

## Fractionation of Polymers by Liquid-Liquid Distribution

### V. Countercurrent Fractionation of Polyglycols in the Solvent System Trichloroethylene-Chloroform-Water

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Three polyglycol preparations have been countercurrent distributed in the solvent system trichloroethylene-chloroform-water. Weights and limiting viscosity numbers of the different fractions have been determined. Curves of weight frequency *vs.* limiting viscosity number have been calculated. The influence of formation of emulsions in the distribution experiments is discussed.

In the preceding paper of this series<sup>1</sup>, data from the liquid-liquid countercurrent distribution analysis of three polyglycol preparations in the solvent system trichloroethylene-alcohol-water (TAW) were reported. The present paper will deal with analogous experiments in another solvent system, trichloroethylene-chloroform-water (TCW).

Preliminary liquid-liquid distribution experiments with the solvent system TCW have shown that the partition coefficients of polyglycols are more dependent on the temperature than is the case with the solvent system trichloroethylene-alcohol-water (TAW)<sup>2</sup>. For this reason, the countercurrent experiments with the solvent system TCW were carried out in a thermostat set at 25°C. This temperature is about five degrees higher than that used in the preliminary experiments reported in Ref.<sup>2</sup>

Difficulties have, however, arisen because of the ease of formation of emulsions in the solvent system TCW. The emulsions were especially prone to appear when the concentration was high, when the molecular weight of the polyglycol was large and when the partition coefficient of the polyglycols differed from unity. In these countercurrent experiments, the emulsions were allowed to remain with the stationary upper phases since the lower surfaces of the emulsions were smoother than the upper ones. The amount of emulsion was, however, found to decrease during the course of the distribution experiment. This was probably due to the decrease in the concentration of polyglycol. The volumes of especially the first ( $p = 0$ ) and the last ( $p = 19$ ) fractions

were thus appreciably less than the others at the end of the distribution experiments, these volume losses being more pronounced when the amount of emulsion formed was larger.

The influence of the emulsion formation can also be seen in the  $W(p)$  vs.  $p$  curves and in the  $[\eta]_p$  values. For symbol notation see Ref.<sup>3</sup> The  $W(p)$  vs.  $p$  curves became shifted towards lower  $p$  values and the relation between  $[\eta]_p$  and  $p$  became steeper when the sample weight and thus the amount of emulsion were increased. These changes can be explained in the following way. The emulsion layers contain varying amounts of the high molecular weight parts of the preparation which should belong to the lower phases. When the phases are separated, these high molecular weight parts remain with the upper phases. The possibility of accumulation of polymer and/or either of the solvents in the emulsion layer on account of surface phenomena will not be discussed.

The experimental data from experiments in which the mean partition coefficient differed appreciably from unity had to be discarded because of the very large emulsion formation. It has therefore not been possible to extend the range of validity of the relation between partition coefficient and limiting viscosity number in the same way as was possible in the case of the solvent system TAW<sup>1</sup>.

In the cases where the formation of emulsion was less pronounced, the data from each experimental series were treated individually, exactly as if no emulsion formation had occurred. The curves of frequency vs. partition coefficient,  $f(k)$ , thus obtained are consequently more compressed than in the cases where no emulsions were obtained. At the same time, the curves of  $[\eta]$  vs. partition coefficient,  $k$ , are steeper. The final frequency functions in terms of the limiting viscosity number can, however, be expected to be correct or nearly correct since the two above-mentioned effects counteract each other.

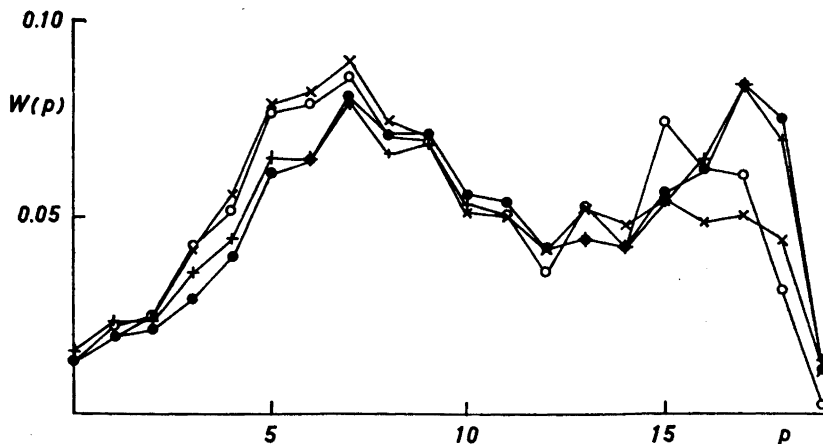


Fig. 1. Experimental  $W(p)$  values obtained in the countercurrent experiments in TCW ( $v = 0.165$ ) with polyglycol A 6000.  $\times$  5 g,  $\circ$  2 g,  $\bullet$  1 g and  $+$  0.5 g sample weight.

