

Investigations of the Phenomena of Coacervation

E. TURSKA and L. UTRACKI

Polish Academy of Science, Department of Physical Chemistry, Politechnika Łódzka, Łódz, Poland

INTRODUCTION

In one-phase liquid (condensed) multicomponent systems containing polymer, a change in the proportions of particular components or in temperature causes the system, under certain conditions, to separate into two phases, the new phase being either a liquid or solid.

The new liquid phase is defined, in certain described cases,^{1,2} as the coacervate.

Quite a number of works discuss the phenomenon of coacervation of polymers and give its theoretical interpretation. The following should be cited among the first: Dobry,² Bandenberg de Jong,³ Voorn,⁴ and Bamford and Tompa.⁵ In our opinion, however, a precise formulation of qualities distinguishing the separation of the system into two liquid phases with a simultaneous formation of the

coacervate from that resulting from the limited miscibility of liquid components has yet to be found in the literature.

The object of our work was to determine the qualities distinguishing the phase separation with the formation of the coacervate from the other cases in which a one-phase system changed into a two-phase one.

Consequently we decided to investigate, under various conditions, the formation of the second phase in the one-phase systems which certainly do not form coacervates, as well as the systems known from the literature as capable of forming coacervates.

As there were no doubts as to how to distinguish a case in which a solid phase is formed from that in which coacervates appear, we did not consider this problem. The object of our investigations was various cases in which the system divided into two liquid phases. The phase volume was the first quantity that we chose for the purpose of characterizing the investigated phenomenon.

EXPERIMENTAL

Apparatus

The measurements were carried out in two types of glass apparatus.

The first one (Fig. 1) served to measure small changes in the volume of the lower liquid phase. For this purpose, the bottom of the apparatus was provided with a narrow calibrated vessel. A propeller-worm stirrer was used. It could be removed from the liquid after stirring. The nonsolvent feeding device and the air escape tube were placed on one side.

The other type of apparatus was used for determining changes in the volume of both the upper and the lower liquid phase. One of the two small calibrated tubes built in at the upper part was used to add the solvent, the other one to add the nonsolvent. Both the tubes were joined with the air

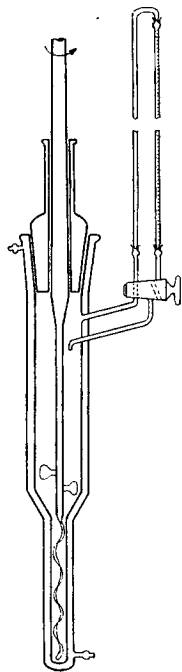


Fig. 1. Apparatus for measuring volume changes of the lower layer of the coacervate.

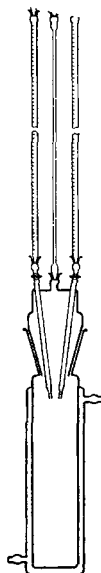


Fig. 2. Apparatus for measuring changes in the volume of the phases.

escape tube. Magnetic stirring was applied and a uniform temperature maintained with an accuracy of $\pm 0.05^\circ\text{C}$.

Description of Experiments

After filling the apparatus with a solution of the polymer and as soon as the temperature of the system had become uniform, the initial level of the liquid was determined by means of a cathetometer with an accuracy of ± 0.05 mm. and then the drop-

ping of the nonsolvent began. When the solution became turbid under the influence of the added quantity of nonsolvent, its level was measured again and the systematic dropping of the nonsolvent resumed. After each addition of the nonsolvent, the system was stirred for some time. On formation of the layers, we determined the level of each phase surface. The time necessary for the formation of the layers ranged from 0.5 to 40 hr., depending on the system and temperature. On the basis of the previously worked out curve indicating the dependence of the volume of the liquid on its level in the vessel used, the volumes of the layers were determined.

Description of Reagents

The following polymers were used during the work:

Laboratory produced polyethylene terephthalate, $\bar{M}_w = 9300$

Laboratory produced polycaprolactam, unstabilized, $\bar{M}_n = 15,300$

Polystyrene (industrial product), $\bar{M}_w = 175,000$
These nonsolvents were used:

n-Heptane $d_{20} = 0.6838$, $n_D^{20} = 1.3877$,
b.p. = 98.35°C .

Dimethyl sulfate $d_{20} = 1.328$, $n_D^{20} = 1.38735$,
b.p. = 188°C .

