

## Investigations of the Phenomena of Coacervation. Part II. Coacervation of Polyethylene Terephthalate

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### Introduction

In the first part of our work<sup>1</sup> we found that, depending on the choice of such parameters as temperature, initial concentration of polymer in the solution, and composition of the solvent (when the solvent is composed of two or more components), it was possible to obtain information on the phenomenon of formation of the new liquid phase in two different ways.

If the volume of the newly formed phase as a function of the quantity of the nonsolvent changes extremely, the phase has been called a coacervate.

The other way in which the phenomenon appears is characterized by a nonextreme (monotonous) shape of the curves illustrating the change of phase volumes. This we have called a demixing.

In agreement with the above, the system polyethylene terephthalate-phenol-tetrachloroethane-*n*-heptane has been defined as capable of forming coacervates.

The present work is aimed at a more detailed investigation of the system mentioned, and at giving its characteristics from the viewpoint of phase equilibrium.

### Experimental

All the experiments have been carried out with nonfractionated polyethylene terephthalate ( $\bar{M}_w = 22,200$ ) dissolved in a solution of tetrachloroethane in phenol and titrated with *n*-heptane as a nonsolvent. The experiments and the apparatus were similar to those used in the first part of our work. Polyethylene terephthalate content in the particular phases has been determined by the usual gravimetric method.<sup>2</sup>

### Results of the Experiments

On the basis of the first series of measurements, we have studied the influence of the particular parameters on the character of the phenomenon.

### I. Influence of Temperature

A series of measurements have been made to study the changes in volume of the lower phase as a function of the quantity of *n*-heptane for the system containing 6% polyethylene terephthalate in a 50% solution of tetrachloroethane in phenol. Measurements were made at 25, 35, 60, and 80°C. The results are shown in Figure 1.

The results from an analogous investigation of a system with an initial concentration of 1.0% polyethylene terephthalate in a solvent composed of 10% tetrachloroethane and 90% phenol at temperatures of 25 and 50°C. are illustrated in Figure 2.

It is evident that a rise in temperature is followed by a gradual transition from one form of the phenomenon to the other. It should be pointed out that in a case such as is shown in Figure 1, even at the lowest measured temperature, i.e., 25°C., the solvent and the nonsolvent give a one-phase solution in any proportion. In a case such as is shown in Figure 2, the curves corresponding to the measurement at 40°C. are below the critical temperature of mixing of the liquid components of the system ( $t_{cr} = 49.5^\circ\text{C}.$ ).

### II. Influence of Solvent Composition

Measurements have been carried out at 25°C. for a 1% solution of polyethylene terephthalate in a 10% and a 50% solution of tetrachloroethane in phenol. Figure 3 shows that with an increase of tetrachloroethane in the solvent the shape of the curve changes extremely.

### III. Influence of Initial Concentration of Polymer

In order to investigate the influence of the initial concentration of polyethylene terephthalate, another series of measurements were made of the changes in the volume of phases as a function of the

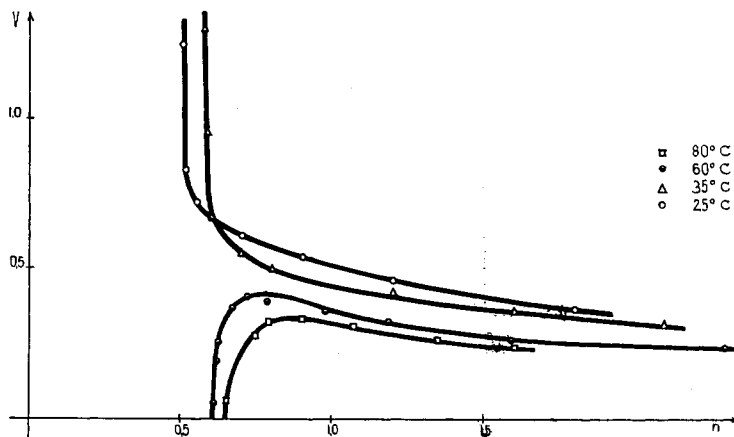


Fig. 1. Lower phase volume as a function of nonsolvent volume  $V_c = f(n)$  at 25, 35, 60, and 80°C. for the system: 6% polyethylene terephthalate dissolved in a 50% solution of tetrachloroethane in phenol titrated with *n*-heptane.

quantity of added *n*-heptane. The temperature was now 50°C. and the solvent was a 50% solution of tetrachloroethane in phenol. In the measurements shown in Figure 4 only the initial concentration of polyethylene terephthalate in the solvent was changed from 1 to 8%.

