

Fractionation of Polymers by Liquid-Liquid Distribution

II. Selection of Experimental Conditions

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Polyglycols have been distributed between selected solvents in order to establish proper experimental conditions for countercurrent experiments. The concentration dependence of the partition coefficient has been discussed and the resolving power of a Craig apparatus has been discussed from theoretical point of view.

In previous communications^{1,2} the fractionation of polymers by means of countercurrent methods was discussed from a theoretical point of view. In this paper, experiments will be reported which give information about the most suitable experimental conditions. The polymer used in these experiments was polyglycol



SOLVENT SYSTEMS

The choice of solvents for these experiments must be made with due consideration to several factors. The mean partition coefficient of the polymer must not deviate too much from unity. This ensures that we do not have to use a volume ratio for the two phases which differs too much from one in order to get suitable amounts of the polymer in the different phases. A system composed of two immiscible or partly immiscible pure liquids cannot be expected to fulfil, at a fixed temperature, the requirements with respect to the partition coefficient since the polymer will most probably pass completely into one of the phases. A two phase liquid system composed of at least three pure liquids would therefore appear necessary. In a three component system, changes in the composition of the phases can be made in order to make it possible to obtain a suitable mean partition coefficient for the polymer. It is important from a practical point of view that the phases should separate easily, thus avoiding loss of time or the use of a centrifuge.

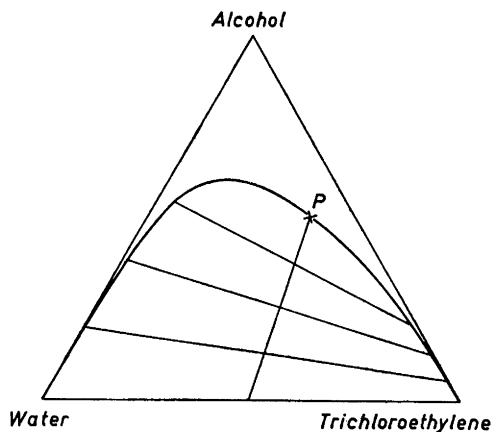


Fig. 1. Approximate phase diagram of the liquid system, trichloroethylene, alcohol (95 %) and water. P = plait-point.

Schulz and Nordt³ have reported that the liquid system, water-chloroform-benzene, is not satisfactory for the fractionation of polyglycols because of the ease of formation of emulsions. For this reason, some other three component liquid systems have been chosen. The three component system, trichloroethylene-alcohol-water (TAW), proved to be very satisfactory in this respect. The three component system, trichloroethylene-chloroform-water (TCW), was nearly as good in this respect and had — as will be shown in the experiments — very good properties with respect to the resolving power.

In order to examine the possibility of using the liquid system TAW, the ternary phase diagram was first determined. The binodal curve was obtained by mixing suitable amounts of trichloroethylene and alcohol or water and alcohol and titrating with water or trichloroethylene, respectively, to the point of first appearance of turbidity. Approximate tie-lines were determined in the following way. The three components were mixed in suitable amounts in a graduated vessel and the volume ratio of the two phases was determined. The tie-lines were then considered to be divided into this ratio by the point which gives the composition of the system. The plait-point was obtained as the point where the binodal curve and the curve joining the middle points of the approximate tie-lines intersect. The phase diagram obtained, see Fig. 1, is thus not theoretically correct. On the other hand, it gave all the information necessary for the subsequent experiments. One can see how the three components should be mixed in order to obtain a two phase system with a predicted composition and volume ratio for the two phases. The author only dealt with equal volumes for the two phases and since the plait-point corresponds to the volume ratio 0.40: 0.51: 0.09 for trichloroethylene, alcohol (95 %) and water, it can be calculated that the three liquids should be mixed in the volume ratio