Twice-distilled water

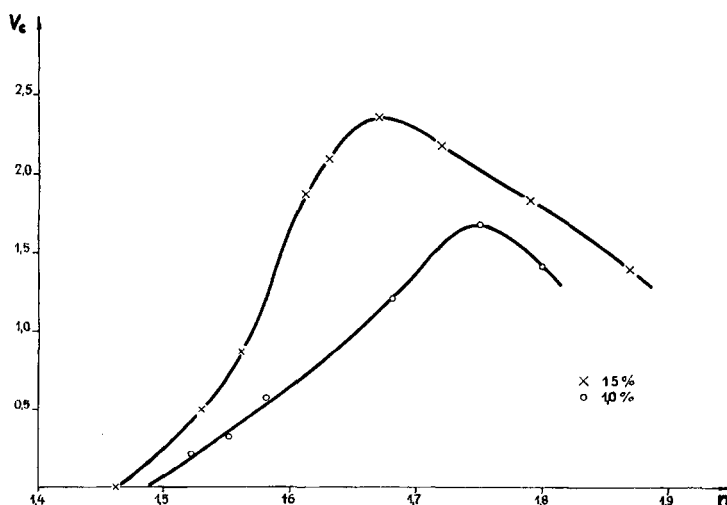


Fig. 3. Diagram of the volume of the coacervate phase as a function of the volume of the nonsolvent: $V_c = f/n$ for the solution of polystyrene in tetrachloroethane precipitated by *n*-heptane at 20°C . The upper curve pertains to the solution with an initial concentration of 1.5% polystyrene, the lower one for 1.0%

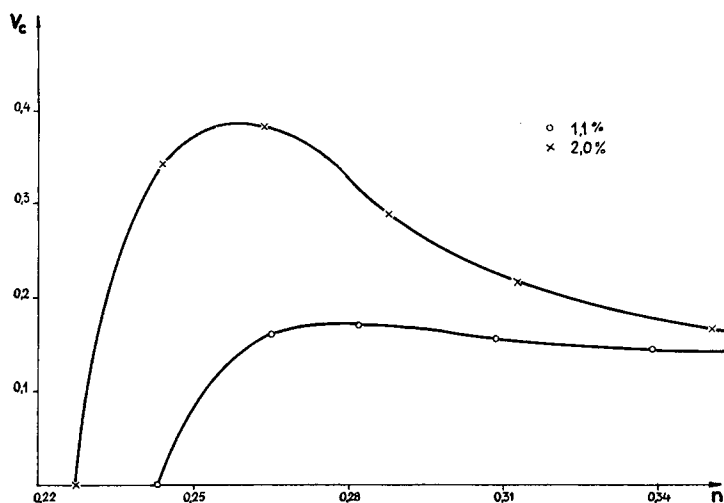


Fig. 4. Curves $V_c = f/n$ for the system polystyrene-carbon tetrachloride-dimethyl sulfate. Temperature 20°C. The upper curve for the initial polystyrene concentration of 2.0%, the lower one for 1.1%.

The following solvents were used:

Phenol	$d = 1.0526$, $n_D = 1.5391$, m.p. = 40.3°C.
Tetrachloroethane	$d = 1.5873$, $n_D = 1.4940$, b.p. = 146.6°C.
Ethylene glycol	$d = 1.015$, $n_D = 1.4313$, b.p. = 196.45°C.
Carbon tetrachloride	$d = 1.5940$, $n_D = 1.4603$, b.p. = 76.65°C.

RESULTS

To comprise a model system in which the coacervate would certainly not be formed, we chose adipic

acid as the solute, phenol in tetrachloroethane as the solvent, and *n*-heptane as the nonsolvent. We chose this system in view of the fact that the adipic acid has, in relation to the other components, a solubility very much like that of the polyethylene terephthalate, i.e., on the one hand, it dissolves well in phenol and its mixture with the chloroethane, while on the other hand, it does not dissolve in the *n*-heptane. We could also assume that since it is a small-molecule substance, it certainly did not possess the ability to form coacervates.

We could ascertain that the system containing the polyethylene terephthalate⁶ as the solute be-