Figure 4 indicates that the extreme character of the curves begins to be visible below a certain initial concentration of polymer.

In the course of further study we have been able to determine the concentrations and content of polymer in both phases for a phenomenon with an extreme (Figs. 5 and 5a) and a nonextreme (Figs. 6a and 6b) course of the curves of the volume changes.

Figures 5a and 5b illustrate a solution with an initial concentration of 1.37% of polyethylene terephthalate in a 10% solution of tetrachloroethane in phenol. The temperature of the measurement was 40°C.

Figures 6a and 6b illustrate the results obtained from the determination of phase volumes and polymer content for a system with an initial polyethylene terephthalate concentration of 3.76%. The temperature and the solvent used were identical with those applied to the system of volume changes of the lower phase. In Figures 5 and 6  $V$  is the change of phase volume,  $C$  is the change of polymer concentration, and  $m$  is the change of polymer content for the lower phase as a function of the quan-

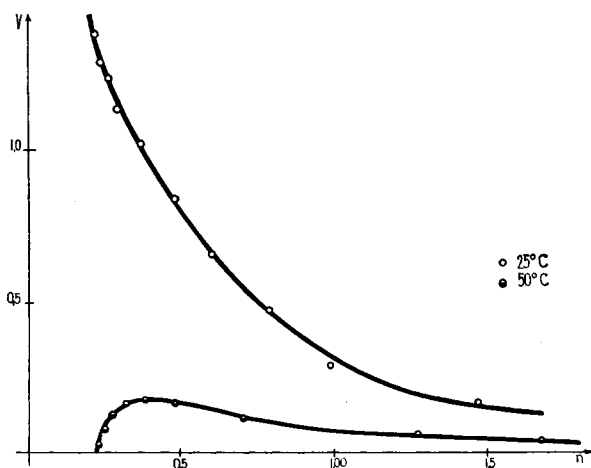


Fig. 2. Lower phase volume as a function of the nonsolvent  $V_c = f(n)$  at 25 and 50°C. for the system: 1% polyethylene terephthalate dissolved in a 10% solution of tetrachloroethane in phenol titrated with *n*-heptane.

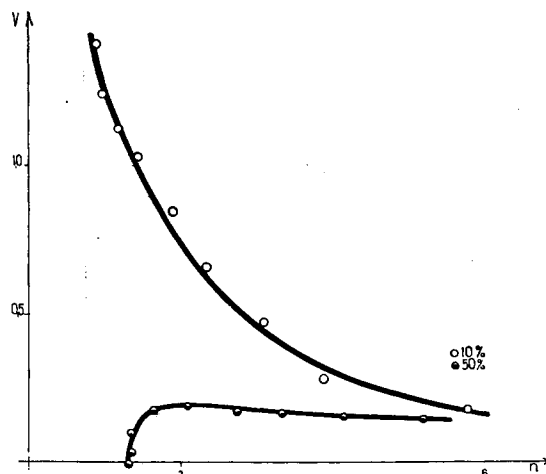


Fig. 3. Curves  $V_c = f(n)$  for various systems of nonsolvent a 10% and a 50% solution of tetrachloroethane in phenol at 25°C. for an initial concentration of polymer of 1%.

