Investigations of the Phenomena of Coacervation.   Part III. Phase Equilibrium in the Three-Component System Toluene–Ethanol–Polystyrene

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Parts I and II of this work[1,2] presented the results of investigations of the phase changes of systems known in the literature as capable of forming coacervates or those we considered as such. The complete regularity with which—depending on the temperature, the composition of the solvent, and the concentration of the polymer—there appeared the two types of separation that we denoted as coacervation and demixing, as well as the possibility of giving a logical and thorough explanation of the phenomenon made us assume that coacervation is one of the phenomena of phase separation and can be expressed by means of known thermodynamic laws.   The aim set for this work is to test the above assumption.

THEORETICAL TREATMENT

The theoretical conditions of phase equilibrium for nonelectrolyte solutions have been given by Tompa[3] and Scott[4] and for electrolytes by Voorn.[5] From the binodial and the critical points of miscibility and through comparison with experimental results obtained by Dobry,[15] Bamford and Tompa[6] tried to prove the coincidence of the investigated phenomenon with simple phase separation.   However, the theoretical results did not quite agree with the experimental data.   In the author's opinion, therefore, the coincidence between the phase separation determined by the thermodynamic conditions and coacervate separation has not up to now been proved.   The main reason for the divergence will probably be the fact that the expression for the thermodynamic potential of mixing is not sufficiently precise.

Maron[7] in his publication of 1959 gave an equation for the thermodynamic potential of mixing for a two-component system.   In further works[8] it was shown that the values calculated on the basis of the given theory agreed very well over the entire concentration range with those obtained experimentally.

Generalizing Maron's expression for the thermodynamic potential of mixing ΔG_m and applying it to an n-component system, we obtain:

$$\Delta G_m / RT = \Sigma n_i \ln v_i + \ln (V^\circ/V) \Sigma n_i$$
$$+ \Sigma n_i \ln (\epsilon_i / \epsilon^\circ_i) + \Sigma m_i n_i \Sigma \chi_{ij} v_i v_j \quad (1)$$

Here, n_i denotes the mole fraction of component i; v_i is the volume fraction of component i; V° and V are the volumes of components of the system before and after mixing, respectively; ϵ_i and ϵ°_i are coefficients of effective volume of component i in the pure liquid state and in solution, respectively; χ_{ij} is the coefficient of molecular interaction between components i and j; and m_i is the ratio of molar volumes of pure component i and solvent.

If eq. (1) is used to calculate the conditions of the phase equilibrium in a three-component system, the parametric equation of the binodial will be given by eqs. (2):

$$\ln \frac{v'_1}{v''_1} + \left(1 - \frac{1}{m_2}\right)(v'_2 - v''_2) + \left(1 - \frac{\epsilon'}{\epsilon_0 m_3}\right) v'_3$$
$$+ \left(1 - \frac{\epsilon''}{\epsilon_0 m_3}\right) v''_3 + \chi_{12}(v'^2_2 - v''^2_2)$$
$$+ \chi_{13}(v'^2_3 - v''^2_3) + (\chi_{12} + \chi_{13} - \chi_{23})$$
$$\times (v'_2 v'_3 - v''_2 v''_3) = 0$$

$$\ln \frac{v'_2}{v''_2} + (1 - m_2)(v'_1 - v''_1) + \left(1 - \frac{m_2' \epsilon}{m_3 \epsilon_0}\right) v'_3$$
$$+ \left(1 - \frac{m_2 \epsilon''}{m_3 \epsilon_0}\right) v''_3 + m_2[\chi_{12}(v'^2_1 - v''^2_1)$$
$$+ \chi_{23}(v'^2_3 - v''^2_3) + (\chi_{12} + \chi_{23} - \chi_{13})$$
$$\times (v'_1 v'_3 - v''_1 v''_3)] = 0$$

$$\ln \frac{v'_3}{v''_3} + \ln \frac{\epsilon'}{\epsilon''} + \left(\frac{\epsilon'}{\epsilon_0} - m_3\right) v'_1 - \left(\frac{\epsilon''}{\epsilon_0} - m_3\right)$$

$$\times v''_1 + \left(\frac{\epsilon'}{\epsilon_0} - \frac{m_3}{m_2}\right) v'_2 - \left(\frac{\epsilon'}{\epsilon_0} - \frac{m_3}{m_2}\right) v''_2$$

$$+ \, m_3[\chi_{13}(v'^2_1 - v''^2_1) + \chi_{23}(v'^2_2 - v''^2_2)$$

$$+ \, (\chi_{13} + \chi_{23} - \chi_{12})(v'_1 v'_2 - v''_1 v''_2)] = 0 \quad (2)$$

The symbols with primes relate to data in the pre-
cipitated phase (of the coacervate) and those with
double primes to data in the equilibrant phase.

