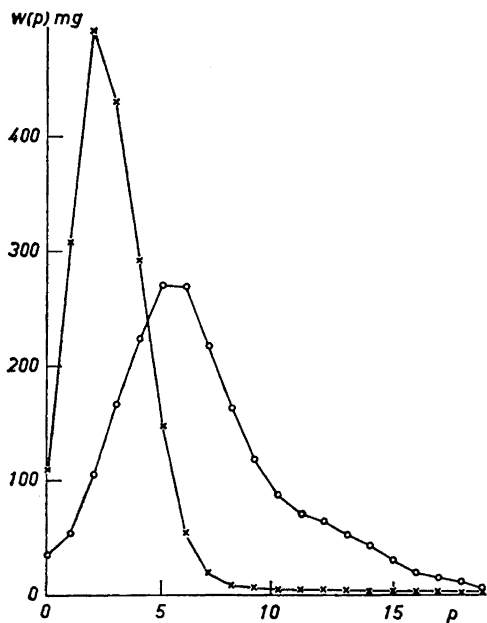


Fig. 1. Countercurrent distribution of Preps. I and II. Solvent system: trichloroethylene-alcohol-water = 2:2:1.

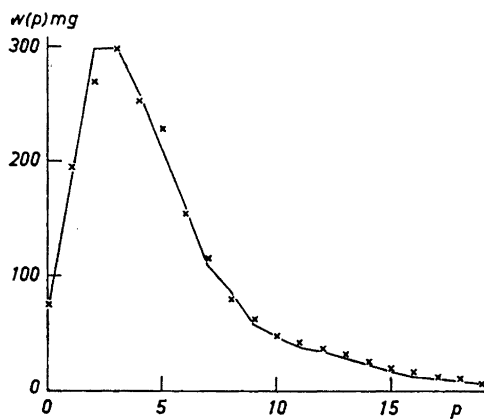


Fig. 2. Countercurrent distribution of Prep. III. Solvent system: trichloroethylene-alcohol-water = 2:2:1. Points: experimental values. Curve: calculated values.

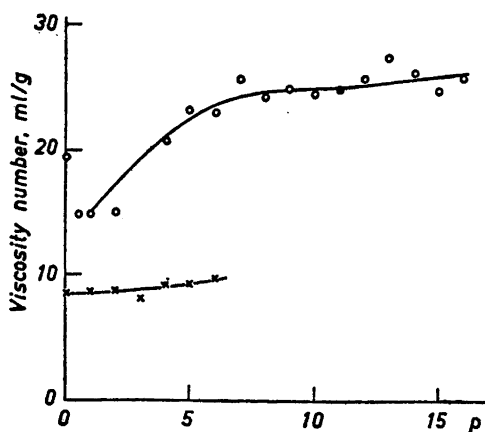


Fig. 3. Viscosity numbers for the fractions obtained from Preps. I and II.

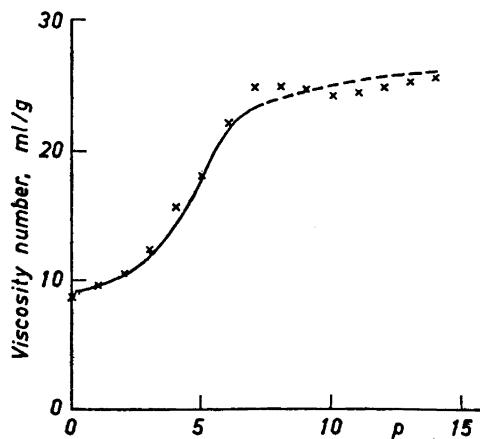


Fig. 4. Viscosity numbers for the fractions obtained from Prep. III. Points: experimental values. Curve: calculated values.

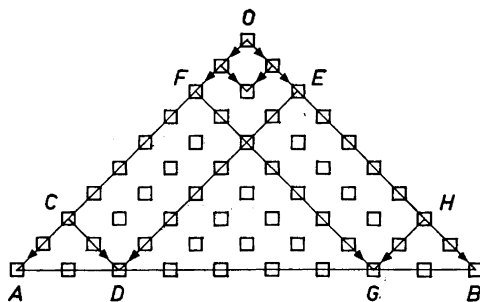


Fig. 5. Schematic diagram for large scale fractionation of polyglycol samples A 1 500 and A 6 000.

equilibrium conditions for the distribution of the polymer between the two solvents does not occur in this case. In the subsequent work, it will be assumed that this is valid at all compositions of the solvent system.

#### EXPERIMENTAL

Concerning temperature, solvents and purification of the polyglycols, see Experimental of Ref.<sup>1</sup> The solvent system used in this investigation was prepared by mixing trichloroethylene, alcohol (95 %) and water in the volume ratio 2:2:1. This volume ratio corresponds closely to  $v = 0.39$  (cf. Ref.<sup>1</sup>).

*Large scale fractionation.* The purpose of this experiment was to prepare two polyglycol specimens, with relatively narrow molecular frequency curves and with greatly different mean molecular weights, by means of a 10 tube ( $n = 9$ ) countercurrent fractionation according to the fundamental Craig procedure. The low molecular weight specimen was prepared from polyglycol A 1 500 and the high molecular weight specimen from polyglycol A 6 000. The procedure could be appreciably shortened since not more than one fraction was of interest in each fractionation series. The complete fractionation scheme for a 10 tube fractionation is shown by the triangle OAB in Fig. 5. The low molecular preparation from polyglycol A 1 500 was obtained by performing the operations within the rectangle OCDE and the high molecular weight preparation from polyglycol A 6 000 by performing the operations within the rectangle OFGH. The experiments were carried out using large separatory funnels.

The weight of sample was 200 g for A 1 500 and 600 g for A 6 000. The yields were 57.7 g and 11.8 g respectively. These two fractions (called Prep. I and Prep. II) were used for the three series of countercurrent experiments. (A mixture of equal parts of these two fractions was designated Prep. III.)

*The countercurrent experiments* were carried out as described in Ref.<sup>1</sup> The weight of sample was in all three cases 2.0000 g. The difference between the sample weight and the sum of the weights of the fractions was for Prep. I 5.6 mg, for Prep. II 19.0 mg and for Prep. III 31.6 mg.

Viscosity measurements were performed on solutions obtained by dissolving about 50 mg of the different fractions in 10.00 ml chloroform. Cannon-Fenske pipettes recommended for the range between 0.3 and 5.0 centipoises were used at  $25^\circ\text{C} \pm 0.02$ .

#### REFERENCES

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2. Almin, K. E. *Acta Chem. Scand.* **11** (1957) 1541.

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