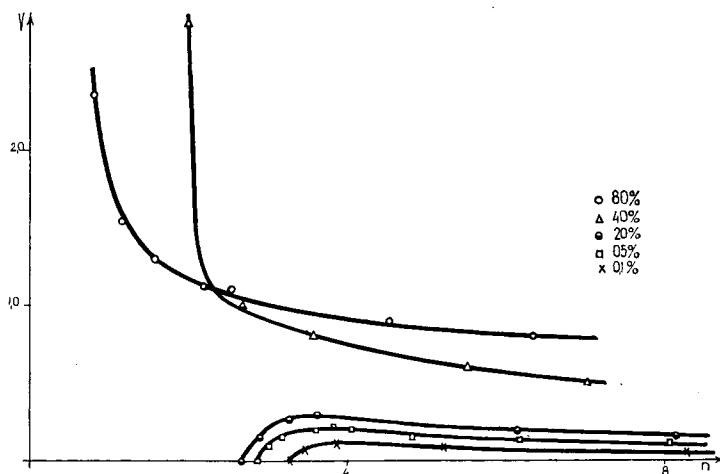


Fig. 4. Curves  $V = f(n)$  for systems with various initial concentrations of polyethylene terephthalate (8, 4, 2, 0, 5 and 0, 1%) dissolved in a 50% solution of tetrachloroethane in phenol at 50°C.

tity of the added nonsolvent. Figures 5b and 6b show the same dependencies for the upper phase.

Considering that the shape of the curves illustrating changes in phase volumes should be dependent on the shape of the binodial in the triangle of Gibbs, we determined this curve for the system investigated. The results are shown in Figures 7 and 8. These figures present by means of sections of the triangle of Gibbs the conditions of coexistence of the liquid phases of the following system: polyethylene terephthalate, solvent (tetrachloroethane in phenol: Fig. 7, 50%; Fig. 8, 10%), and nonsolvent (*n*-heptane). For the sake

of simplification, polyethylene terephthalate was considered as a single component. This approximation, repeatedly employed by other authors,<sup>3</sup> should have, in our opinion, no serious effect on the character of the phenomenon. With this assumption the triangle of Gibbs evidently forms the secant area of a quadrangle illustrating the system polyethylene terephthalate-tetrachloroethane-phenol-*n*-heptane. The intersections have been effected for constant values of 10% and 50% tetrachloroethane in phenol. The measurements in one case were made at 25, 40, and 50°C. (Fig. 7) and in the other at 40 and 50°C. For easy com-

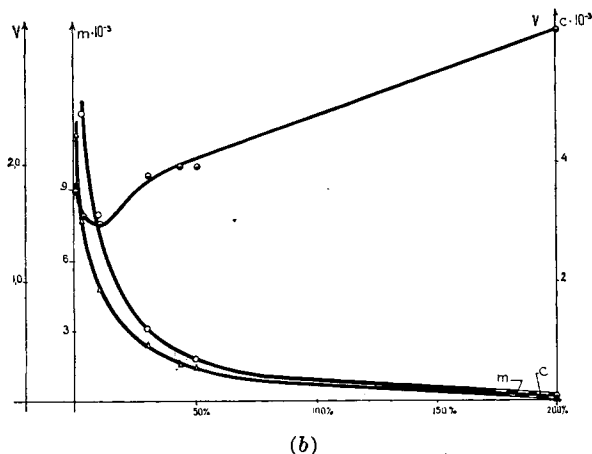
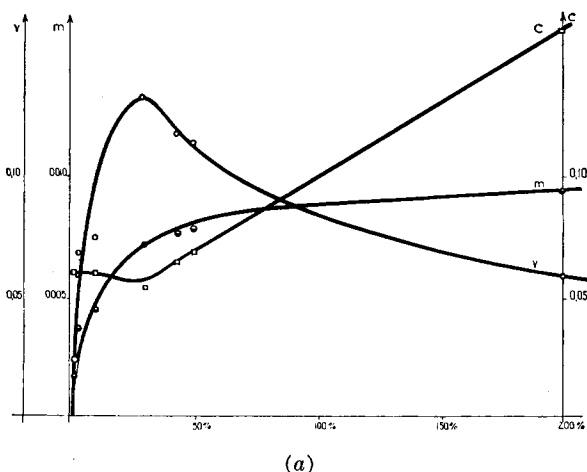


Fig. 5. Change of (a) lower and upper (b) phase volume ( $V$ ) concentration of polymer ( $C$ ) and its content in the phase ( $m$ ) as a function of the quantity of added nonsolvent:  $V$ , lower phase volume in milliliters per gram of initial solution;  $C$ , concentration of polymer in grams per milliliter;  $m$ , polymer content in the lower phase per gram of the initial solution. Measurement at 40°C. Initial concentration 1.37% in a 10% solution of tetrachloroethane in phenol. Ordinate: per cent of *n*-heptane in relation to the quantity of same necessary for turbidity.