In the process of developing the above system of
equations and effecting calculations given later in
the work it was assumed that the changes in (a)
the total volume of components in the process of
dissolving, (b) coefficients of molecular interac-
tions with a change in concentration, and (c) the
coefficients of effective volume of liquid components
with a change in concentration are only slight ones
and can be neglected. These assumptions will be
discussed in the portion of the present work dealing
with calculations.

The spinodial equation and that of the critical
points of miscibility were calculated by the method
of Tompa.[3]

$$\frac{v_1}{(1 - 2\chi_1 v_1)} + \frac{m_2 v_2}{(1 - 2\chi_2 m_2 v_2)}$$

$$+ \, \frac{m_3 v_3}{(1 - 2\chi_3 m_3 v_3) + [1 - (\epsilon/\epsilon_0)]^2} = 0 \quad (3)$$

$$\frac{v_1}{(1 - 2\chi_1 v_1)^3} + \frac{m_2^2 v_2}{(1 - 2\chi_2 m_2 v_2)^3}$$

$$+ \left[\frac{m_3^2 v_3}{(1 - 2\chi_3 m_3 v_3)^3}\right] A_3 = 0 \quad (4)$$

$$A_3 = \frac{[1 + (\epsilon_0 - \epsilon) v_3]^2}{1 + 2(\epsilon_0 - \epsilon) v_3}$$

$$+ \, \frac{2(\epsilon_0 - \epsilon)^2 v_3^2}{[1 + 2(\epsilon_0 - \epsilon) v_3][1 + (\epsilon_0 - \epsilon) v_3]} \quad (4a)$$

The above expressions are equivalent to those of
Tompa only if we assume that $\epsilon = \epsilon_0$. On the
basis of experimental data of Maron, Nakajima,
and Krieger[9] it can easily be stated that this as-
sumption can introduce some error into the calcu-
lations.

Equations (3) and (4), together with eq. (5):

$$v_1 + v_2 + v_3 = 1 \quad (5)$$

can be used to calculate the coordinates of the
critical points of miscibility. In order to solve

this system of equations we used the method of
iteration. Before the iteration was started the
system had been rearranged:

$$\psi_1 = v_1/(1 - 2\chi_1 v_1)$$

$$\psi_3 = m_3 v_3/(1 - 2\chi_3 m_3 v_3)$$

$$\psi_2 = - \left\{\psi_1 + \psi_3 \frac{1 - 2\chi_3 m_3 v_3}{1 - 2\chi_3 m_3 v_3 + [1 - (\epsilon/\epsilon_0)]^2}\right\}$$

$$\hspace{10cm} (6)$$

$$v_1 = 1 - v_2 - v_3$$

$$v_3 = \frac{1}{2\chi_3 m_3} \left\{1 \pm (1 - 2\chi_1 v_1)(1 - 2\chi_2 m_2 v_2)\right.$$

$$\left. \times \left[\frac{-A_3 m_3 \psi_3}{\psi_1(1 - 2\chi_2 m_2 v_2)^2 + m_2 \psi_2(1 - 2\chi_1 v_1)^2}\right]^{1/2}\right\}$$

$$v_2 = \psi_2/m_2(1 + 2\psi_2 \chi_2)$$

If the method of successive approximations and
several iterations is used, results of the required
accuracy will be obtained easily and relatively
quickly.

Similarly the system of eqs. (2) was solved by
iteration. The numerical solution of that system
was achieved with the aid of a type XYZ electronic
calculating machine.

CALCULATIONS

In order to verify the assumption it was neces-
sary to compare the theoretical results obtained by
calculation of conditions of thermodynamic equilib-
rium of a system capable of forming coacervates
with those obtained experimentally from investiga-
tions of the phase equilibrium of the same system.

The system used for testing the basic assump-
tions had to be, first, known to be capable of
forming coacervates and, second, relatively simple
and easily handled in experimental work. These
conditions were best complied with by the toluene–
ethanol–polystyrene system.

Before attempting a numerical solution of eqs.
(2) and (6), we considered it necessary to determine
the value of the semiempirical coefficients χ_{ij}
and to examine the correctness of the assumptions
made previously. These values were determined
for the conditions under which the system was to
be investigated experimentally, i.e., for a tempera-
ture of 25°C. and $\bar{M}_v = 162{,}000$.

