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Thermodynamic Perturbation Theory of Phase Separation in Macromolecular Multicomponent Systems. 2. Concentration Dependence[†‡]

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ABSTRACT: A perturbation-theoretical approach to the concentration dependence of phase separation in quasiternary macromolecular solutions consisting of polymer, solvent, and nonsolvent is developed. It results in a linear semilogarithmic phase equation $\gamma_F{}^* = A_c - \sigma_c{}^* \ln c_0$, where $\gamma_F{}^*$ denotes the precipitant fraction (volume fraction of the precipitant at the cloud point) and c_0 the initial polymer concentration in g/cm^3. Here, A_c and $\sigma_c{}^*$ are constants with A_c as the precipitant fraction at $c_0 = 1$ g/cm^3 and $\sigma_c{}^*$ the inverse value of the change of the relative perturbation density $(\Delta\mu^*{}_{\mathcal{P}F,c})$. The theory is verified experimentally at 25 °C by investigation of the three different systems: (a) polystyrene–benzene–methanol; (b) poly(methyl methacrylate)–benzene–cyclohexane; (c) poly(ϵ-caprolactam)–*m*-cresol–petroleum ether. Fast turbidimetric titration measurements on the basis of the dynamic volume pulse technique were used. The perturbation-theoretical approach is confirmed furthermore by numerous experimental results taken from the literature. The results are compared critically with the earlier approaches on the basis of statistical thermodynamics, partition equilibria, and solution equilibria. In this context, the effect of the constant ratio of the solvent/nonsolvent in the gel phase is interpreted theoretically.

I. Introduction

This paper is concerned with a perturbation-theoretical approach to the initial concentration dependence of phase separation in macromolecular multicomponent systems after the addition of nonsolvent (precipitant), and with applications of the theory. The approach is based on concepts that I have developed in previous papers.[1-3] The assumptions and basic equations have been set out in the first paper of this series.[3]

Firstly, it is shown how the perturbation relations can be applied to calculating the functional dependence of the precipitant fraction (volume fraction of the nonsolvent at the precipitation threshold, $\gamma_F{}^*$) from the original polymer concentration, taking into account the macromolecular phase concentrations. Then, the theory is applied to various multicomponent macromolecular systems. The results obtained are scrutinized and compared critically with earlier attempts at problem solution such as, e.g., partition equilibria[4,5] and solution equilibria.[6,7]

II. Fundamentals: The Perturbation-Theoretical Approach of Phase Separation in Fluid Macromolecular Multicomponent Systems

Addition of nonsolvent to a homogeneous macromolecular solution may cause its disintegration by polymer precipitation. The simplest system here is now a fluid heterogeneous ternary one. Generally, however, solutions of macromolecules in solvent/nonsolvent mixtures are quasiternary multicomponent systems. In the following, the assumptions and the notation of ref 3 are used.

Let the finite set of a multicomponent macromolecular solution of nonelectrolytes $|K_0 = \{1, 2, ..., L_\lambda, ..., \mathcal{P}_j, ..., F_{\varkappa-1}, F_{\varkappa+1}, ..., r\}$ be perturbed by the admixture of a nonsolvent $F_\varkappa \notin |K_0$. Then, the system passes from the reference state $|K_0 \rightarrow |K = \{1, 2, ..., L_\lambda, ..., \mathcal{P}_j, ..., F_\varkappa, ..., r\} = |K_0 + \{F_\varkappa\}$, $F_\varkappa \in |K \supset |K_0((j,\lambda,\varkappa) \in N_{r(j,\lambda,\varkappa)})$. Let the statistical polymer component in the precipitation equilibrium which is

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[†] This paper is dedicated to Professor Maurice L. Huggins on the occasion of his 80th birthday, but publication unfortunately had to be delayed.

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perturbed be the main component $\mathcal{P}_j \in |P \subset |K_0$, the perturbing precipitant be the secondary component of the first kind $F_\varkappa \in |F \subset |K$, and the remaining members of set $|K$ be the additional components of the second kind $|K'' = |K - \{\mathcal{P}_j,F_\varkappa\}$; $(\mathcal{P}_j,F_\varkappa) \notin |K'')^3$. The corresponding r-tuples of volume fractions are (see ref. 3, eq 5): $\tilde{\gamma}_0 = (\gamma_1, \gamma_2, ..., \gamma_{L_\lambda}, ..., \gamma_{\mathcal{P}_j}, ..., \gamma_{F\varkappa-1}, \gamma_{F\varkappa+1}, ..., \gamma_r)$ and $\tilde{\gamma} = (\gamma_1, \gamma_2, ..., \gamma_{L_\lambda}, ..., \gamma_{\mathcal{P}_j}, ..., \gamma_{F\varkappa}, ..., \gamma_r)$. In this context, the subscripts $\mathcal{P}_j$, L_λ, and $F_\varkappa$ designate the respective polymer, solvent, and nonsolvent components. In the following, since there is no risk of confusion, the simplified perturbation notation will be used (see ref 3, section IV.1).

As pointed out in ref 3, the investigation of the most important quasiternary systems ($\overline{K} \equiv r > 3$, $\overline{\mathcal{P}} > 1$, $\overline{L} = \overline{F} = 1$) can be restricted to the analysis of ternary systems ($\overline{K} \equiv r = 3$, $\overline{\mathcal{P}} = \overline{L} = \overline{F} = 1$). Hence, for $(\alpha-\beta)$ phase separation in (quasi-) ternary macromolecular solutions the difference of the perturbed chemical phase potentials of the polymer $\Delta\mu_{\mathcal{P}}^{(\alpha-\beta)}$ and the related change of the chemical polymer potentials of the unperturbed reference states $\Delta\mu_{\mathcal{P}}(0)$ are linearly combined with the precipitant fraction γ_{F}

$$\Delta\mu_{\mathcal{P}}^{(\alpha-\beta)} = \Delta\mu_{\mathcal{P}}(0) + \Delta\mu^*{}_{\mathcal{P}\mathrm{F}}\gamma_{\mathrm{F}} = \Delta\mu_{\mathcal{P}}(0) + \frac{RT}{\sigma^*}\gamma_{\mathrm{F}} \quad (1)$$