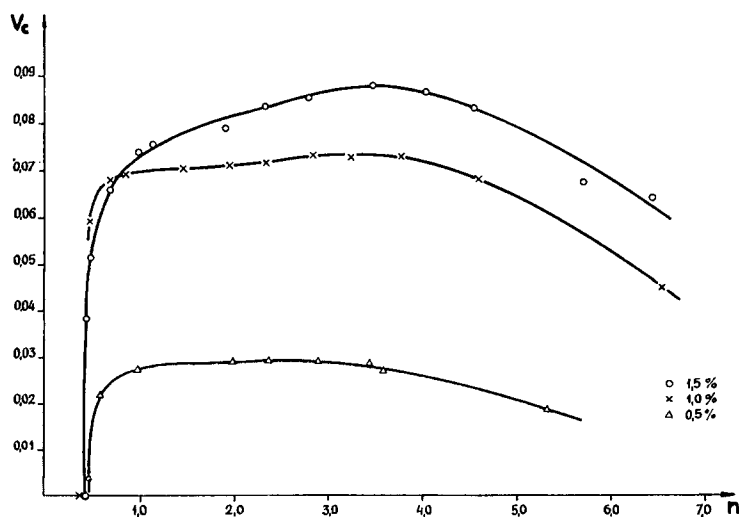


Fig. 5. Curves $V_c = f/n$ for the system Polycaprolactam-75% phenol + 25% ethylene glycol-water. Temperature 50°C. The curves refer (from top to bottom) to initial polymer concentrations 1.5%, 1.0%, and 0.5%, respectively.

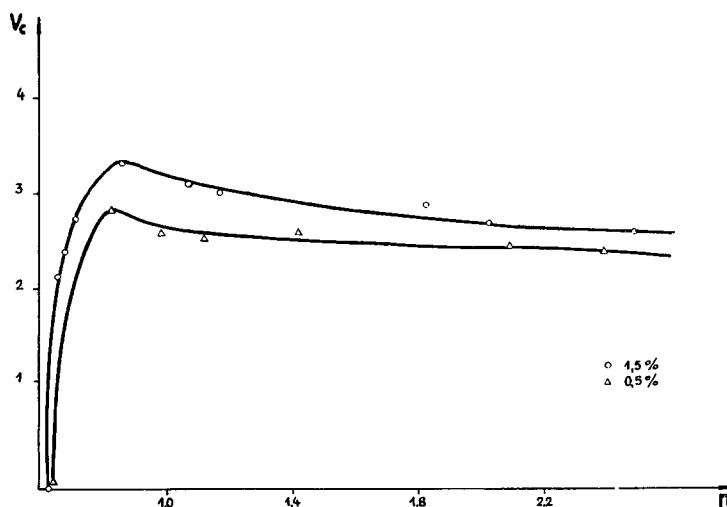


Fig. 6. Dependence $V_c = f/n$ for the system polycaprolactam-phenol-water at 70°C. The upper curve is for the initial polymer concentration of 1.5%, the lower one for 0.5%.

haves in the same way as the polycaprolactam-phenol-ethylene glycol-water system which had been proved before⁷ to be capable of forming coacervates.

The following systems were examined:

A. Systems without the polymer:

1. Adipic acid solutions (concn. 0.01-4.96%) in phenol, titrated with *n*-heptane at 50°C. We stated that the excess of *n*-heptane necessary for formation of a new phase depended on the initial concentration of the solution. The new upper phase had a much lower concentration of the solute than the lower phase. With further additions of *n*-heptane, the new phase increased in volume and the lower phase decreased until the latter completely disappeared.

2a. Adipic acid solutions (concn. 2.3-5%) in phenol

containing 2% tetrachloroethane. It was established that addition of *n*-heptane resulted in the precipitation of the acid in a crystalline form before the phase separation.

2b. For concentrations of the adipic acid up to 1.83%, we could observe the separation into two liquid phases whose disappearance preceded the precipitation of the acid.

2c. For adipic acid concentrations from 1.83 to 2.30%, both phenomena appeared simultaneously.

3. In the solutions of adipic acid (at any of the above named concentrations) in phenol containing, in turns, 5.0, 10.0, and 20.0% of tetrachloroethane, only the precipitation of solid acid was observed.

B. Systems containing the polymer.

1. Systems capable of forming the coacervate, according to the data available in literature.⁸ The behavior of the following systems was investigated qualitatively: polystyrene in (a) tetrachloromethane, (b) methyl ethyl ketone,

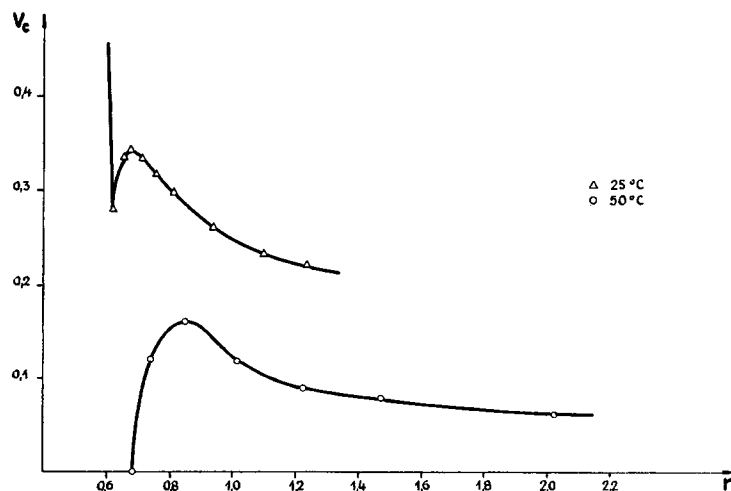


Fig. 7. Curves $V_c = f/n$ demonstrate the temperature dependence of the phenomenon of coacervate formation in the system polycaprolactam-50% phenol + 50% tetrachloroethane-*n*-heptane. Upper curve for 25°C., lower curve for 50°C.