$$(0.5 - 0.20 v) : v : (0.5 - 0.80 v) \text{ with } v < 0.51.$$

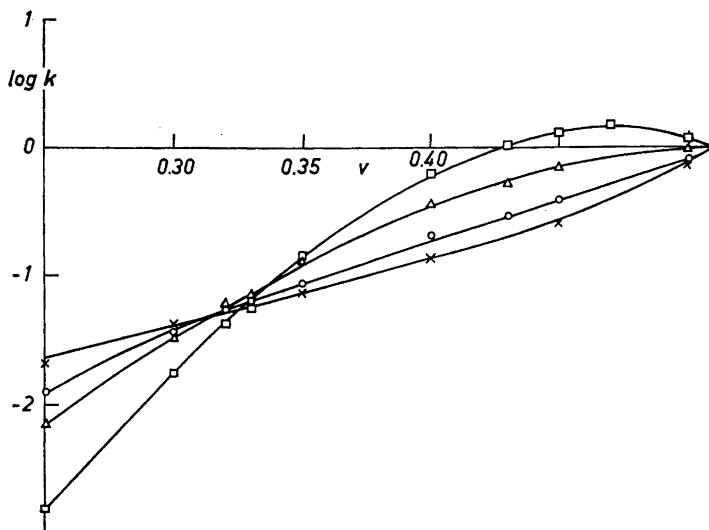


Fig. 2. Apparent partition coefficient for polyglycol in the liquid system TAW as a function of the composition. \times A 300, \circ A 1 500, Δ A 4 000, \square A 6 000.

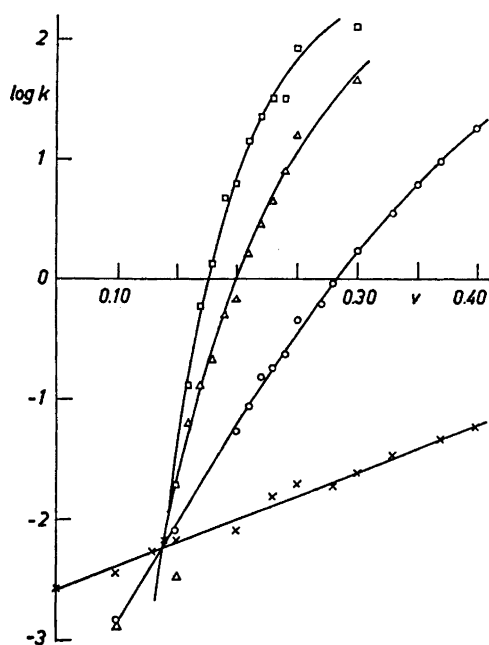


Fig. 3. Apparent partition coefficient for polyglycol in the liquid system TCW as a function of the composition (for notation see Fig. 2).

Both trichloroethylene and chloroform are practically immiscible with water. Equal volumes of the two phases of the liquid system TCW are thus obtained when the three liquids are mixed in the volume ratio $(0.5 - v) : v : 0.5$.

An analysis of this type is necessary in order to facilitate the planning of a systematic investigation of these liquid systems. Furthermore, any undesirable waste of solvents can be avoided.

APPARENT PARTITION COEFFICIENTS

In Fig. 2, the apparent partition coefficients for four commercial polyglycols in the liquid system TAW are plotted as a function of the composition parameter v . Since the upper phases will be used as the stationary phases in the forthcoming countercurrent experiments, the partition coefficient is, in accordance with the definition given in Ref.¹, the ratio between the weights of polyglycol in the lower and the upper phases. In Fig. 3, the apparent partition coefficients for the polyglycol preparations in the liquid system TCW are plotted as a function of the composition parameter v .

From Figs. 2 and 3, it can be seen that both solvent systems are suitable for fractionation purposes. The system TCW, in particular, shows large changes in partition coefficient for a change in molecular weight. At the same time it is very sensitive to small changes in the composition. For this reason, it was considered convenient to study the system TAW first.

However, a few comments of general interest must be made. The curves in Figs. 2 and 3 intersect each other. Owing to the experimental inaccuracy, it is impossible to decide whether the curves have a common point of intersection. The same observation has been reported by Schulz⁴. However, he has not investigated more than two polyglycol preparations in the solvent system chloroform-benzene-water. According to his theories, the point of intersection should occur for $k = 1$. Neither in his own experiments nor in those reported in this paper does this occur. Schulz explained this as being due to the difference in temperature which existed between the two series of experiments performed by him. In the present work, however, all experiments at a specified composition of the solvent system were carried out simultaneously. Thus, there is no doubt that the curves cut in a point or points at which the partition coefficient differs appreciably from unity. The reason for this deviation is that the Brønsted equation⁵ for the relation between partition coefficient and molecular weight, on which Schulz' theories are based, is too approximate. In addition, the linear relation between the logarithm of the partition coefficient and the composition of the solvent system, proposed by Schulz⁴, cannot be regarded as satisfactory.