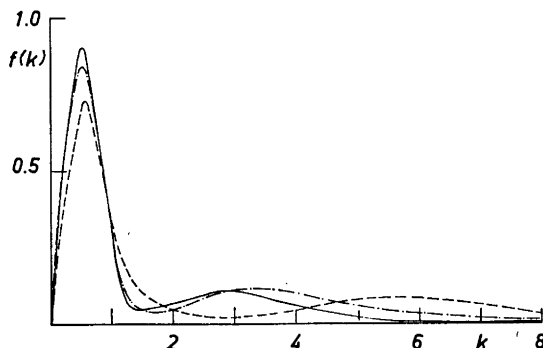


Fig. 2. Curves of weight frequency vs. partition coefficient, calculated from the experimental  $W(p)$  values obtained in the experiments with polyglycol A 6 000. — 5 g, -.-.-.- 2 g and - . - . - 1.0 and 0.5 g sample weight.

The calculation of the relation between  $[\eta]$  and  $k$  was found to be much simpler with the present solvent system than with the solvent system TAW<sup>1</sup> inasmuch as  $[\eta]_p$  proved to be, in all cases, a linear function of the derivative  $\frac{d \ln S(p)}{d p}$  (cf. Ref.<sup>3</sup>). The relation between limiting viscosity number and partition coefficient can thus be written,

$$[\eta] = C_0 + B \ln k \quad (1)$$

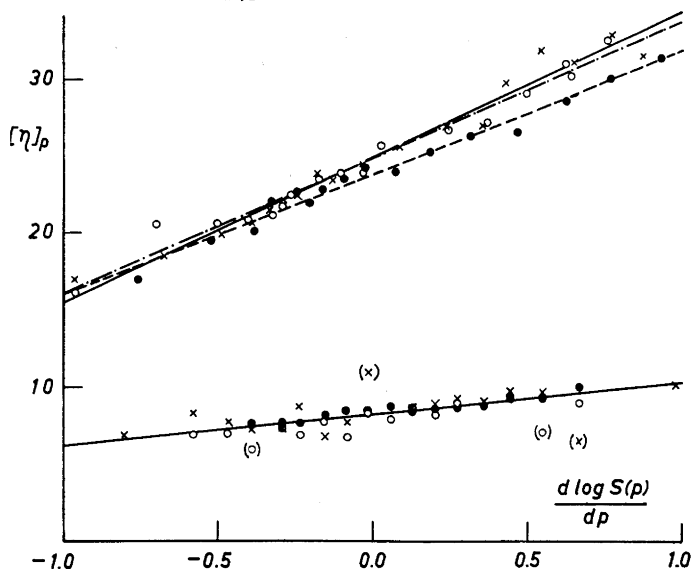


Fig. 3. Relation between limiting viscosity number and the derivative  $d \log S(p)/d p$  for polyglycol A 6 000 and A 1 500 (Sample weights: cf. Fig. 1).

Table 1. The constants  $B$  and  $C_0$  of eqn. 2 calculated from viscosity data.

Sample	Weight of sample, g	$C_0$	$B$
A 6 000	5	24.90	4.03
	2	24.87	3.86
	1 and 0.5	23.78	3.47
A 4 000	5	15.41	2.03
	2	14.88	2.23
	1 and 0.5	15.10	1.96
A 1 500	5, 2 and 1	8.19	0.93

The  $W(p)$  values obtained from the experiments with polyglycol A 6 000 are given in Fig. 1. The composition of the solvents corresponds to  $v = 0.165$  (cf. Ref.<sup>2</sup>). The influence of emulsion formation is obvious — especially in the 5 g and 2 g experiments. From the curves, it can be seen that the  $W(p)$  values of every second fraction seem too low and those of every other one too high. The cause of these irregularities is unknown to the author. It may be pointed out that they seem to be more pronounced when the emulsion formation is large. The  $f(k)$  curves calculated from the experimental data are given in Fig. 2. The experimental  $[\eta]_p$  values are plotted in Fig. 3 as a function of the derivative  $\frac{d \ln S(p)}{d p}$ . The numerical values of the constants  $C_0$  and  $B$ , calculated from the lines in Fig. 3, are given in Table 1. In Fig. 4, the frequency vs. limiting viscosity number curves are reproduced. The agreement is good in spite of the differences in the  $f(k)$  curves. The differences in the frequency curves in the range  $[\eta] > 32$  must be ascribed to slight errors in the experimental and numerical methods.