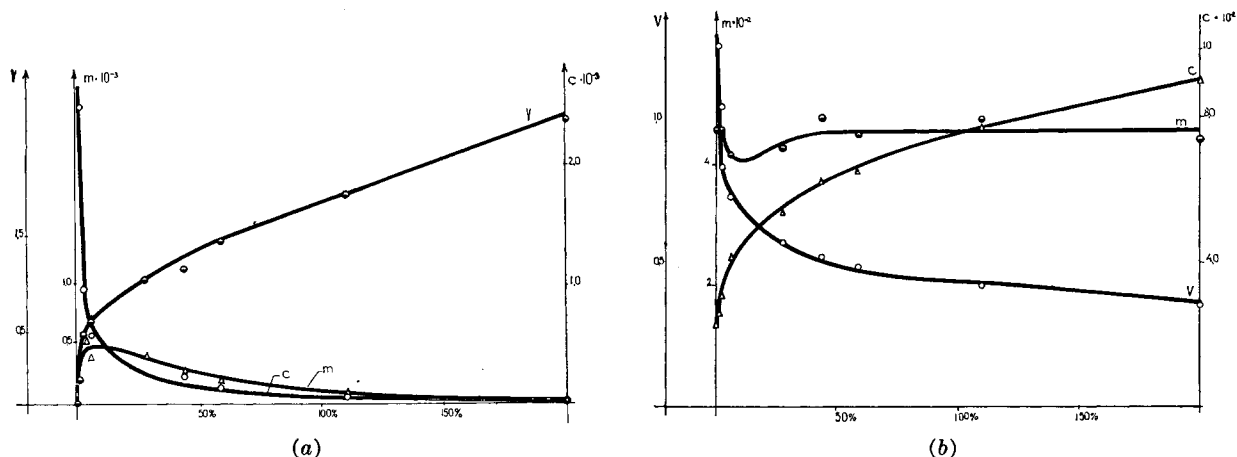


Fig. 6. Same dependencies as in Figure 5 for the system 3.76% polyethylene terephthalate in a 10% solution of tetrachloroethane at 40°C.: (a) lower phase; (b) upper phase.

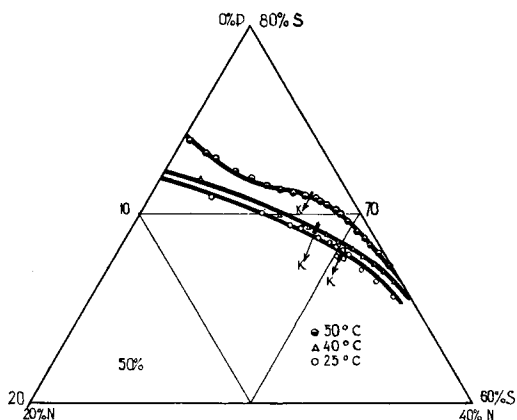


Fig. 7. Section of Gibbs triangle corresponding to the system: polyethylene terephthalate, a 50% solution of tetrachloroethane in phenol, and *n*-heptane; The liquid-phase binodials represent measurements at 25, 40 and 50°C.

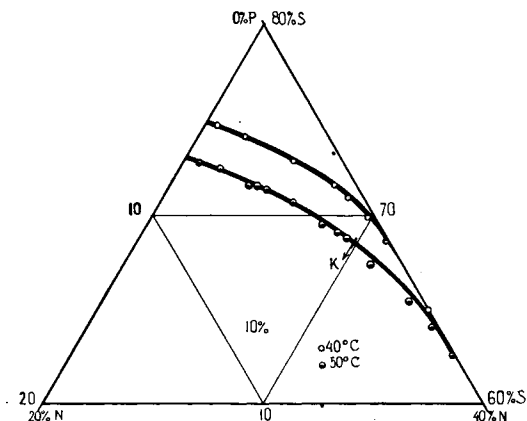


Fig. 8. Section of Gibbs triangle corresponding to the system: polyethylene terephthalate, a 10% solution of tetrachloroethane in phenol, and *n*-heptane; binodials determined at 40 and 50°C.

parison the respective binodials for the same solvent are shown in the same graph.