EQUILIBRIUM CONDITIONS

Preliminary experiments with a conventional 20 tube allglass countercurrent apparatus, constructed according to Craig, showed that the amount of polyglycol in the different fractions was not independent of the shaking time unless at least a 30 min shaking time was used at each step.

Table 1. Countercurrent distribution of polyglycol A 6 000. Solvent system: TAW ($v = 0.43$).

Time of shaking at each step	30 min	240 min
Weight of sample (w_0)	2.0002 g	2.0002 g
p	$w(p)$ mg	$w(p)$ mg
0	2.1	2.9
1	3.3	3.1
2	5.4	6.2
3	13.8	13.2
4	32.8	30.2
5	64.3	63.4
6	108.5	112.1
7	171.4	162.5
8	216.8	226.9
9	259.0	250.5
10	256.6	249.2
11	238.0	234.5
12	203.0	204.3
13	156.3	152.5
14	113.4	111.0
15	73.9	71.3
16	43.3	41.5
17	23.4	19.7
18	9.5	9.7
19	4.3	3.9
$\sum w(p)$	1.9991 g	1.9686 g

Table 1 contains the results from two series of experiments in which polyglycol was distributed according to the fundamental countercurrent process, separatory funnels being used as contacting vessels. The two series only differ in the time of shaking at each step. In one case, the shaking time was 30 min, in the other 120 min. The differences in the results of the two series must be ascribed to random errors. For this reason, a shaking time of 30 min was used at each step in the subsequent countercurrent experiments.

In order to investigate the reversibility of the distribution process, two series of experiments were carried out, one in which the sample was dissolved in the upper phase before the lower phase was added, and one in which the sample was first dissolved in the lower phase. The results are shown in Fig. 4. It can be seen that the value of k is independent of the direction in which the distribution process proceeds. This means that the process is reversible and that no obstacles exist for its treatment as a real equilibrium process.

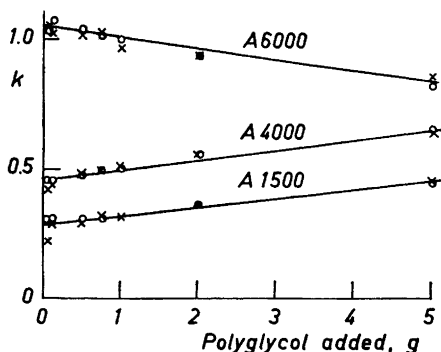


Fig. 4. Apparent partition coefficient for polyglycol at different sample weights. Solvent system: TAW ($v = 0.43$). Volume of each phase = 50 ml. \times sample first dissolved in the upper phase. \circ sample first dissolved in the lower phase.

CONCENTRATION DEPENDENCE

The problem is, as can be seen from Fig. 4, complicated by the appreciable concentration dependence of the partition coefficient. This effect can be quite considerable at high concentrations. The slopes of the lines drawn in Fig. 4 have different signs, implying that reverse distribution conditions at high and low concentrations are conceivable. However, the matter is further complicated in the distribution experiments reported in this paper. The solvent system used was a three component system. Upon adding an appreciable quantity of a fourth component, polyglycol, the composition of the two solvents might have been changed. This change may have been different for different molecular weights of the polyglycol. No attempts have been made to determine whether such a change takes place. Corrections were introduced which were thought to make this effect negligible in the author's results.

In a multiple-contact-countercurrent experiment, the concentration of the substance to be distributed decreases appreciably as the experiment proceeds. This is especially striking when the partition coefficient is close to unity. The errors introduced due to the concentration dependence of the partition coefficient must therefore be most serious during the first stages of the countercurrent process. However, the results obtained are, at least qualitatively, comparable with the results obtained in a countercurrent experiment where the partition coefficient is independent of the concentration but where the sample has been added to more than one tube at the start of the process. As shown by Craig ⁶, no appreciable errors are introduced in this way. However, a mathematical analysis of the problem will be made.

As can be seen from Fig. 4, 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. (Indications of a slight curvature, at least for preparation A 4 000, are left out of consideration).