The results of the experiments with polyglycol A 4 000 in the solvent system TCW ( $v = 0.192$ ) are quite analogous to those reported for polyglycol

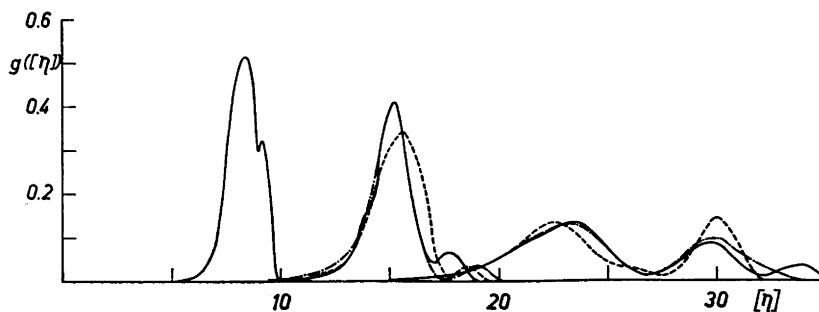


Fig. 4. Curves of weight frequency vs. limiting viscosity number for polyglycols A 6 000, A 4 000 and A 1 500 calculated from the corresponding curves in terms of partition coefficient. (Sample weights: cf. Fig. 2.)

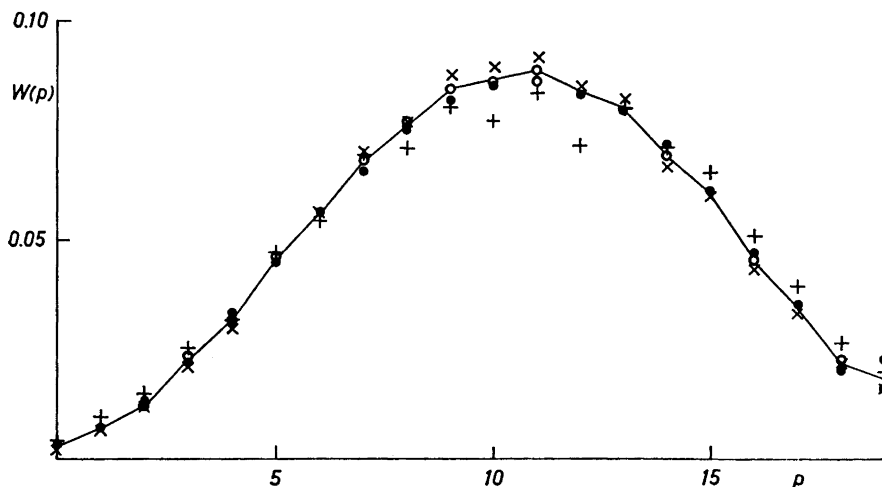


Fig. 5.  $W(p)$  values obtained in the countercurrent experiments in TCW ( $v = 0.83$ ) with polyglycol A 1500. (Sample weights: cf. Fig. 1.) The curve represents the arithmetical mean of the  $W(p)$  values from the 5 g, 2 g and 1 g experiments.

A 6 000. The irregularities in the experimental  $W(p)$  vs.  $p$  curves were, however, less pronounced. The final results of the calculations can be seen in Table 1 and Fig. 4. The small peaks in the frequency curves at about  $[\eta] = 18$  must, once again, be ascribed to slight errors in the experimental and numerical methods.

No emulsions appeared in the experiments in the solvent system TCW ( $v = 0.283$ ) with polyglycol A 1500. The experimental  $W(p)$  values are given in Fig. 5. It can be seen that the points form curves with somewhat higher maxima at high concentrations. Craig<sup>4</sup> ascribes such a phenomenon to a nonmonotonic partition isotherm. The phenomenon is thus not equivalent to the concentration effect found in the experiments with the solvent system TAW<sup>2</sup>. The differences between the  $W(p)$  values obtained at different sample weights are, however, small and the limiting viscosity numbers of the fractions proved to be independent of the sample weights. The calculations have therefore been made using the arithmetical mean of the experimental  $W(p)$  values. The final results can be seen in Table 1 and Figs. 3 and 4. The small peak at  $[\eta] = 9$  in Fig. 3 must be regarded as insignificant.

The final discussion concerning the accuracy of the frequency curves obtained will be given in the next paper of this series. It shall only be pointed out here that the double peak of the frequency curve of polyglycol A 6 000, as found in earlier experiments<sup>1</sup>, has been verified once more.

From the experimental point of view, the work with the solvent system TCW did not differ from that with TAW, apart from the ease of emulsion formation and the dependence on temperature. As a compensation, however, the solvent system TCW has a higher resolving power. Furthermore, it has

been shown that small deviations from ideality do not appear in the final results provided that the experimental data are treated in the proper way.

#### EXPERIMENTAL

For experimental details, see earlier papers of this series <sup>1,2</sup>. The constant temperature (25°C) in the countercurrent experiments was obtained by placing the shaking device in an air thermostat.

The frequency *vs.* limiting viscosity number curves were calculated from the corresponding curves with respect to partition coefficient by means of a Litton digital differential analyzer equipped with graph follower and graph plotter.

#### REFERENCES

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