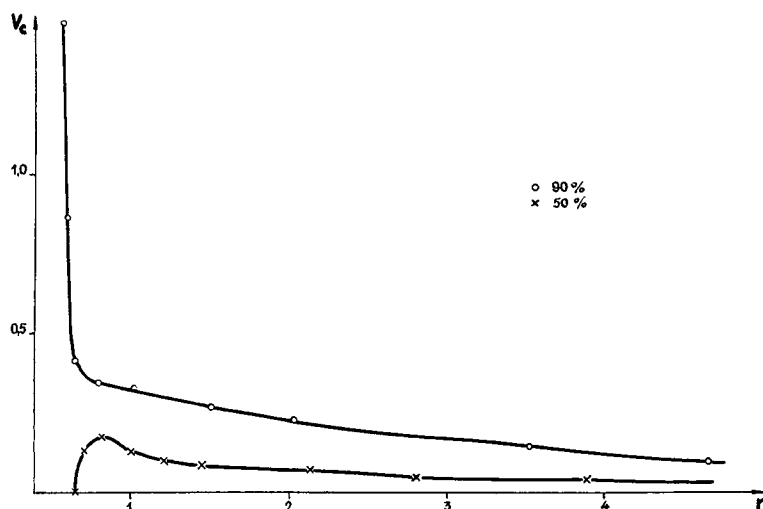


Fig. 8. Dependence of $V_c = f/n$ for the system polycaprolactam- $X\%$ phenol + $(100-X)\%$ tetrachloroethane- n -heptane at 50°C . For the upper curve $X = 90\%$; for the lower one, $X = 50\%$.

and (c) benzene. As nonsolvents we used in all three cases n -heptane, isopropyl alcohol, and acetic acid. Measurements were carried out at the temperature of 50°C . In all the combinations of these systems (referred to in the literature as forming coacervates) the phenomenon took a similar course. Successive additions of the nonsolvent resulted, after a period of mutual solubility, in the formation of a lower phase with a greater concentration of the polymer. As the dropping proceeded, the lower phase increased until it reached its maximum, after which any further addition of the nonsolvent produced a gradual decrease in its volume.

For a quantitative examination of the phenomenon the following system was chosen: the solutions of polystyrene in tetrachloroethane to which n -heptane was added. From the qualitative point of view, the process was analogous to that described above. The results obtained for the two different

concentrations of the polymer are shown in Figure 3. For both the concentrations, the maximum is obtained on the curve $V_c = f/n$ ($V_c =$ volume of the coacervate phase, $n =$ ml. of nonsolvent). For a higher concentration of the polymer in the initial solution, this extremum will increase and be displaced in the direction of the axis of ordinates.

In our experiments we had observed so far an extreme change in volume of the precipitated lower phase of the coacervate, i.e., of the phase richer in polymer. By means of a suitable choice of components from the point of view of their specific weights, a system may be obtained in which the coacervate should form the upper phase. In order to obtain a fuller view of the phenomenon, we examined the following new system: polystyrene-tetrachloromethane-dimethyl sulfate. The results obtained were similar, i.e., the phase volume of the coacervate was found in its extremal change,

