

The Interpretation of Data from Countercurrent Distributions at Non-ideal Conditions

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By assuming a linear relation between the partition coefficient and the concentration an equation is derived indicating how to plot data obtained from countercurrent distributions. The plot gives information about the concentration dependence of the partition coefficient and the purity.

The interpretation of data obtained from countercurrent distribution experiments is often difficult because of deviations of the shape of the experimentally obtained relation between the amount of sample in a tube *vs.* tube number from the theoretical one. Such deviations can be explained in different ways. One possibility is that a peak in the distribution pattern arises from more than one component of the original sample. Another possibility is thermodynamic non-ideality of the constituent in one or both of the solvents. A third possibility is that the solute system is undergoing chemical reactions, *e.g.* the formation of dimers or trimers under reversible conditions in the two phases.

The last case was analyzed by Bethune and Kegeles¹ using an electronic computer. They concluded that many bizarre countercurrent distribution patterns could be explained on the basis of molecular associations taking place during the distribution rather than on the basis of thermodynamic non-ideality. This means that it is sometimes difficult to distinguish between the last two possibilities given above. From an analytical point of view, this matter is of no great importance, but the necessity of using an electronic computer for the interpretation of experimental data seriously limits the method. In chemical analysis one is often met with small but significant deviations from the ideal laws and in many cases a simple graphical method to handle such data is preferred. In the case of countercurrent analysis, methods of this type do not seem to exist. Almin² has derived a formula giving the difference between the experimental and ideal amounts in each fraction when it is assumed that the apparent partition coefficient can be expressed by

$$k = k_0(1 + \epsilon m) \quad (1)$$

where k_0 is the partition coefficient at infinite dilution, m the amount of substance distributed between the two phases and ε a constant. The formula derived under the assumption that $\varepsilon m \ll 1$ is too unwieldy for practical use.

The author has, however, been successful in condensing the above mentioned formula to a rather handy form, and from this new formula, conclusions can be drawn as to how to treat the experimental data.

From Ref.² it is evident that if eqn. 1 is valid, the difference between the real and ideal (*i.e.* $\varepsilon = 0$) amount of sample is a linear function of (εw_0^2) , where w_0 is the total amount of a pure substance added to a Craig distribution apparatus working according to the fundamental procedure.³ We then have the amount of substance in the p th tube, n being the number of transfers:

$$w_n(p) = w_n^*(p) \left[1 + \varepsilon \cdot \frac{w_0}{\binom{n}{p}} \cdot f_n(p) \right] \quad (2)$$

where $f_n(p)$ is a function which has to be calculated, and

$$w_n^*(p) = \binom{n}{p} \cdot \frac{k_0^p}{(1+k_0)^n} \cdot w_0 \quad (3)$$

We further have eqn. 2 of Ref.² which after a slight approximation can be written

$$w_n(p) = \frac{k_0}{1+k_0} \cdot w_{n-1}(p-1) \left[1 + \frac{\varepsilon}{1+k_0} w_{n-1}(p-1) \right] + \frac{1}{1+k_0} \cdot w_{n-1}(p) \cdot \left[1 - \frac{\varepsilon k_0}{1+k_0} w_{n-1}(p) \right] \quad (4)$$

Inserting eqn. 2 into eqn. 4 and rearranging, we obtain after neglecting terms containing ε^2

$$f_n(p) = f_{n-1}(p-1) + f_{n-1}(p) + \binom{n-1}{p-1}^2 \cdot \frac{k_0^{p-1}}{(1+k_0)^n} - \binom{n-1}{p}^2 \cdot \frac{k_0^{p+1}}{(1+k_0)^n} \quad (5)$$

The author has found that

$$f_n(p) = \binom{n}{p} \left[\sum_{i=0}^{p-1} w_n^*(i) - \sum_{i=p+1}^n w_n^*(i) \right] \quad (6)$$

The proof for this formula can be performed as an induction proof. It is a little tedious but quite straightforward.