Equation 1 can be assumed to be a first-order perturbation series expansion in powers of (small) γ_{F}. The product terms on the right-hand sides mean the perturbation. Hereby, $\Delta\mu^*{}_{\mathcal{P}\mathrm{F}}$ denotes the $(\alpha-\beta)$ change of the perturbation density, σ^* the dimensionless inverse relative phase change of the perturbation density, and γ_{F} the relative strength of perturbation by the addition of nonsolvent. Its minimum is $\gamma_{\mathrm{F,min}} = 0$ and its maximum $\gamma_{\mathrm{F,max}} = 1$. In this context, regarding the reference states of the sol ($\gamma_{\mathcal{P}}{}^\alpha \to 0$) and gel phases ($\gamma_{\mathcal{P}}{}^\beta \to 1$), it was borne in mind that the original (quasi-) binary macromolecular solutions are highly diluted ($\gamma_{\mathcal{P}}(0) \to 0$). Therefore, one can assume $\mu_{\mathcal{P}}{}^\alpha(0) = \mu_{\mathcal{P}}(0)$ and $\mu_{\mathcal{P}}{}^\beta(0) = \mu_{0\mathcal{P}}$ where $\mu_{\mathcal{P}}(0) = \mu_{\mathcal{P}}(\tilde{\gamma}_0)$ denotes the chemical polymer potential of the original (quasi-) binary solution and $\mu_{0\mathcal{P}}$ is the chemical standard polymer potential (see ref 3).

For practical applications these facts are in accordance with the two limit cases discussed in ref 3, Section III.2. Hence, according to ref 3, the application of eq 9, 11, 12 to eq 21b results approximately in ($\mu_{0\mathcal{P}}(0) = \mu_{0\mathcal{P}} + RT \ln b_{0\mathcal{P}}(0)$)

$$\Delta\mu_{\mathcal{P}}(0) = \mu_{\mathcal{P}}(0) - \mu_{0\mathcal{P}} \approx \hat{\mu}_{0\mathcal{P}} + RT \ln \gamma_{\mathcal{P}}(0) - \mu_{0\mathcal{P}} = RT(\ln \gamma_{\mathcal{P}}(0) + \ln b_{0\mathcal{P}}(0)) \quad (2)$$

Combining eq 15 of ref 3 and eq 1, one obtains

$$\Delta\mu_{\mathcal{P}}{}^{(\alpha-\beta)} = RT[\ln \gamma_{\mathcal{P}}(0) + \ln b_{0\mathcal{P}}(0)] + \Delta\mu^*{}_{\mathcal{P}\mathrm{F}}\gamma_{\mathrm{F}} = RT[\ln \gamma_{\mathcal{P}}(0) + \ln b_{0\mathcal{P}}(0)] + \frac{RT}{\sigma^*}\gamma_{\mathrm{F}} \quad (3)$$

according to ref 3, Section III.2. Here,

$$b_{0\mathcal{P}}(0) = f_{\mathcal{P}}/\hat{f}_{\mathcal{P}} = \exp[(\hat{\mu}_{0\mathcal{P}} - \mu_{0\mathcal{P}})/RT] = \exp[-(\Delta^{\mathrm{E}}\hat{\mu}_{\mathcal{P}} - \Delta^{\mathrm{E}}\mu_{\mathcal{P}})/RT] \quad (4)$$

designates the limit polymer activity coefficient of the initially highly diluted (quasi-) binary macromolecular solution.

Applying the analogous considerations, including the two thermodynamic limit cases cited in ref 3, to the sol and gel phases, it results (see ref 3, eq 1, 9, 11, 12; $\mu_{0\mathcal{P}}{}^\alpha = \mu_{0\mathcal{P}}{}^\beta = \mu_{0\mathcal{P}}$; $\gamma_{\mathcal{P}}{}^\alpha \to 0$; $\gamma_{\mathcal{P}}{}^\beta \to 1$):

$$\mu_{\mathcal{P}}{}^\alpha = \mu_{0\mathcal{P}} + RT \ln a_{\mathcal{P}}{}^\alpha \approx \hat{\mu}_{0\mathcal{P}}{}^\alpha + RT \ln \gamma_{\mathcal{P}}{}^\alpha = \mu_{0\mathcal{P}} + RT(\ln \gamma_{\mathcal{P}}{}^\alpha + \ln b_{0\mathcal{P}}{}^\alpha) \quad (5a)$$

$$\mu_{\mathcal{P}}{}^\beta = \mu_{0\mathcal{P}} + RT \ln a_{\mathcal{P}}{}^\beta \approx \mu_{0\mathcal{P}} + RT \ln \gamma_{\mathcal{P}}{}^\beta \approx \mu_{0\mathcal{P}} \quad (5b)$$

$$\Delta\mu_{\mathcal{P}}{}^{(\alpha-\beta)} = RT \ln (a_{\mathcal{P}}{}^\alpha/a_{\mathcal{P}}{}^\beta) \quad (5c)$$

Introducing these expressions on the left-hand sides of eq 1 to 3, after transformation one obtains for the precipitant fraction ($\gamma_{\mathcal{P}}(0)b_{0\mathcal{P}}(0) = a_{\mathcal{P}}(0)$):

$$\gamma_{\mathrm{F}} = \frac{RT}{\Delta\mu^*{}_{\mathcal{P}\mathrm{F}}}[\ln (a_{\mathcal{P}}{}^\alpha/a_{\mathcal{P}}{}^\beta) - \ln a_{\mathcal{P}}(0)] \approx \sigma^*\left[\ln (\gamma_{\mathcal{P}}{}^\alpha/\gamma_{\mathcal{P}}{}^\beta) - \ln \gamma_{\mathcal{P}}(0) + \ln\frac{b_{0\mathcal{P}}{}^\alpha}{b_{0\mathcal{P}}(0)}\right] \quad (6)$$

Here, $a_{\mathcal{P}}(0)$ is the polymer activity of the original solution and $b_{0\mathcal{P}}{}^\alpha$ the polymer limit activity coefficient of the sol phase. In the case of the most important quasiternary macromolecular solutions ($\overline{K} \equiv r > 3$, $\overline{\mathcal{P}} > 1$, $\overline{L} = \overline{F} = 1$), subscripts $\mathcal{P}_j$ in lieu of $\mathcal{P}$ should formally be used.