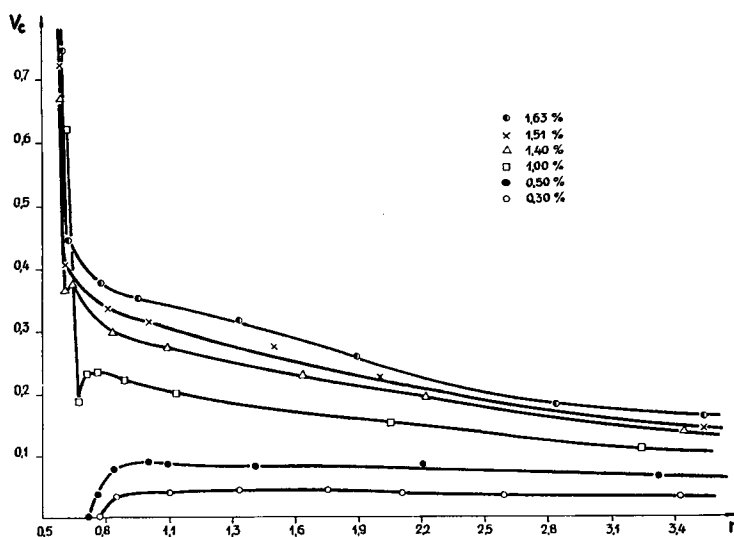


Fig. 9a. Changes in the character of the curves $V_c = f/n$ dependent on the initial concentration of the solution (1.63% of polymer, upper curve; down to 0.30%, lower curve). System: polycaprolactam-90% phenol + 10% tetrachloroethane- n -heptane. Temperature, 50°C .

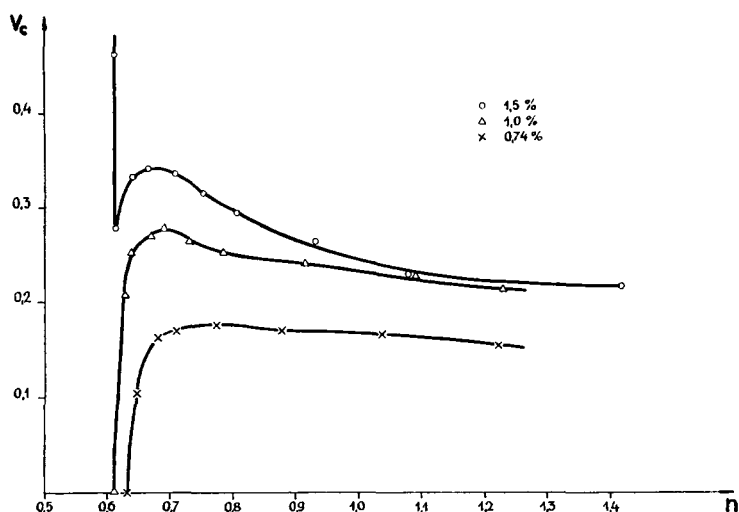


Fig. 9b. Change in the character of the curves $V_c = f/n$ for the system: polycaprolactam-50% phenol + 50% tetrachloroethane-*n*-heptane at 25°C. Uppermost curve, 1.5% of polymer in the initial solution; the following curves, 1.0% and 0.74%, respectively.

and, for a higher concentration, the displacement of the extremum towards the axis V_c was observed. These results are shown in Figure 4.

2. We had formerly acknowledged the system⁷ (polycaprolactam-phenol-ethylene glycol-water) as the one in which the coacervate may be formed. The results of the measurements are given in Figure 5. As it is evident from the figure, in this case also there is a maximum reached on the curve of the change in the volume of the coacervate as a function of the quantity of the nonsolvent used. With increasing concentration of the solution, we can observe an increase in the maximum and a displacement of it away from the ordinate axis.

In order to ascertain the ability of the polyamide to form coacervates in other systems, the following systems were examined:

a. Polycaprolactam-phenol-water, Figure 6. A similar system had been used by Taylor for fractionation.⁹ The measurements were carried out at 70°C., i.e., above the critical point for the phenol-water mixture. In this case as well, we ascertained the existence of the maximum on curve $V_c = f/n$ and the direction in which it displaced was the same as in the system (polycaprolactam-phenol-ethylene glycol-water), i.e., away from the ordinate axis.

b. Polycaprolactam-phenol-tetrachloroethane-*n*-heptane. The following measurements were carried out:

(1). For two identical systems (1.5% of polycaprolactam in a 50% solution of tetrachloroethane in phenol titrated with *n*-heptane) at two different temperatures, $t_1 = 50^\circ\text{C}$. and $t_2 = 25^\circ\text{C}$. The results are shown in Figure 7. As is evident from the diagram, the general character of the curves for different temperatures is similar.

(2). In systems containing the same percentage of the polymer (1.5%) at 50°C. with different compositions of the solvent, i.e., 10.0% and 50.0% of tetrachloroethane in phenol (Fig. 8). The curve in the diagram shows the dependence of the phenomenon on the composition of the solvent. The maximum was not reached for a lower tetrachloroethane concentration.

(3). For systems with a constant composition of the solvent: 10% tetrachloroethane in phenol at 50°C. The polyamide concentration was the changeable parameter. The respective results of the measurements are given in Figure 9a. In this case as in the preceding one, the phenomenon depended distinctly on the changeable parameter. According to the concentrations applied, we could obtain maxima of different ranges. With increasing concentration of the solution, the maxima showed the tendency to displace towards the axis of ordinates. For concentrations exceeding 1.40%, no maximum was observed. Similar measurements were carried out for the system (polycaprolactam-50% phenol + 50% tetrachloroethane-*n*-heptane) at a temperature of 25°C. The results obtained bear a general resemblance to those shown in Figure 9b.