From eqns. 2 and 6 we obtain the final expression:

$$w_n(p) = w_n^*(p) \left[1 + \varepsilon \cdot \left(\sum_{i=0}^{p-1} w_n^*(i) - \sum_{i=p+1}^n w_n^*(i) \right) \right] \quad (7)$$

When the numerical values of ε and k_0 are known it is thus possible to calculate the amount of substance in each tube using eqn. 7. This equation is analogous to eqn. 2 of Ref.² It is, however, superior to that one owing to its much simpler form.

From eqn. 7 it is possible to derive an equation well adapted for graphical treatment of the experimental data. By dividing the amounts of substance in two adjacent tubes and multiplying this ratio with $(p + 1)/(n - p)$ we obtain from eqn. 7 after neglecting corrections of higher order

$$\frac{(p + 1) \cdot w_n(p + 1)}{(n - p)w_n(p)} = k_0[1 + \varepsilon \cdot (w_n^*(p) + w_n^*(p + 1))] \approx k_0 + \varepsilon \cdot k_0(w_n(p) + w_n(p + 1)) \quad (8)$$

By plotting the left member of eqn. 8 as a function of the sum of the amounts of substance in the p th and $(p + 1)$ th tubes, a straight line should be obtained with the intercept k_0 and the slope εk_0 .

To illustrate the method it will be applied to experimental data from countercurrent distributions of polyglycols having average molecular weights of about 1500 and 4000 in a solvent system obtained by mixing trichloroethylene, alcohol, and water in proper amounts. The experimental details are given in Ref.² and the experimentally obtained amounts of substance in each fraction is given in Ref.⁴ The data are plotted in Fig. 1 according to the

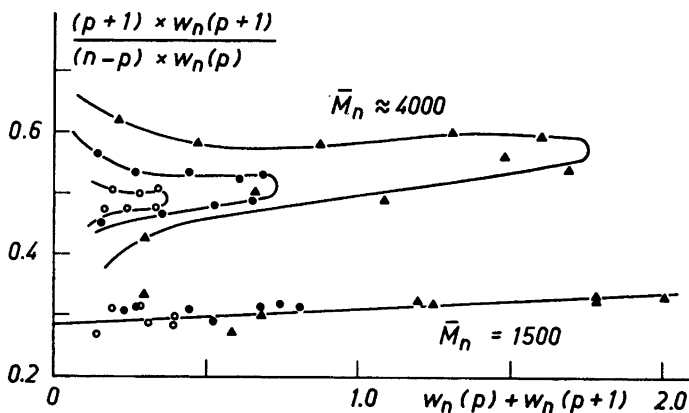


Fig. 1. Data from countercurrent distributions with polyglycols plotted according to eqn. 8. \blacktriangle , $w_0 = 5$ g; \bullet , $w_0 = 2$ g; \circ , $w_0 = 1$ g.

analysis given above. The data from the experiments with the polyglycol of the average molecular weight 1500 describe a straight line within experimental accuracy, indicating that the sample acts as one containing molecules of only one size in the solvent system used. The intercept of the line corresponds to $k_0 = 0.285$, which is in good agreement with the value 0.284 obtained by direct measurement (Ref.).² In the plot only points corresponding to $(w_n(p) + w_n(p + 1))$ values higher than 0.150 g have been taken into consideration. Points corresponding to lower values show a considerable scatter, partly

owing to the polymolecularity of the sample and partly owing to experimental inaccuracy.

The experimental data from the experiments with the polyglycol sample with the average molecular weight about 4000 do not form a straight line when plotted in the same way. They form bell shaped curves indicating that components of different partition coefficients were present in the original sample. As can be seen in Fig. 1, the peaks of the curves do not form a horizontal line. This must be ascribed to the concentration dependence of the partition coefficients. The same conclusion must also be drawn from the asymmetrical form of the curves.

Thus this method for interpreting experimental data obtained from countercurrent distribution does not only give information about the concentration dependence of the partition coefficient of pure components of the original sample, but also indicates the apparent purity of the component. It further gives information about the existence of a concentration dependence of the partition coefficient of components which — owing to low resolving power — have not been separated from each other.

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Received July 7, 1964.