III. Perturbation-Theoretical Approach to the Concentration Dependence of Phase Separation in Fluid Macromolecular Multicomponent Systems

To determine the concentration dependence of phase separation in (quasi-) ternary macromolecular solutions, eq 3 or 6 can be used according to choice. At phase equilibrium and constant molecular weight (M) of the statistical polymer component involved, according to eq 1 and 15 of ref 3, it is (($T,p,M,\dot{w}$) = constant; $\dot{w}$ = injection rate)

$$\mu_{\mathcal{P}}{}^\alpha = \mu_{\mathcal{P}}{}^\beta \quad (7a)$$

$$\Updownarrow$$

$$a_{\mathcal{P}}{}^\alpha = a_{\mathcal{P}}{}^\beta \quad (7b)$$

$$\Downarrow$$

$$\gamma_{\mathcal{P}}{}^\alpha f_{\mathcal{P}}{}^\alpha = \gamma_{\mathcal{P}}{}^\beta f_{\mathcal{P}}{}^\beta \quad (7c)$$

Hence, from eq 21a of ref 3 and eq 5c it follows that $\Delta\mu_{\mathcal{P}}{}^{(\alpha-\beta)} = 0$. Combining this result with eq 3, after rearrangement one obtains

$$\gamma_{\mathrm{F}}^* = -\frac{RT}{\Delta\mu^*{}_{\mathcal{P}\mathrm{F,c}}}[\ln b_{0\mathcal{P}}(0) + \ln \gamma_{\mathcal{P}}(0)] = \sigma_{\mathrm{c}}^*\left[\ln \frac{1}{b_{0\mathcal{P}}(0)} - \ln \gamma_{\mathcal{P}}(0)\right] \quad (8)$$

where γ_{F}^* denotes the precipitant fraction at the cloud point. Going over from the volume fraction to the initial weight concentration of the polymer ($c_0 = \gamma_{\mathcal{P}}(0)\bar{\rho}_{\mathrm{P}}$ g/cm^3; $\bar{\rho}_{\mathrm{P}}$ = partial density of the polymer), we arrive at the linear semilogarithmic function

$$\gamma_{\mathrm{F}}^* = \sigma_{\mathrm{c}}^*\left[\ln \frac{\bar{\rho}_{\mathrm{P}}}{b_{0\mathcal{P}}(0)} - \ln c_0\right] = A_{\mathrm{c}} - \sigma_{\mathrm{c}}^* \ln c_0 \quad (9)$$

This is the phase equation when ($T,p,M,\dot{w}$) = constant and

$$A_{\mathrm{c}} = \sigma_{\mathrm{c}}^* \ln (\bar{\rho}_{\mathrm{P}}/b_{0\mathcal{P}}(0)) \quad (10)$$

In eq 8–10 the perturbation parameters $\Delta\mu^*{}_{\mathcal{P}\mathrm{F,c}}$ and σ_{c}^* were labeled by the subscript c. A_{c} designates the precipitant fraction at $c_0 = 1$ g/cm^3. The corresponding volume fraction is equal to the dimensionless quantity of $\gamma_{\mathcal{P}}(0) = |1/\bar{\rho}_{\mathrm{P}}| = |\bar{v}_{\mathrm{P}}|$.

Plotting γ_{F}^* vs. $\ln c_0 = 2.303 \log c_0$, one should get a linear decreasing function of the slope $\mathrm{d}\gamma_{\mathrm{F}}^*/\mathrm{d} \ln c_0 = -\sigma_{\mathrm{c}}^*$. Accordingly, the decrease of the precipitant fraction at incipient phase separation should be proportional to the reciprocal relative perturbation density σ_c^*, as well as to the relative increase of the initial polymer concentration, $-d\gamma_F^* = \sigma_c^*\, dc_0/c_0$.

According to eq 4 and in addition to $\bar{\rho}_P$ and σ_c^* in eq 9 and 10, the polymer limit activity coefficient of the original (quasi-) binary macromolecular solution $b_{0\mathcal{P}}(0)$ is a further constant. In connection with A_c which may be obtained experimentally as the intercept at $c_0 = 1$ g/cm^3, $b_{0\mathcal{P}}(0)$ can be determined at known polymer density according to

$$\ln b_{0\mathcal{P}}(0) = \ln \bar{\rho}_P - A_c/\sigma_c^* \qquad (11a)$$

$$b_{0\mathcal{P}}(0) = \bar{\rho}_P \exp(-A_c/\sigma_c^*) \qquad (11b)$$

Therefore, all the constants of eq 9–11 can be determined experimentally.

Starting the perturbation calculations from eq 7b,c we arrive at the same expressions for the concentration dependence of γ_F^* as given by eq 9. Beyond that, however, one obtains additional information with regard to the "interior" state of phase equilibria in (quasi-) ternary macromolecular multicomponent systems, because it follows

$$\gamma_{\mathcal{P}}{}^{\alpha}/\gamma_{\mathcal{P}}{}^{\beta} = f_{\mathcal{P}}{}^{\beta}/f_{\mathcal{P}}{}^{\alpha} \approx 1/b_{0\mathcal{P}}{}^{\alpha} \qquad (12)$$

Here, the right-hand side is obtained by applying the two thermodynamic limit cases cited in ref 3, Section III.2 ($\gamma_{\mathcal{P}}{}^{\alpha} \rightarrow 0, f_{\mathcal{P}}{}^{\alpha} \rightarrow b_{0\mathcal{P}}{}^{\alpha}; \gamma_{\mathcal{P}}{}^{\beta} \rightarrow 1, f_{\mathcal{P}}{}^{\beta} \rightarrow 1$). Equation 12 means a constant ratio of the equilibrium polymer volume fractions in the sol and gel phase irrespective of the initial polymer concentration c_0. In the case of a quasiternary macromolecular solution with a finite polymer subset $|\mathrm{P}$ of cardinal number $\bar{\mathcal{P}} > 1$, eq 12 is valid obviously for each statistical polymer component, and subscripts $\mathcal{P}_j$ instead of $\mathcal{P}$ must be used.