We assume that a pure compound containing molecules of only one size is distributed between two solvents according to the fundamental Craig distribution procedure. The partition coefficient is assumed to obey eqn. 1. The concentration is chosen so that $\varepsilon m \ll 1$. Using the notations given in Ref.², we obtain

$$\begin{aligned} w_n(p) &= \frac{k_o[1 + \varepsilon w_{n-1}(p-1)]}{1 + k_o[1 + \varepsilon w_{n-1}(p-1)]} w_{n-1}(p-1) + \frac{1}{1 + k_o[1 + \varepsilon w_{n-1}(p)]} w_{n-1}(p) = \\ &= \frac{k_o}{1 + k_o} w_{n-1}(p-1) + \frac{1}{1 + k_o} w_{n-1}(p) + \Delta_n(p) \end{aligned} \quad (2)$$

where $\Delta_n(p)$ is a correction term which has to be calculated. Rearrangement gives

$$\Delta_n(p) = \frac{\varepsilon k_o}{1 + k_o} \left[\frac{[w_{n-1}(p-1)]^2}{1 + k_o[1 + \varepsilon w_{n-1}(p-1)]} - \frac{[w_{n-1}(p)]^2}{1 + k_o[1 + \varepsilon w_{n-1}(p)]} \right]$$

Approximating this expression by neglecting the terms in the denominators containing ε and exchanging the w 's for their idealized values (*i.e.* ε is considered to be 0) gives

$$\Delta_n(p) = \frac{\varepsilon}{k_o} \cdot \frac{p^2 - k_o^2 \cdot (n-p)^2}{n^2} \cdot [w_n^*(p)]^2 \quad (3)$$

where the asterisk indicates idealized values. From eqn. 2, we obtain by successive additions

$$w_n(p) = \binom{n}{p} \cdot \frac{k_o^p}{(1 + k_o)^n} w_o(0) + \sum_{i=0}^{n-1} \sum_{r=0}^i \binom{i}{i-r} \cdot \frac{k_o^{i-r}}{(1 + k_o)^i} \cdot \Delta_{n-i}(p-i+r)$$

Insertion of the Δ values from eqn. 3 and division with $w_o = w_o(0)$ give

$$\begin{aligned} W_n(p) - W_n^*(p) &= \\ \frac{\varepsilon w_o}{k_o} \cdot \sum_{i=0}^{n-1} \sum_{r=0}^i \frac{(p-i+r)^2 - k_o^2(n-p-r)^2}{(n-i)^2} \cdot W_{i-r}^* \cdot [W_{n-i}^*(p-i+r)]^2 \end{aligned} \quad (4)$$

This expression thus gives the difference between the experimental and the idealized relative amounts of the sample in each fraction as a function of the total amount of sample distributed, the partition coefficient of the sample at infinite dilution and ε . In Fig. 5, the expression

$\frac{W_n(p) - W_n^*(p)}{\varepsilon w_o}$ is plotted as a function of the fraction number p for $k_o = 1$ and $n = 19$ (full-drawn curve). This curve is compared with the curve obtained when it is assumed that the partition coefficient of an ideal substance is changed by a small amount Δk_o . The expression for $W_n(p)$ (eqn. 2 in Ref.²) is differentiated with respect to k . Then

$$\Delta W_n(p) = W_n(p) \cdot \left(\frac{p}{k_o} - \frac{n}{1 + k_o} \right) \cdot \Delta k_o \quad (5)$$

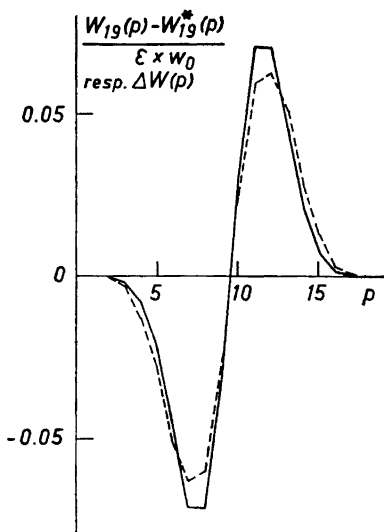


Fig. 5. Full-drawn curve: Graphical representation of eqn. 4 for $k = 1$ and $n = 19$. Dotted curve: Graphical representation of eqn. 5 for $k = 1$, $n = 19$ and $\Delta k = 0.28$.

The dotted curve in Fig. 5 gives this expression calculated for $k_0 = 1$, $n = 19$ and $\Delta k_0 = 0.28$.