The value of χ_{12}, the coefficient of molecular
interaction between toluene (1) and ethanol (2),
was determined by linear extrapolation to 25°C.

of the value found by Kretchmer and Viebe[10] for temperatures of 35 and 55°C.; this yielded, for the temperature of measurement (25°C.), $\chi_{12} = 1.971$. Kretchmer and others have shown that the coefficient of molecular interaction in this system does not depend on concentration.

The value of χ_{13}, the coefficient of molecular interaction between toluene (1) and polystyrene (3), was calculated on the basis of the equation of Krigbaum et al.:[11]

$$A_2 = (v_3{}^2/V_1)\psi[1 - (\Theta/T)]F(Z,\delta) \qquad (7)$$

and by a logarithmic interpolation of data of Frank and Mark[12] for the corresponding molecular weight of polystyrene. The value accepted for further calculations was $\chi_{13} = 0.445$.

From the work quoted above[12] it is evident that the value of χ_{13} remains unaltered for the concentrations range of 0–1.2 g./100 ml. of solution. The experimental data given in other works indicate that the coefficient in question is constant over a much wider concentration interval than this; e.g., Bawn, Freeman, and Kamaliddin[13] give information according to which χ_{13} remains uninfluenced within the limits of the experimental error up to a concentration of 10 g./100 ml. It follows that it is permissible to assume invariability of the molecular interaction coefficient for low and medium concentrations in this system. In the case of higher concentrations, the error is relatively small and admissible for the problems under investigation.

The value of χ_{23} was determined as follows: the Θ concentration was determined at 25°C. by viscometric measurements and its average molecular interaction coefficient amounted to 0.5. If it is assumed that:

$$\bar{\chi} = \frac{\chi_{13}v_1 + \chi_{23}v_2}{v_1 + v_2} - \frac{\chi_{12}v_1v_2}{(v_1 + v_2)^2} \qquad (8)$$

the required value is found to be: $\chi_{23} = 2.231$. In this case the assumption of invariability of the molecular interaction coefficient in relation to concentration was natural.

As had been proved by Maron, Nakajima, and Krieger,[9] the functional dependence of the effective volume coefficient on concentration was the following:

$$\epsilon/\epsilon_0 = l/[1 + (\epsilon_0 - \epsilon_\infty)v_3] \qquad (9)$$

The value of ϵ_0 was determined from viscosity measurements; the value of $\epsilon_\infty = 4.00$ was based on the data of Maron et al.[9] Thus:

$$\epsilon = 37.90/(1 + 33.90 \, v_3)$$

From eq. (9) it can easily be found that the changes in the effective volume coefficients of liquid components are very small and to neglect them results in only a slight calculation error.

The admissibility of neglecting the influence of total volume changes in the components in the course of solution on the thermodynamic data under consideration was tested by direct measurements and from the data on density changes in the toluene–ethanol system as given by Timmermans.[16] The error resulting from the assumption in question was found to be within the limits of the normal measurement error.
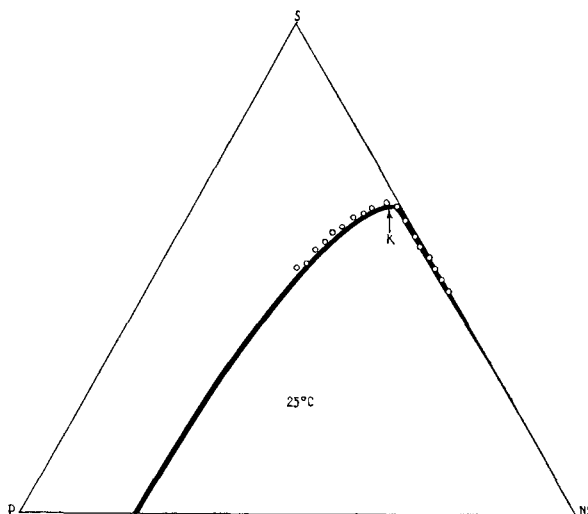

Fig. 1. Phase diagram of the system: toluene–ethanol–polystyrene at 25°C., $\bar{M}_v = 162,000$: (O) experimental points; (——) theoretical separation curve calculated from eqs. (2). K is the critical point of miscibility calculated from eqs. (6).

As a result of substituting the numerical semiempirical values of coefficients in the system of eqs. (2) and (6) and of iteration as mentioned above, numerical data were obtained which permitted determination of the binodial curve and the coordinates of critical points. This is shown in Figure 1.

In the course of calculations with eq. (6) use was made of Scott's remark[4] that if $m_3 \geq 1000$, then, with a certain approximation, $m_3 \to \infty$, and results obtained are given in the first line of Table I. Another approximation was the assumption that $\epsilon = \epsilon_0$, i.e., that the system of eqs. (6) can be reduced to Tompa's system. The results obtained for this assumption are given in the second line of Table I. The final solution of system of eqs. (6) is shown in the third line of this table.