Finally, on account of the concentration eq 6 of ref 3 one can calculate the course of the boundary curves of phase separation in macromolecular multicomponent systems according to

$$1 = \sum_{j,\varkappa,\lambda}(\gamma_{\mathcal{P}_j}{}^* + \gamma_{F\varkappa}{}^* + \gamma_{L_\lambda}{}^*), \qquad (\bar{K} > 3;\ (j,\varkappa,\lambda) \in |N_{r(j,\varkappa,\lambda)}) \qquad (13a)$$

$$1 = \gamma_{\mathcal{P}}{}^* + \gamma_F{}^* + \gamma_L{}^*, \qquad (\bar{K} = 3;\ \bar{\mathcal{P}} = \bar{F} = \bar{L} = 1) \qquad (13b)$$

Here, the asterisks designate the cloud-point concentration of the various components of a mixture, calculated according to eq 14 of the following section IV.

IV. Experimental Section

The precipitant fractions were determined by fast turbidimetric titration, according to the dynamic volume pulse technique (see ref 9 and 10). For that purpose, a thermostated semiautomatic recording turbidity measuring device for the fast optical precipitation analysis of polymer solutions was applied as previously described.[9] The precipitations were carried out at injection rates of ca. $\dot{w} \approx 20$ cm^3/min. For the computation of γ_F^*, the linear portion of a recorder curve was extrapolated to the point of intersection with the time axis (abscissa) which is correlated, via the injection rate $\dot{w}$, with the injected precipitant volume (V_F). The measuring periods were less than a minute. The measurements were carried out with white light at 25 °C, using solutions of polystyrene, poly(methyl methacrylate), and poly(ϵ-caprolactam). They were adapted to optimum precipitation conditions by the preaddition of certain amounts of precipitant. Hereby, "tilted states" (in German "Kippzustände") were approached, just within the cloud-point thresholds.[9,11]

The turbidimetric precipitation conditions are summarized in Table I. Details of the evaluations are given in ref 9. The accuracy equals 0.1% (cf. ref 9). Mixing additivity of the volumes was presumed. The solvents employed were of analytical grade, mainly from Merck (Darmstadt) or Riedel de Haen (Seelze). Some characteristic properties are given in Table II. The refractive indices were measured by the aid of an Abbê refractometer (Zeiß, Oberkochen).

Table I

Solution and Precipitation Conditions to Polystyrene, Poly(methyl methacrylate), and Poly(ϵ-caprolactam) at 25 °C[a]

	polystyrene	poly(methyl methacrylate)	poly(ϵ-caprolactam)
type	fractionated	fractionated	unfractionated
U	<0.2	<0.2	0.7
$\bar{M}_\eta$	99000	43000	25000
solvent	benzene	benzene	*m*-cresol
precipitant	methanol	cyclohexane	petroleum ether
$c_0 \times 10^3$ (g/cm^3)	0.1–1.0	0.2–2.0	0.1–1.0
adaptation ratio ($V_{F,0}/V_{L,0}$)	5/22	6/10	3/10

[a] c_0 = original polymer concentration, $V_{F,0}$ = initial precipitant volume, $V_{L,0}$ = initial solvent volume, $\bar{M}_\eta$ = viscometric molecular weight average, U = nonuniformity.

Table II

Properties of the Solvents and Nonsolvents at 25 °C

solvent	uncorrected bp, °C	refractive index ($n^{25}{}_D$)
benzene	80.0	1.4980
m-cresol	202.5	1.5388
cyclohexane	80.9	1.4236
methanol	64.5	1.3265
petroleum ether	36–38	1.3570

The polystyrene (PS) and the poly(methyl methacrylate) (PMA) samples were radically polymerized under nitrogen, using azobis(isobutyronitrile) as initiator. Both samples were practically unbranched and double fractionated from benzene–methanol and benzene–light gasoline (C_5–C_8 cut) mixtures, respectively. The nonuniformities[4] amounted to about 0.1 to 0.2. The poly(ϵ-caprolactam) (PA 6) was hydrolytically autoclave polymerized. Most of the low molecular compounds, about 10% by weight, were removed by washing with hot water, followed by drying under vacuum (2 Torr/110 °C). The conditions of polymerization and treatment are published in detail elsewhere.[12-14] The PA 6 sample was unfractionated.

The molecular weight determinations (Table I) were carried out viscometrically at 25 °C, using a modified Ubbelohde suspended level viscometer.[15] Corrections for shear were not necessary. Reduced specific viscosities were extrapolated to the intrinsic viscosities $[\eta]$ by graphic or mathematical methods, using the improved single-point determination.[16] The calculation of the molecular weights ($\bar{M}_\eta$) was performed by the use of the Staudinger–Kuhn–Mark equation $[\eta] = K_\eta M^a$ with the aid of known $[\eta]$–M calibration curves (see: PME in benzene;[17] PS in benzene;[18] PA 6 in *m*-cresol[19]).

The partial specific volumes and densities were determined pycnometrically, for the evaluation see ref 20 and 21. The polymer concentration at the cloud point followed from

$$c^* = c_0(1 - \gamma_F^*) \qquad (14a)$$

$$\gamma_{\mathcal{P}}{}^* = \gamma_{\mathcal{P}}(0)(1 - \gamma_F^*) \qquad (14b)$$

V. Results

In Figure 1 the precipitant fractions of the three systems (a) polystyrene–benzene–methanol, (b) poly(methyl methacrylate)–benzene–cyclohexane, and (c) poly(ϵ-caprolactam)–*m*-cresol–petroleum ether at 25 °C are plotted vs. the logarithm of the initial concentration c_0. The semilogarithmic graphs are linear, thus verifying, also at the high injection rates applied, the perturbation-theoretical approach to the concentration dependence of phase

Table III
Parameter Values to the Concentration Dependence of the Precipitant Fraction at 25 °C (the Magnitudes are Explained in the Text)

	system a[b]	system b[c]	system c[d]
$\overline{M}_\eta$	99000	43000	25000
$\Delta\mu^*_{PF,c} \times 10^{-4}$ (cal/mol)	5.378 ± 0.013	2.820 ± 0.007	5.524 ± 0.022
$\Delta\mu^*_{PF,c} \times 10^{-4}$ (J/mol)	22.50 ± 0.05	11.80 ± 0.03	23.11 ± 0.09
$\sigma_c^* \times 10^2$	1.101 ± 0.003	2.100 ± 0.005	1.072 ± 0.004
A_c	0.2168 ± 0.0002	0.3177 ± 0.0004	0.5518 ± 0.0003
$b_{0P}(0)$	3.057×10^{-9}	3.334×10^{-7}	5.110×10^{-23}
$\bar{v}_P$ (cm³/g)	0.9174[a]	0.8080[a]	0.8779
$\bar{\rho}_P$ (g/cm³)	1.0900[a]	1.2376[a]	1.1391

[a] After ref 22. [b] Polystyrene-benzene-methanol. [c] Poly(methacrylate)-benzene-cyclohexane. [d] Poly(ϵ-caprolactam)-m-cresol-petroleum ether.