(4). As a further system for our investigations, we chose the one in which we had previously⁶ carried out the fractionation of polyethylene terephthalate, viz., polyethylene terephthalate-phenol-tetrachloroethane-*n*-heptane. The measurements were carried out for different concentrations of polymer dissolved in a mixture of 90% phenol and 10% tetrachloroethane during titration with *n*-heptane (Figure 10). The curves obtained show a very distinct maximum that displaces, with increasing concentration of the polymer, towards the axis of ordinates.

In order to achieve a full characterization of the phenomenon, we examined in addition the following system: polyethylene terephthalate-phenol-ethylene glycol-water. As a result of the measurements, it can be stated that at 50°C., solutions of 0.15-1.5% polyethylene terephthalate prepared in phenol containing from 0-25.0% of ethylene glycol, and titrated with water in all cases do not form two liquid phases. On the contrary, a solid polymer is precipitated.

Even without a detailed analysis of the results obtained, it can be stated that the systems de-

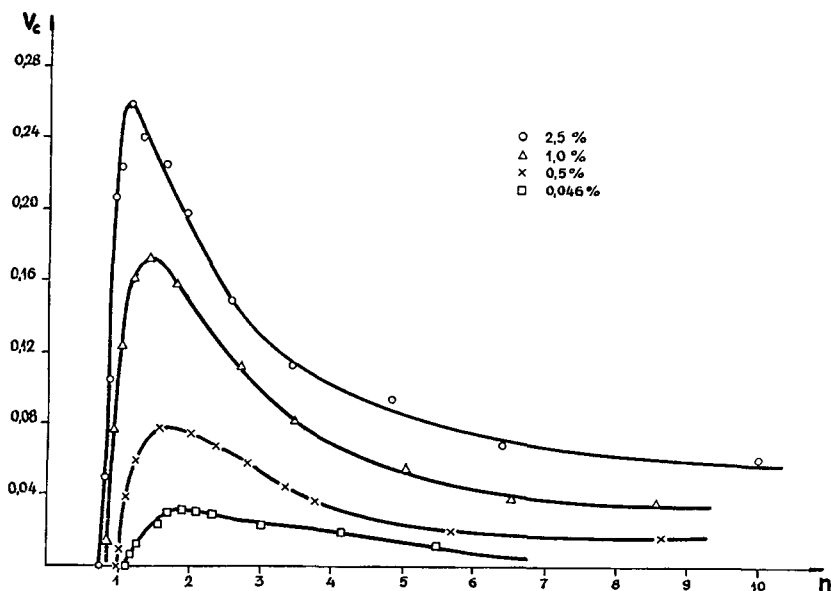


Fig. 10. Curves $V_c = f/n$ for the increasing concentrations of the initial polymer solution from 0.046% (the lowest curve), up to 2.5%. Temperature, 50°C. System: polyethylene terephthalate-10% phenol + 10% tetrachloroethane-*n*-heptane.

scribed in the literature and those which we ascertained as capable of forming coacervates possess the common characteristic of reaching a maximum on the curve of volume change of the coacervate layer vs. the amount of the nonsolvent used in the system.

In order to confirm the precipitation of the polymer as the liquid phase, additional measurements were carried out with a view of establishing the quantities of polymer contained in the two phases. The results thereof are shown in Figure 11.