The agreement between the two curves is good. The concentration dependence of the partition coefficient thus results in an effect comparable to an overall change in the partition coefficient rather than a broadening of the $W(p)$ vs. p curve. From eqn. 4, it can be seen that the $W(p)$ values at infinite dilution can be obtained by determining the $W(p)$ values at different values of w_0 and extrapolating them as a function of w_0 to the value $w_0 = 0$. Because of the initial assumptions, this extrapolating method is only applicable to substances containing molecules of the same size. The method will, however, be applied to common polymers as a first approximation. It is assumed that such a method, in addition, automatically corrects for small changes in the composition of the two liquid phases which might occur due to the addition of the polymer.

The reason for the concentration dependence is that there probably exists an interaction between molecules of the same size. The question now arises as to what extent molecules of different sizes interact in the distribution experiments. It is necessary to know whether micelles or complexes of some other type between molecules of different sizes occur, resulting in an effect closely related to the coprecipitation found in polymer precipitation fractionation. This problem will be treated in a separate paper. In the subsequent parts of this paper, this effect will be considered to be negligible.

RESOLVING POWER

As was pointed out by Craig ⁷, the peak of the curve representing the relation between the amount in each fraction and the fraction number in the funda-

mental Craig countercurrent distribution procedure can be approximately expressed by

$$p_{\max} = \frac{nk}{1+k} \quad (6)$$

if molecules of only one size are present and if the volumes of the two phases are equal. If the ratio between the volumes of the lower and upper phases is φ , then the relation can be written

$$p_{\max} = \frac{n\varphi k}{1+\varphi k} \quad (7)$$

When a polymer is distributed in a Craig apparatus, the derivative $|\partial p_{\max}/\partial M|$ can be regarded as a measure of the resolving power of the apparatus. This derivative should of course be as large as possible, *i.e.* the positions of the peaks caused by two samples differing in molecular weight by an infinitesimal amount should differ as much as possible. By differentiation of eqn. 7 we obtain

$$\left| \frac{\partial p_{\max}}{\partial M} \right| = \frac{\partial p_{\max}}{\partial k} \cdot k \cdot \left| \frac{d \ln k}{dM} \right| = n \cdot \frac{\varphi k}{(1+\varphi k)^2} \cdot \left| \frac{d \ln k}{dM} \right| \quad (8)$$

The expression $\frac{\varphi k}{(1+\varphi k)^2}$ attains its highest value, *viz.* 1/4 for $\varphi k = 1$ and the derivate $d \ln k/dM$ is independent of φ . The highest resolving power is thus obtained if the distribution experiment is carried out employing a φ value equal to the inverse of the apparent partition coefficient of the substance. However, φk can differ appreciably from unity without the above expression and thus the resolving power being too far below the maximum value.

It now remains to find the maximum value of $|d \ln k/dM|$. No current theory about the activity of polymer solutions is able to provide an acceptable expression for this derivative. The expressions provided are either too approximate or too unwieldy for the present purpose. An empirical method must therefore be used. The author has chosen to regard the curves in Figs. 2 and 3 as representative for polyglycols containing molecules of only one size, the molecular weight being identical with the one given by the manufacturer. By means of graphical methods, it was found that, for the solvent system TAW, the derivative $|d \ln k/dM|$ attains its maximum value for $v = 0.43$ independent of the molecular weight. For the solvent system TCW, the derivative attains its maximum value for each preparation when k is about unity, the latter condition being far from critical.

As can be predicted by the theory of Schulz, it is possible that, with the solvent system TAW, an extremely good resolving power can be obtained at compositions corresponding to $v < 0.32$ and, with the system TCW, at $v < 0.13$ or at v values rather close to 0.50. It is however probable that the gain is not sufficient to compensate for the enormous increase in experimental difficulty. Furthermore, when the experiments are carried out at a volume ratio for the two phases which differs appreciably from unity, the concentration of

polymer in the phase of less volume must be kept very high if sufficient quantities of polymer are to be obtained in the final fractions. In view of the above discussion of the concentration dependence of the partition coefficient, such experimental conditions should be avoided.

An exact analysis of the resolving power problem cannot be carried out until a more accurate relation between molecular weight and the partition coefficient is known. The above analysis was, however, regarded as sufficient for planning the subsequent countercurrent distribution experiments.

EXPERIMENTAL

All experiments reported in this paper were carried out at room temperature (20–21°C). Variations in temperature have been avoided.

Chemicals used. Trichloroethylene: Technical grade quality, distilled before use. Chloroform: pro analysi quality, stabilized with 1 % alcohol. Alcohol: 95 % ethyl alcohol ("Extra finsprit"). In the countercurrent experiments, spectroscopic grade quality alcohol was used. All solvents were checked with respect to evaporation residue before use.