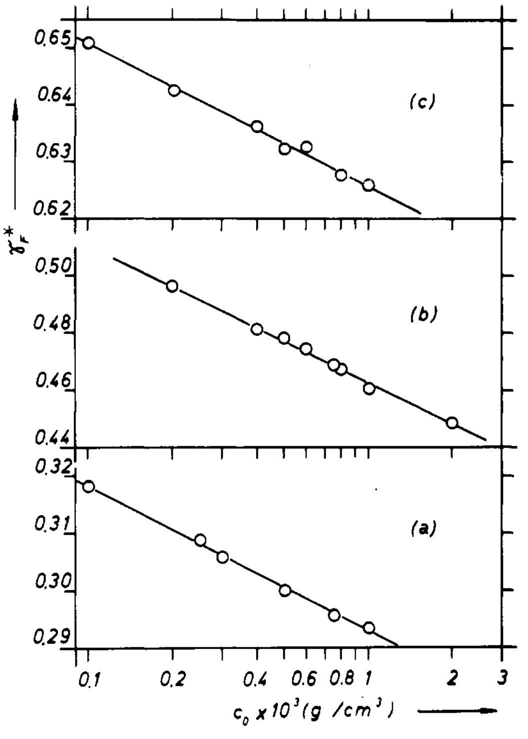

Figure 1. Plot of the precipitation fraction γ_F^* vs. log c_0 at 25 °C where c_0 in g/cm³ is the initial polymer concentration. The systems studied are: (a) polystyrene ($\bar{M}$ = 99000)-benzene-methanol; (b) poly(methyl methacrylate) ($\bar{M}$ = 43000)-benzene-cyclohexane; (c) poly(ϵ-caprolactam) ($\bar{M}$ = 25000)-m-cresol-petroleum ether.

separation in (quasi-) ternary macromolecular solutions which led to the corresponding phase eq 9. Therefore, eq 9 may be applied to evaluate the experiments. The results for the three systems studied are summarized in Table III. Here, $\Delta\mu^*_{PF,c}$ denotes the change of the perturbation densities as energies per amount of substance and σ_c^* the respective nondimensional relative inverse values, related to RT. The A_c values designate the values of the precipitant fractions of the various systems if the initial polymer concentration is taken to be c_0 = 1 g/cm³. In this instance, the initial volume fractions of the polymer $\gamma_P(0)$ would be equal to the nondimensional amounts of the partial specific volumes $\bar{v}_P = 1/\bar{\rho}_P$ (see section III).

Applying the experimentally obtained parameter values of Table III to eq 9, by making use of eq 14 and according to eq 13, we can calculate all the volume fractions at incipient phase separation which yield the (quasi-) ternary phase diagrams of the macromolecular solvent-precipitant systems investigated. The results for the polystyrene, the poly(methyl methacrylate), and the poly(ϵ-caprolactam) systems are shown in Figures 2-4 where "P" denotes the polymer, "L" the solvent and "F" the nonsolvent angles.

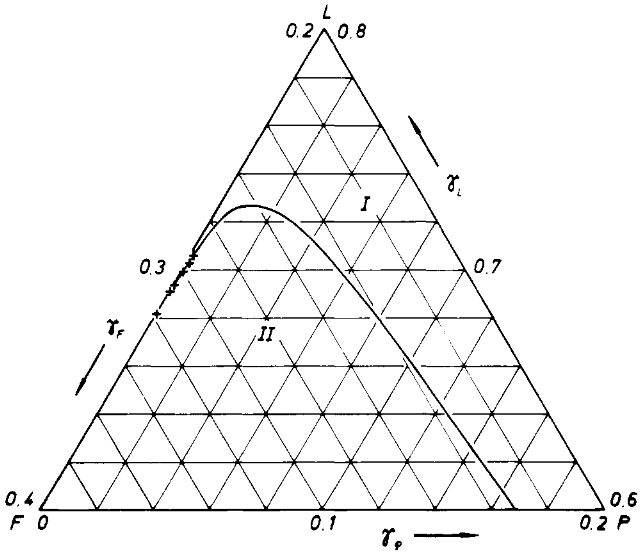

Figure 2. Phase diagram at 25 °C for the (quasi-) ternary system polystyrene ($\bar{M}$ = 99000; P)-benzene (L)-methanol (F). The crosses are the experimental values (+). Plotted are the volume fractions at incipient phase separation. The phase line (—) was calculated by the use of eq 9 and 13 in accordance with the parameter values of Table III, system a. Here, (P) means the polymer, (L) the solvent, (F) the precipitant, and (I) the homogeneous and (II) the heterogeneous region.

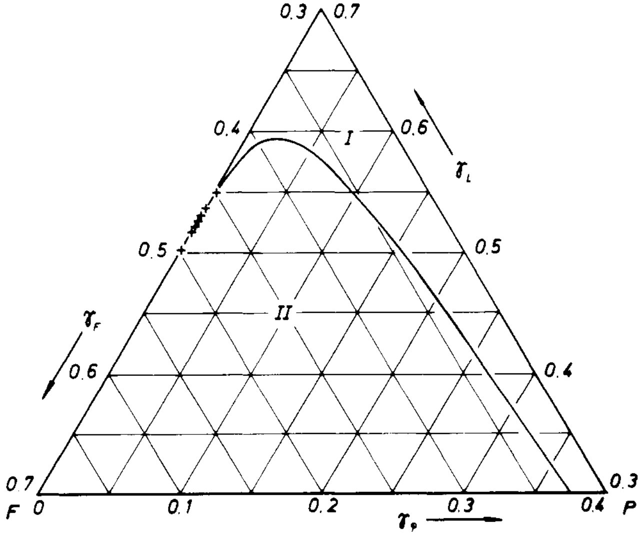

Figure 3. Phase diagram at 25 °C for the (quasi-) ternary system poly(methyl methacrylate) ($\bar{M}$ = 43000; P)-benzene (L)-cyclohexane (F). The crosses are the experimental values (+). Plotted are the volume fractions at incipient phase separation. The phase line (—) was calculated by the use of eq 9 and 13 in accordance with the parameter values of Table III, system b. Here, (P) denotes the polymer, (L) the solvent, (F) the nonsolvent, and (I) the homogeneous and (II) the heterogeneous region.