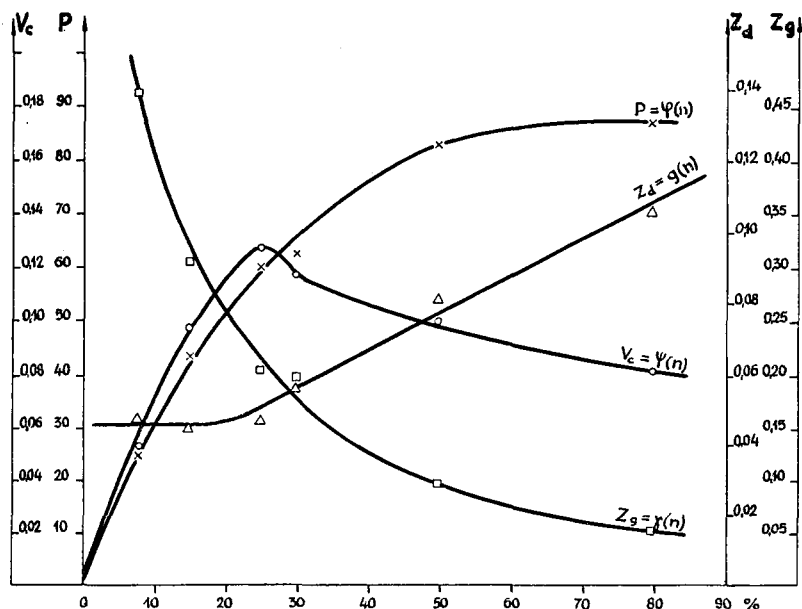


Fig. 11. Changes in the concentration as a function of the quantity of the added nonsolvent. System: polyethylene terephthalate-90% phenol + 10% tetrachloroethane-*n*-heptane. Initial concentration of polymer, 1.0%. Temperature, 50°C. Z_d = concentration in the coacervate phase. P = per cent of the precipitated polymer. Z_g = concentration in the upper layer. V_c = volume of the coacervate phase.

DISCUSSION

On the basis of the above measurements, we ascertained that in systems consisting of a polymer, a solvent (or a mixture of solvents), and a nonsolvent, there is a possibility of distinguishing between two ways in which a new liquid phase may be formed. The first type of phenomenon is the formation of a liquid phase (generally an upper one) possessing only a slight solute content or even containing no solute at all. With further additions of the nonsolvent, there is an increase of this phase volume and a simultaneous decrease in the volume of the other liquid phase. This was observed first of all in the following system: adipic acid-phenol-*n*-heptane. The same process was also ascertained for the system polycaprolactam (1.5% of solvents)-90% phenol + 10% tetrachloroethane-*n*-heptane at 50°C. (Fig. 9a), as well as for all the systems of the same composition but with higher initial concentrations of polyamide (Fig. 9b). The other type consists in the formation of a liquid phase richer in solute. It is a lower phase, as a rule, and it results from the density of the polymer relative to that of the nonsolvent and the solvent. Further additions of the nonsolvent are followed, at the beginning, by an increase in volume until the maximum is reached. The upper phase, on the other hand, after a transitory check corresponding to the extreme point on the curve $V_c = f/n$, increases its volume linearly. The latter type corresponds to all the systems described in literature and those we ourselves have determined as forming coacervates. These are: polystyrene-tetrachloroethane-dimethyl sulphate (Fig. 4), polystyrene-tetrachloroethane-*n*-heptane (Fig. 3), and polycaprolactam-phenol-ethylene glycol-water (Fig. 5).

Moreover, we were able to establish that there were systems in which the process was similar, although they had not yet been considered as coacervates. The following such systems are to be mentioned here: polycaprolactam-phenol-water, polycaprolactam-phenol-tetrachloroethane-*n*-heptane, and polyethylene terephthalate-phenol-tetrachloroethane-*n*-heptane.

It is known from the literature that a similar curve was observed by Boyer when he precipitated polystyrene in the form of gel.¹⁰ From our own observations, as well as taking into consideration the above-mentioned work, we can establish that a maximum on the curve of the new phase volume is a characteristic feature for precipitation of the polymer, and consequently, in the case of a liquid phase, of formation of the coacervate. Thus, all

the systems we examined and ascertained as possessing this characteristic are coacervates.

A full characterization of the described phenomenon of a liquid phase with an extreme change in volume may be achieved with Figure 1. As is shown in the diagram, the total quantity of the "precipitated polymer" in the lower phase is constantly increasing with gradual additions of the nonsolvent. Within the scope of our investigations, however, it did not reach the full quantity of the polymer contained in the solution. The curve of the volume changes as they approach the maximum and the curve showing the polymer content in the lower phase are similar. The maximum is followed by a decrease in the values of the ordinates in spite of the continuing increase in quantity of the polymer in the lower phase. These facts may only be explained as a precipitation of the polymer with a simultaneous extraction of liquid components from the lower phase. This hypothesis is confirmed by the character of the curve indicating the polymer content in the lower phase. In its initial part, it is almost parallel to the axis of abscissae, i.e., the polymer concentration in the lower phase is constant; approaching the maximum, the curve begins to bend upwards with the increasing values of the concentration. This is caused both by the continuing precipitation of the polymer and the extraction of liquid components. The results of this experiment allow us to assume that the extremum on the volume curve corresponds to the process of precipitation of the polymer in the liquid phase, i.e., to the formation of the coacervate. A further analysis of the results obtained makes us advance the statement that, oftentimes, in the same system and with change in only one of the parameters (temperature, composition of solvent, or polymer concentration in the initial solution), a separation into two liquid phases with or without an extremum in the volume of the phase richer in polymer may be obtained.