Four different polyglycol preparations, *viz.* A 6 000, A 4 000, A 1 500, A 300, manufactured by Mo och Domsjö AB were used in the experiments — the figures indicating their approximate, number-average molecular weights. The first three samples were purified by dissolving them in trichloroethylene, shaking with water, shaking the water phase with chloroform and evaporating the chloroform. The preparations were finally dried in vacuum at 50°C.

Fisher & Porter Co 250 ml separatory funnels equipped with glass stoppers and teflon valve taps were used — they permitted an almost perfect separation of the two phases.

The one-stage extraction experiments were carried out by shaking a weighed amount of polyglycol with 50 ml of both solvents (the solvents had previously been shaken to equilibrium in separatory funnels). If nothing to the contrary is stated, the amount of polyglycol in each experiment was 500 mg. A 25 ml portion of each phase was evaporated to dryness and weighed after drying in vacuum at 50°C.

The countercurrent experiments. An all-glass countercurrent apparatus according to Craig could not be used because the transfer of liquid could not be performed without preventing parts of the lower phase following the upper phase and parts of the upper phase remaining with the lower stationary phase. For this reason, separatory funnels of the type described above were used as contacting vessels. The transfer of liquid was of course more laborious and time-consuming but the phases could be separated almost exactly from each other.

The shaking device consisted of a horizontal metal rod along which 20 clamps for the separatory funnels were attached on opposite sides. The funnels were situated at right angles to the rod at a distance of about 20 cm from the rod. Equilibrium was obtained by automatically turning the rod back and forth around its axis through an angle of $\pm 40^\circ$ for 30 min, the mean position of the funnels being horizontal. The number of periods per min was 33. After allowing the two liquid layers to separate, the lower phases were transferred according to the general fundamental distribution pattern.

The substance to be distributed was added in the solid state to tube No. 0 which contained 50 ml of both phases. Equal volumes were used in all steps. At the end of the distribution experiment, the contents of the twenty tubes together with the necessary rinsing liquid were evaporated to dryness in warm air. The fractions were finally dried in vacuum at 50°C and weighed.

In order to show that the phases separate well and that no appreciable loss of solvents by evaporation or other reasons occurs, the volumes of both phases in each tube were determined at the end of a distribution experiment. The losses were small and were partly due to the liquid adhering to the walls of the funnels.

In order to demonstrate that the apparatus can be used as an analytical tool, a pure compound, *N,N*-dimethylaniline, twice distilled in vacuum, was distributed in the apparatus. The solvents used were *cyclohexane* and aqueous phosphate-citrate buffer according

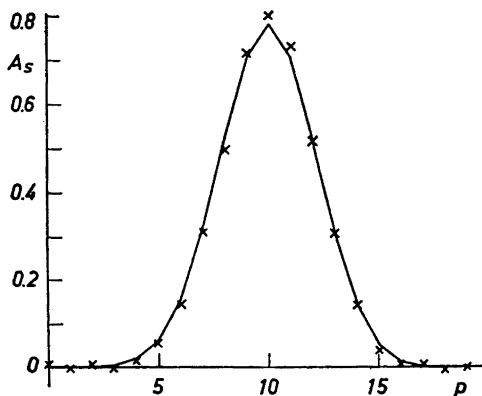


Fig. 6. Comparison at 251 $m\mu$ between experimental (points) and theoretical (curve) absorbancies of the upper phase for countercurrent distribution of N,N-dimethylaniline. Solvent system: Cyclohexane aqueous buffer (pH=2.75). Equal volumes of both phases.

to McIlvaine with pH = 2.75, the two liquids being shaken to equilibrium before use. A solution containing about 3×10^{-5} g N,N-dimethylaniline in 50 ml of the equilibrated cyclohexane was prepared and used as the upper phase in tube No. 0. After completion of the distribution, the upper phases were collected and their absorbancies measured at 250 $m\mu$ in a Beckman spectrophotometer, the equilibrated cyclohexane being used as the reference substance. The results are given in Fig. 6 where a comparison can be made with the theoretical values for a compound with a partition coefficient = 1.10. This value is in fairly good agreement with the value 1.16 which can be calculated from the paper of Columbic and Goldbach⁸. The agreement between experimental and calculated absorbancies must be regarded as good.

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