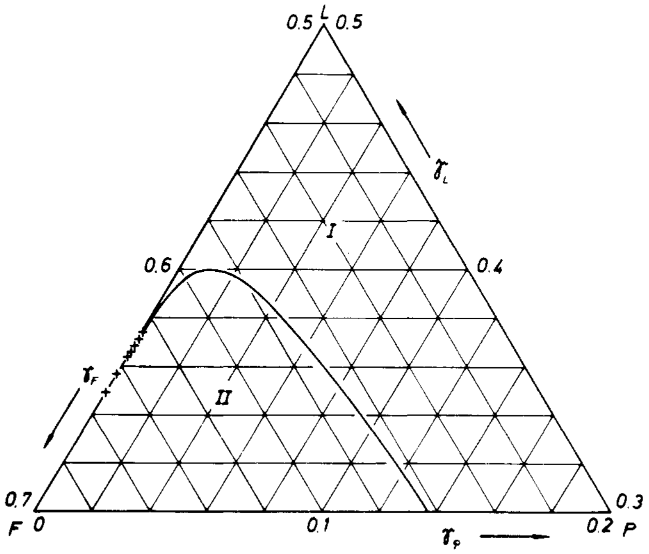

Figure 4. Phase diagram at 25 °C for the quasiternary system poly(ϵ-caprolactam) ($\bar{M}$ = 25 000; P)–*m*-cresol (L)–petroleum ether (F). The crosses are the experimental values (+). Plotted are the volume fractions at incipient phase separation. The phase line (—) was calculated by the use of eq 9 and 13 in accordance with the parameter values of Table III, system c. Here, (P) means the polymer, (L) the solvent, (F) the precipitant, and (I) the homogeneous and (II) the heterogeneous region.

The broad lines are the computed boundary curves (binodials), distinguishing the coexisting phases by separating the homogeneous (I) and the heterogeneous regions (II) of the three (quasi-) ternary macromolecular systems investigated. They can be assumed to be correct within the experimental error limits (Table III) and the range of validity of the theoretical first-order perturbation approximation up to about $\gamma_{\mathcal{P}} \lesssim 0.1$ (cf. sections III and VI). Initially, they are compressed against the zero borderlines of the polymer concentrations. The crosses correspond to the experimental values.

VI. Discussion

Regarding phase separation in fluid macromolecular multicomponent systems and its practical applications, "the lack of any proper theoretical basis has hampered development" (cf. ref 23). As discussed in ref 3, up until now a full quantitative understanding of polymer phase separation by statistical thermodynamics has not been achieved.[24,25] Assuming solution equilibria,[6,7] a double-logarithmic relationship was deduced between the precipitation fraction γ_F^* and the polymer cloud-point concentration c^* or $\gamma_{\mathcal{P}}^*$. However, according to Sections II and III of ref 3 and eq 14, c^* is a function of γ_F^*, but not an independent variable. Furthermore, in case of quasiternary solutions there is a relatively large number of parameters. The most frequently used treatment rests on the assumption of partition equilibria.[4] The equations obtained in this context are marked by a relatively large number of adaptable constants. For thermodynamic[5–7] as well as for experimental reasons[6] there are serious objections against the assumption of such partition equilibria which "can hardly be assumed to be responsible for the problems in question" (cf. ref 6 and 7).

Restricting ourselves to the analysis of the concentration dependence from the standpoint of the thermodynamic perturbation theory, these objections[5–7] are further confirmed. For example, to arrive at the linear semilogarithmic relation between the precipitant fraction and the polymer cloud-point concentration, in ref 4 the polymer sol concentration was assumed to be equal to the total cloud-point concentration. This assumption, however, must be assumed to be at fault, since according to eq 12 and 14 and ref 6 one is in no case permitted to set $\gamma_{\mathcal{P}}^{\alpha}$ equal to the polymer concentration at the precipitation threshold $\gamma_{\mathcal{P}}^*$. Furthermore, there are serious objections to the application of $\gamma_{\mathcal{P}}^*$ itself. As it is discussed above, $\gamma_{\mathcal{P}}^*$ is not an independent variable, such as, e.g., $\gamma_{\mathcal{P}}(0)$, and one should bear in mind that the gel phase is only generated in the course of phase separation, but does not exist at the outset. Therefore, the concept of partition equilibria should be regarded as fundamentally unsound.

With the perturbation-theoretical approach, one has for the first time a quantitative phase boundary relationship between γ_F^* and the initial polymer concentration c_0 as the independent variable derived theoretically. The corresponding semilogarithmic eq 9 is equal to a first-order approximation with regard to γ_F^* which characterizes the strength of perturbation. Principally, there are only two constants at $(T,p,M,\bar{w})$ = constant. These are the change of the perturbation density $\Delta\mu^*_{\mathcal{P}F,c}$ or likewise the dimensionless relative inverse quantity σ_c^* and the intercept A_c of the precipitant fraction at $c_0 = 1\ \mathrm{g/cm^3}$. The latter is connected with the limit activity coefficient $b_{0\mathcal{P}}(0)$ of the original macromolecular solution (not to be confused with the limit activity coefficient of the sol phase $b_{0\mathcal{P}}{}^{\alpha}$) and the polymer density $\bar{\rho}_P$. All these parameters are thermodynamically well defined, building up the pertinent phase boundary eq 9. Here, the precipitant fraction γ_F^* is given as a function of the initial polymer concentration $\gamma_{\mathcal{P}}(0)$ $\Longleftrightarrow$ $c_0 = \gamma_{\mathcal{P}}(0)\bar{\rho}_P$ as the independent variable. In this context, according to eq 12 the ratio of the sol and gel phase concentrations of the polymer should be approximately constant and independent of the magnitude of the initial polymer concentration. The phase parameters themselves, such as $\gamma_{\mathcal{P}}^{\alpha}$, $\gamma_{\mathcal{P}}^{\beta}$, $f_{\mathcal{P}}^{\alpha}$, $f_{\mathcal{P}}^{\beta}$, are not necessary to determine the conditions of phase separation. They have to be measured independently (see, e.g., ref 6).