Let us assume that we are to deal with two different phenomena: the formation of layers, which is the result of the limited miscibility of liquid components of a system, and the precipitation of the polymer as a liquid phase, the coacervate. Whether one or the other phenomenon will appear depends upon the parameters mentioned before. By changing them, it should be possible to obtain a system which, under suitable conditions and the influence of the nonsolvent, will be able to assure a direct transition from one phenomenon to the other. The experimentally obtained curves in Figures 7, 8, 9a,

and 9b confirm this hypothesis. It is worthwhile to note that, beginning from a certain value of the abscissa (the quantity of the added nonsolvent), the curves are almost alike, irrespective of whether there was an extremum in the initial part of the diagram.

Consequently, independently of the way in which the phenomenon appeared at the beginning of the process, the curves later become analogous. This fact is liable to encourage the advancing of some far-reaching general statements; in our opinion, however, it cannot be properly interpreted until more comprehensive experimental material of the kind on which our own investigations were based is available.

CONCLUSIONS

Based on the above analysis of the results, the following statements can be made:

(1). The appearance of a maximum on the curve $V_c = f/n$ (where V_c denotes the volume of the phase richer in polymer and n stands for the quantity of the added nonsolvent) determines the examined phase as the coacervate (the polymer precipitated as a liquid phase).

(2). The systems (polyethylene terephthalate-phenol-tetrachloroethane- n -heptane), (polycaprolactam-phenol-tetrachloroethane- n -heptane), and polycaprolactam-phenol-water) are capable of forming coacervates. Note: Both the first and the second systems were used by us for fractionation.^{6,7}

(3) Changes in the polymer concentration, temperature, and composition of the solvent are decisive for the formation of the coacervate or, alternatively, for the phase separation as a result of the limited miscibility of liquid components.

We wish to express our thanks to Mr. S. Szapiro for his participation in the first stage of our investigations.

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Synopsis

The object of the work was to ascertain the characteristic features which could provide a basis for distinguishing between the formation of the coacervate and that of a new liquid phase resulting from the limited miscibility of components. Various multicomponent systems containing the polymer were examined, and as a model we examined a system unable to form coacervates in which the polymer was replaced by a small-molecule substance of a similar solubility. Measurements of the changes in the volumes of the liquid phases were carried out and the polymer content in the particular phases was determined. It was ascertained that the characteristic feature for the coacervate is a maximum on the curve which indicates the dependence of the volume of the phase richer in polymer on the quantity of the nonsolvent used. The polyethylene terephthalate coacervate was obtained and certain new systems containing polyamides were proved to be able to form coacervates.

Résumé

Ce travail a été entrepris en vue de déterminer les différences entre le phénomène de formation d'un coacervat et la formation d'une nouvelle phase liquide par suite de la miscibilité limitée des composants liquides du système. On a étudié plusieurs systèmes à composants multiples contenant le polymère et un système-modèle, qui ne forme certainement pas de coacervats et contenant au lieu de polymère une substance de poids moléculaire faible et de solubilité semblable. Les variations de volume des phases liquides ont été mesurées, de même que leurs teneurs en polymère. On a constaté que la propriété caractéristique d'un coacervat est l'existence d'un maximum sur la courbe exprimant la dépendance du volume de la phase la plus riche en polymère, en fonction de la quantité du nonsolvant. On a obtenu des coacervats de polyteréphthalate d'éthylène glycol de même que de certains systèmes nouveaux contenant des polyamides qui ont également été caractérisés.

Zusammenfassung

Diese Arbeit wurde unternommen, um Eigenschaften festzustellen, die die Koazervatbildung von der Bildung einer neuen flüssigen Phase (wegen der begrenzten Mischbarkeit der Komponenten) unterscheiden. Es wurden zahlreiche Mehrkomponenten-Systeme untersucht die

Polymer enthielten, wie auch ein Modell-System, das eine niedermolekulare Substanz von einer dem Polymer ähnlichen Löslichkeit enthielt. Es wurden Messungen der Volumenänderungen der flüssigen Phasen, wie auch Messungen der Polymermenge in den Phasen durchgeführt. Es wurde festgestellt, dass ein Maximum auf der Kurve der Abhängigkeit des Volumens der polymerreichen Phase von

der Menge des Nichtlösers, eine für Koazervate charakteristische Eigenschaft ist. Es wurde ein Koazervat des Polyäthylenglykolterephthalats erhalten, sowie einige neue Systeme, die Polyamide enthielten—als für die Bildung von Koazervaten fähig, charakterisiert.

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