TABLE I

Approximation	v_1	v_2	v_3
Scott	0.6638	0.3362	0.0000
Tompa	0.6332	0.3490	0.0178
This work, eq. (6)	0.6303	0.3504	0.0193

Table I shows the influence that the simplifying assumptions have on the final result. They are of greatest importance for v_3 which, in turn, is fairly essential for the problems of phase equilibria in the systems that are now under consideration.

EXPERIMENTAL

The reagents used, the apparatus, and the method of determining the binodial curve were analogous to those described in the two previous parts of the present study.[1,2] As stated before, the temperature at which experiments were carried out was 25°C. and $\bar{M}_v = 162,000$. The points in Figure 1 lying just over the theoretical separation curve (continuous line) illustrate the results of the experiments.

The deviation of experimental points from the theoretical curve is due mainly to the fact that the viscosity-average molecular weight M_v, instead of E.E. molecular weight as proposed by Tompa,[14] was used in the calculations, and also to the simplification introduced into the calculation of χ_{23} as a result of using eq. (8).

CONCLUSIONS

On the basis of a comparison of theoretical results obtained by applying Maron's theory to the general laws of thermodynamic phase equilibrium with the experimental data the following statements can be advanced.

(1) There exists a satisfactory agreement of theoretical and experiments results.

(2) Coacervate separation is indeed a separation belonging to the group of phase separations described by fundamental thermodynamic dependences.

(3) The application to phase equilibrium calculations of the equation systems above developed instead of those given by Tompa makes the results more accurate and is therefore useful.

(4) The two types of phase separations, coacervation and demixing, discussed in the foregoing parts of this work present, from the thermodynamic point of view, the same phenomenon. In view of the fact that the former of the two types of separation is very useful in fractionation it seems appropriate to establish two different names for the two different forms.

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Synopsis

The goal of this work was to prove that the phenomenon of coacervation was one of the phenomena of phase separation determined by the general laws of thermodynamic phase equilibrium. In this connection, the toluene–ethanol–polystyrene system, known from the literature to be capable of forming coacervates: was studied, and the binodial curve as well as a number of semiempirical coefficients necessary for its theoretical determination established experimentally. For the latter purpose use was made of a generalized form of Maron's equation for the thermodynamic potential of mixing. The experimental and theoretical data showed good agreement. It was therefore concluded that systems capable of forming coacervates are subject to the general laws of thermodynamic equilibrium, and formation of coacervates is a phenomenon within the limits of a simple phase separation.

Résumé

On a étudié le système décrit dans la littérature scientifique comme capable de former des coacervats: toluène–éthanol–polystyrolène, pour prouver que la coacervation n'est qu'un phénomène de séparation de phases, déterminé

par les conditions générales d'équilibre de phases. On a déterminé expérimentalement la courbe binodiale, ainsi que les valeurs numériques des coefficients semi-empiriques qui étaient nécessaires pour la courbe théorique. L'équation de Maron exprimant l'énergie libre de mélange généralisée par l'auteur a été employée pour le calcul théorique de la binodiale. Les résultats expérimentaux sont d'un bon accord avec ceux obtenus par le calcul. On a déduit, en se basant sur les résultats obtenus, que les systèmes capables de former des coacervats sont soumis aux lois générales de la thermodynamique et la formation du coacervat est un phénomène de séparation de phases.

Zusammenfassung

Die vorliegende Arbeit wurde unternommen, um zu beweisen, dass die Erscheinung der Koazervation eine Art der Phasenverteilung ist, die durch die allgemeinen thermodynamischen Bedingungen für Phasengleichgewichte besch-rieben werden kann. Zu diesem Zweck wurde das System Toluol-Äthanol-Polystyrol untersucht, das zur Bildung von Koazervaten fähig ist. Auf Grund der Untersuchungen wurde experimentell die Binodalkurve für die Temperatur von 25°C, sowie eine Reihe von halbempirischen Koeffizienten, die für die theoretische Berechnung der Binodalkurve notwendig sind, bestimmt. Bei der theoretischen Bestimmung der Binodalkurve wurde die verallgemeinerte Formel von Maron für das thermodynamische Potential der Mischung angewandt. Der Vergleich der experimentellen Ergebnisse mit den theoretisch berechneten Werten ergab gute Übereins'immung. Daraus kann man schliessen, dass die Systeme, die zur Bildung von Koazervaten fähig sind, den allgemeinen Gesetzen des thermodynamischen Gleichgewichts unterliegen und dass die Bildung von Koazervaten eine in den Grenzen der normalen Phasenverteilung liegende Erscheinung ist.