In this connection, constancy of the ratio solvent–nonsolvent in the gel phase for a given system independent of c_0 or c^* was found experimentally by Patat and Träxler.[6] This result may be interpreted theoretically in the following way. Let us assume precipitation equilibria (cf. Section III.3 of ref 3) represented by

$$\mathrm{PL}_m + x\mathrm{F} \rightleftharpoons \mathrm{PL}_{m-x}\mathrm{F}_x + x\mathrm{L} \qquad (15)$$

Here, the subscripts m, $m-x$, and x mean the number of molecules of solvent and nonsolvent per macromolecule, respectively. Furthermore, PL_m and $\mathrm{PL}_{m-x}\mathrm{F}_x$ signify the respective solute and precipitate complexes. Simplifying the analysis by using concentrations on an optional scale (denoted by brackets) instead of activities, the equilibrium constant of the precipitation reaction is given approximately by

$$\begin{aligned} K &= [\mathrm{PL}_{m-x}\mathrm{F}_x][\mathrm{L}]^x/[\mathrm{PL}_m][\mathrm{F}]^x = K_1([\mathrm{L}]/[\mathrm{F}])^x, \\ K_1 &= [\mathrm{PL}_{m-x}\mathrm{F}_x]/[\mathrm{PL}_m] \end{aligned} \qquad (16)$$

According to eq 12, K_1 can approximately be assumed to be constant. Therefore, it follows

$$[\mathrm{L}]/[\mathrm{F}] = (K/K_1)^{1/x} \approx \text{constant} \Longrightarrow \gamma_L^{\beta}/\gamma_F^{\beta} \approx \text{constant} \qquad (17)$$

In the case of quasiternary macromolecular solutions, these considerations are valid for each member of the polymer subset |P (cf. ref 3 and the comment to eq 12, section III).

In this context, it is of interest that eq 9 is more accurate than the arguments applied would indicate.[3] This can be seen from the experimental results (see Figures 1 and 5–9). Therefore, it follows that eq 9 is checked in a domain of

Table IV
Linear Semilogarithmic Relationships between Precipitant Fraction γ_F* and Initial Polymer Concentration c_0 for Various Polymer-Solvent-Precipitant Systems (c* Values were Converted to c_0 after eq 14)

authors	polymer	solvent-precipitant	remarks	ref
Morey and Tamblyn	cellulose acetate butyrate	acetone-(ethanol-water) (3:1 v/v mixture)	Figure 7	27
Schulz and Jirgensons	nitrocellulose	acetone-water	Figure 8	30
Jirgensons	gelatine	water-acetone	Figure 5	29
Craubner	poly(ϵ-caprolactam)	*m*-cresol-petroleum ether	Figure 1	this paper
Craubner	poly(methyl methacrylate)	benzene-cyclohexane	Figure 1	this paper
Schulz and Jirgensons	poly(methyl methacrylate)	benzene-cyclohexane	Figure 8	30
Craubner	polystyrene	benzene-methanol	Figure 1	this paper
Schulz and Jirgensons	polystyrene	benzene-methanol	Figure 8	30
Elias	polystyrene	benzene-*n*-hexane		7
Staudinger and Heuer	polystyrene	chloroform-methanol	Figure 6	8
Urwin et al.	polystyrene	butanone-isopropyl alcohol		23, 28
Scholtan	poly(vinyl pyrrolidone)	water-aq Na_2SO_4 solutions	Figure 9	31
Schulz and Jirgensons	starch triacetate	chloroform-ether	Figure 8	30

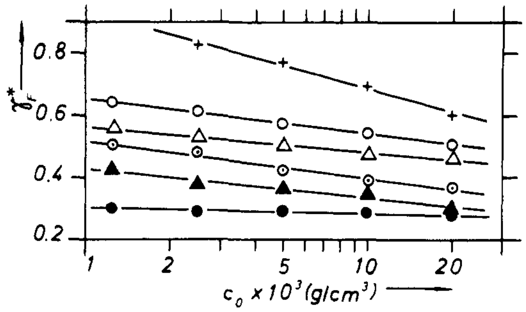

Figure 5. Plot of the precipitant fraction γ_F* vs. log c_0 at 15 °C where c_0 in g/cm^3 is the initial polymer concentration. The systems studied are gelatine and its degradation products (P)-water (L)-acetone (F): (a) gelatine, $\bar{M}$ = 90 000 (●); (b) degradation products, (1) $\bar{M}$ = 31 600 (▲), (2) $\bar{M}$ = 8900 ⊙, (3) $\bar{M}$ = 2500 (△), (3) $\bar{M}$ = 900 (○); (c) glycine, M = 75 (+). Here, (P) means the polymer, (L) the solvent, and (F) the precipitant (after B. Jirgensons, ref 29).

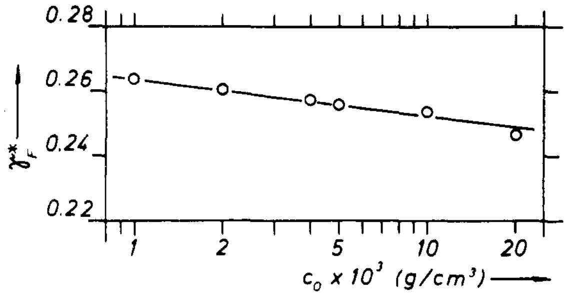

Figure 6. Plot of the precipitant fraction γ_F* vs. log c_0 for the system polystyrene ($\bar{M}$ = 60 000)-chloroform-methanol where c_0 in g/cm^3 is the initial polymer concentration (after Staudinger and Heuer, ref 8).

precipitant volume fractions of $0 < \gamma_F^* < 1$. The physical reasons may be connected with the intermolecular potentials, governing phase separation of macromolecular multicomponent systems. A similar argumentation may be applied, regarding the initial polymer concentration. With respect to eq 22 of ref 3, there is first no limit within $0 < \gamma_P(0) < 1$. However, in the approach to the concentration dependence given by the approximate eq 9, simplifying use of the two thermodynamic limit cases discussed in ref 3 was made. Following therefrom, eq 9 should be valid only for not too high values of $\gamma_P(0)$ or c_0, respectively. For experimental (see Figures 1 and 5–9) as well as theoretical reasons the validity limits may be estimated to be $0 < \gamma_P(0) \lesssim 0.1$. With regard to special systems, the upper polymer concentration limit may be somewhat higher or lower, also depending on the intermolecular potentials mentioned. In the case of higher polymer concentrations the perturbation-theoretical approach should be based on the more exact eq 22 of ref 3.