### Discussion and Conclusions

In our preceding work,<sup>1</sup> based on investigations of systems described in the literature as coacervates, we were able to find that in all of them a basic feature was an extreme course of change in the phase volume at a higher concentration of polymer as a function of the nonsolvent quantity. In distinction to such systems, those characterized by a nonextreme (monotonous) course of the curve have been termed demixings.

Determinations of the content and concentration of polymer in both phases (coacervate in Figs. 5a and 5b and demixing in Figs. 6a and 6b) bring out the following fairly essential difference between the two.

1. *Coacervate.* (a) The lower phase: In agreement with the results presented in the first part of our work under somewhat different conditions we have now observed the following course of the phenomenon with additions of the nonsolvent. The whole polymer content in the phase varies from 0 asymptotically to 100%. Since the phase volume rises quickly in the beginning but after it has reached the extremum tends very much downward—the concentration of polymer accordingly is maintained almost constant at the first stage and then gradually rises. (b) The upper phase: The polymer content decreases from 100% to almost 0; its concentration changes from a value determined by the initial conditions down to a value close to 0.

As is evident from the graph, it is possible to obtain two liquid phases with arbitrarily chosen

proportions of the polymer content in both phases, depending on the quantity of the nonsolvent used. It is also worthy of note that this fact creates specially favorable conditions for making use of these systems for fractionation.

2. *Demixing.* (a) The lower phase: As the nonsolvent is added, the polymer content in the phase changes from a value close to 100% down to somewhat lower values (in our case about 4% less) and back again to a value close to 100%. With the volume falling hyperbolically down to 0 the concentration rises from a value determined by the initial conditions up to a value close to 100%. (b) The upper phase: The polymer content varies over a very small maximum practically up and down from 0 to 0 and the concentration decreases from a value determined by the initial conditions to a value close to zero.

It is obvious that systems of this kind are not suitable for fractionation by a division of polymer between two liquid phases.

From analysis of the results presented in Figures 1 and 2 the conclusion can be drawn that by gradual changes of temperature it is possible to make the system pass in a continuous way from coacervation to demixing as well as the other way around. Similarly, a close examination of Figures 3 and 4 will lead to the observation that successive small changes either in the concentration of tetrachloroethane in the solvent or in the initial concentration of polyethylene terephthalate allow a gradual transition from one form of the phenomenon of the phase division into the other.

A similar phenomenon of formation of a lower phase and then of an upper one is found in the well-known phase division of classic solutions. To bring out the analogy we shall briefly discuss an example.

The system that will be considered consists of three components: two liquids ( $N_1$  and  $N_2$ ) of limited miscibility and entirely soluble in a third one (S). If, when adding  $N_1$ , we intersect the binodial of the phases between the critical point of miscibility and the side of the triangle conforming to the condition  $N_1 = 0$ , the volume of the remaining phase will change from 0 to 100% of the total volume of the system. Should the binodial be intersected on the other side of the critical point the new layer changes over a certain maximum from zero to zero. It is noteworthy that the new layer formed in the second case is due to the course of changes of composition from the original one. An adequate choice of specific weights for

the system can result, in similar experiments, in the same phase being lower or upper. So, for such a course of composition changes, the critical point of miscibility separates the lower and the upper phases. A similar phenomenon is illustrated in Figures 7 and 8.

Consequently, in accordance with the classic interpretation of the phenomenon it is possible, on the basis of the binodial, to determine the conditions for obtaining both the separations. The one we have called a coacervate conforms to a straight line which represents the change in the nonsolvent content in the system intersects the binodial between the critical point and the straight line of the zero content of polymer. The demixing appears when, after addition of the nonsolvent, the binodial is intersected on the other side of the critical point.

On the basis of the results and discussion presented above we suggest the term "coacervate" for the layer in which the polymer concentration during titration with nonsolvent is higher than that in the balancing layer and the polymer content simultaneously varies from 0% up to a value close to 100%. This phenomenon will appear if the straight line representing the change in the nonsolvent content intersects the binodial between the critical point and the straight line corresponding to the zero content of polymer.

We propose to define as systems capable of forming coacervates all liquid systems containing polymer (a) for which the binodial of the liquid phases has a critical point of miscibility, and (b) in which the critical point of miscibility (if the system is represented by means of a steric or a plane figure with sides corresponding to the phase equilibrium of the two components) lies neither on the side of the value of polymer concentration equal to 0 nor beyond it.

Systems unable to form coacervates will therefore be those having three or more components whose critical points of miscibility on the binodial of the liquid phases move to the side of the figure corresponding to the zero content of nonsolvent, and also those which for other reasons do not possess a critical point of miscibility.

The definitions proposed by us do not quite agree with those given in the scientific literature<sup>4</sup> which, however, have repeatedly been interpreted differently.

Although it may seem that the formation of a new liquid phase as suggested by us has no thermodynamical explanation since the whole curve can be

expressed by means of a single equation fulfilling the condition  $\Delta\mu_i' = \Delta\mu_i''$ , nevertheless, considering the essential differences in the manner of division, such a distinction appears to us pertinent and advisable.

It may be repeated that, in contrast to other liquid systems, those defined by us as capable of forming coacervates are particularly good for fractionation.<sup>5</sup>

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### Synopsis

Investigations are reported for the influence of temperature, initial polymer concentration, and solvent composition on the course and character of the phenomenon of a division into two liquid phases of the system polyethylene terephthalate-phenol-tetrachloroethane-*n*-heptane. Some curves presented show changes in volumes of the phases in polymer content in phases, and in binodials of the liquid phases (Gibbs triangles). The term "coacervate" is suggested for the phase in which concentration of polymers during titration with nonsolvent is greater than that in the balancing phase, and in which at the same time the polymer content changes from 0 to 100%. It is shown that such a division into two liquid phases can take place only when the straight line representing the changes of nonsolvent content inter-

sects the binodial between the critical point of miscibility and the side of the triangle of Gibbs corresponding to the zero content of polymer.

### Résumé

On a étudié le système polytéraphthalate de glycol, phénol, tétrachloréthane, *n*-heptane. On a déterminé l'influence de la température, de la concentration initiale du polymère et de la composition du solvant sur le phénomène de la formation de deux phases liquides. Des résultats expérimentaux furent présentés au moyen de courbes indiquant le changement de volume des phases et le changement de la teneur en polymère dans les phases en fonction de la quantité de non-solvant. On a déterminé les binodiales correspondantes dans le triangle de Gibbs. En se basant sur les résultats obtenus, on a proposé comme définition de coacervat: le coacervat est la phase liquide dans laquelle la concentration du polymère est plus grande que celle dans la phase surnageante; simultanément le contenu du polymère peut varier de 0% à 100% de la quantité totale. On a constaté que la formation de telles phases liquides ne peut avoir lieu que dans le cas où la droite indiquant les variations de la teneur en non-solvant coupe la binodiale entre le point critique et le côté du triangle de Gibbs correspondant au contenu nul en polymère.

### Zusammenfassung

Für das System: Polyäthylenglykolterephthalat-Phenol-Tetrachloräthan-*n*-Heptan wurde der Einfluss von Temperatur, anfänglicher Polymerkonzentration und Lösungsmittelzusammensetzung auf den Vorgang und Charakter der Verteilung in zwei flüssige Phasen untersucht. Die Untersuchungsergebnisse werden graphisch als Kurven der Volumsänderung der einzelnen Phasen, der Änderung des Polymergehalts in den einzelnen Phasen, sowie als Binodal-kurven der flüssigen Phasen im Gibb'schen Dreieck dargestellt. Auf Grund der erhaltenen Ergebnisse wurde vorgeschlagen, diejenige Phase als "Koazervat" zu bezeichnen, in welcher die Polymerkonzentration im Verlaufe einer Dosierung des Fällungsmittels grösser ist als in der zweiten Phase, wobei gleichzeitig der Polymergehalt von 0% bis auf 100% ansteigt. Es wurde nachgewiesen, dass eine solche Verteilung in zwei flüssige Phasen nur dann erfolgen kann, wenn die Gerade für die Gehaltsänderung des Nichtlösers die Binodalkurve zwischen dem kritischen Mischungspunkt und der Seite des Gibb'schen Dreieck schneidet, die einer Konzentration Null des Polymeren entspricht.

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