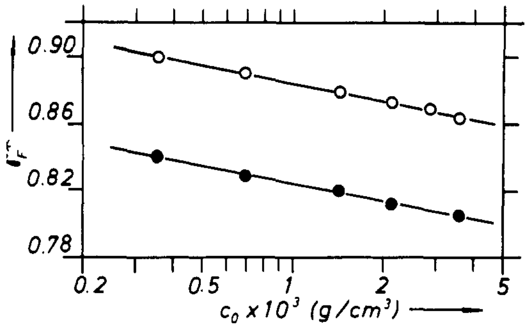

Figure 7. Plot of the precipitation fraction γ_F* vs. log c_0 where c_0 in g/cm^3 is the initial polymer concentration. The systems studied are fractions of cellulose acetate butyrate (P)-acetone (L)-(ethanol-water) (3:1 v/v mixture; F): (a) $\bar{M}$ = 137 500 (●); (b) $\bar{M}$ = 50 000 (○). Here, (P) means the polymer, (L) the solvent, and (F) the precipitant (after Morey and Tamblyn, ref 27).

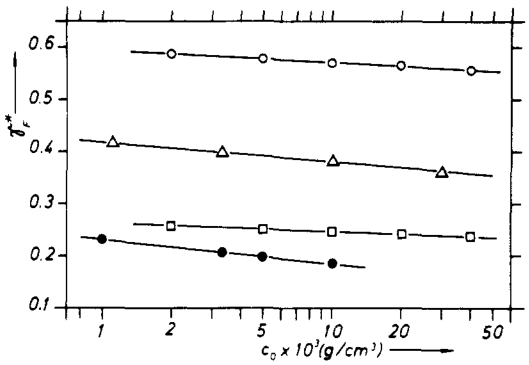

Figure 8. Plot of the precipitant fraction γ_F* vs. log c_0 where c_0 in g/cm^3 is the initial polymer concentration. The systems studied are: (a) nitrocellulose ($\bar{M}$ = 56 800)-acetone-water (●); (b) polystyrene ($\bar{M}$ = 165 000)-benzene-methanol (□); (c) poly(methyl methacrylate) ($\bar{M}$ = 120 000)-benzene-cyclohexane (△); (d) starch triacetate ($\bar{M}$ = 45 000)-chloroform-ether (○) (after Schulz and Jirgensons, ref 30).

Regarding the solubility-concentration dependence, in the literature there are a lot of experimental results (see Table IV and the literature listed in ref 4, 23, and 26). Some of them refer empirically to the semilogarithmic relationship of the initial polymer concentration as the independent variable (see, e.g., ref 23, 27, and 28). The other ones seem to confirm concentration dependence as derived from partition or solution equilibria. However, reexamination showed in each case a functional concentration dependence as given by the thermodynamic perturbation theory. This is illustrated for various polymer-solvent-precipitant systems by, e.g., Figures 5 to 9. The plots of the precipitant fraction vs. the logarithm of

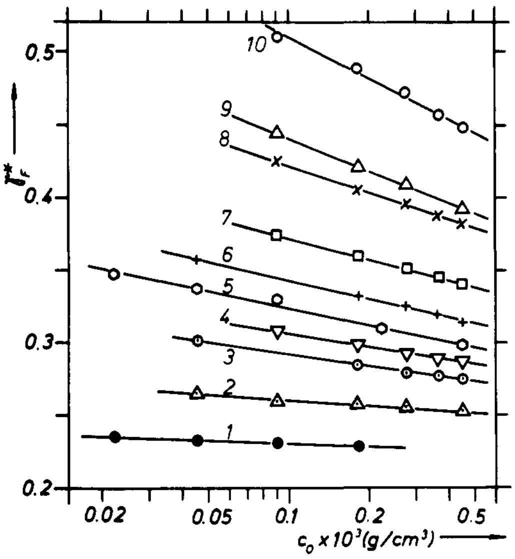

Figure 9. Plot of the precipitant fraction $\gamma_F{}^*$ vs. log c_0 where c_0 in g/cm^3 is the initial polymer concentration. The systems studied are fractions of poly(vinyl pyrrolidone) (P)–water (L)–aqueous Na_2SO_4 solutions (9–33.4 g Na_2SO_4 per 100 cm^3 solution, F): (1) $\bar{M}$ = 1010000 (●); (2) $\bar{M}$ = 280000 (▲); (3) $\bar{M}$ = 58000 (⊙); (4) $\bar{M}$ = 45500 (▽); (5) $\bar{M}$ = 36000 (○); (6) $\bar{M}$ = 31000 (+); (7) $\bar{M}$ = 22000 (□); (8) $\bar{M}$ = 15600 (×); (9) $\bar{M}$ = 13800 (△); (10) $\bar{M}$ = 9300 (○). Here, (P) means the polymer, (L) the solvent, and (F) the precipitant (after W. Scholtan, ref 31).

the initial polymer concentration led to straight lines according to eq 9 (cloud-point concentrations given originally were converted to initial polymer concentrations, according to eq 14). In this context, from Figures 5, 7, and 9 it can be seen that the intercept A_c of eq 9 depends on $\bar{M}$ (cf., e.g., ref 23 and 27). A list of references is recorded in Table IV.

Finally, it can be stated that the perturbation-theoretical approach to the concentration dependence of phase separation in (quasi-) ternary fluid macromolecular systems has been successful in every case investigated so far. This is in accordance with the known fact that perturbation theories have been the most effective theories of the liquid state up to now[3,32-36] and is demonstrated by the excellent agreement with eq 9, as well as by the interpretation of the gel state reported by Patat and Träxler.[6] These results are important for the processes in which polymer phase separation is involved, such as, e.g., the determination of the molecular weight distribution by precipitation[23,26,37] or polymer indicator reactions at fast mixing processes.[9-11] However, further investigations on polymer phase separation especially at higher polymer concentrations are felt to be necessary.

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