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Equilibrium Thermodynamics of a Quaternary Membrane-Forming System with Two Polymers. 1. Calculations

R. M. Boom,* Th. van den Boomgaard, and C. A. Smolders

*Department of Chemical Technology, University of Twente, P.O. Box 217,
7500 AE Enschede, The Netherlands*

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ABSTRACT: Liquid–liquid phase separation phenomena are investigated for a quaternary system containing two polymers, a solvent, and a nonsolvent for one of the polymers which also is a solvent for the other polymer. The phase separation behavior studied is related to the membrane-forming properties of a system containing a macromolecular additive as a second polymer. To visualize the parts of the three-dimensional quaternary phase diagrams, semiternary cross-sections are used in which two components are regarded as a "lumped" component. Cloud point and shadow curves are given. The critical point valid for a ternary system is extended into a *critical curve*. It is found that the critical curve at larger molecular weights of the second polymer is situated at higher concentrations of the membrane-forming polymer. A high molecular weight of this second polymer causes the phase diagram to become insensitive to the various interaction parameters. At constant molecular weight of the second polymer, the critical curve shifts to higher polymer concentrations upon increasing the concentration of the second polymer. Interaction effects appear to have a marginal influence, as long as the component pairs that were assumed to be miscible remain miscible.

Introduction

The formation of symmetric or asymmetric membranes by the immersion precipitation process[1–4] is based on the phenomenon of liquid–liquid phase separation. A concentrated solution (e.g., 10–30 wt %) of the polymer in the solvent is immersed in a bath containing nonsolvent. By the exchange of solvent and nonsolvent the polymer solution becomes unstable, and liquid–liquid demixing starts. Nuclei of a polymer-lean phase grow out into pores until a solidification process inhibits any further changes in morphology. The ultimate morphology of the resulting porous membrane is strongly dependent on the thermodynamic and kinetic properties of the system studied. The membrane formation process in a ternary system has already been extensively studied by, e.g., Hsu and Prausnitz[5] and Altena *et al.*[6]

In a (quasi)ternary system, membrane structures can be obtained that have permeation properties ranging from microfiltration to gas separation. The performance of some of these membranes can be dramatically improved by using a second polymer in the polymer solution that is miscible with the nonsolvent used in the coagulation bath. For micofiltration and ultrafiltration, membrane morphologies can result that are far more regular and show superior permeabilities while retaining the required retention properties.[7–10]

In this paper we will develop a general although qualitative overview of the important characteristics of liquid–liquid phase separation in such a system.

Theory

It is our intention to study the general phase separation characteristics of a quaternary system. We will adopt the Flory–Huggins theory[11,12] for the following reasons:

(i) We are only interested in a qualitative understanding of the phase behavior of the system.

(ii) The Flory–Huggins theory, by its relative simplicity, gives excellent insight into the underlying properties that cause the phase behavior.

(iii) It is our assumption that the essential characteristics of the phase separation phenomena underlying membrane formation are *not* the result of polar effects or hydrogen bonding that the Flory–Huggins approach cannot adequately describe.

(iv) In membrane science all authors have used Flory–Huggins theory as a starting point.[5,6,13–23] Until now, this approach has proven to be most successful in this field. This alone justifies this approach in that it makes comparisons possible.

The authors are, however, completely aware that the Flory–Huggins theory is not adequate in the sense that it cannot describe many important effects. For a better quantitative study, other, more sophisticated, theories must be adopted.

The following indices will be used: 1, nonsolvent; 2, solvent; 3, membrane-forming polymer; 4, second polymer. The (modified) Flory–Huggins theory[11,12] gives the Gibbs energy of mixing as a function of concentration-dependent interaction parameters

$$\Delta G_\mathrm{m}/RT = n_1 \ln \varphi_1 + n_2 \ln \varphi_2 + n_3 \ln \varphi_3 + n_4 \ln \varphi_4 + n_1\,\varphi_2 g_{12}(u_2) + n_1\,\varphi_3 g_{13} + n_1\,\varphi_4 g_{14}(u_4) + n_2\,\varphi_3 g_{23}(\upsilon_2) + n_2\,\varphi_4 g_{24}(w_2) + n_3\,\varphi_4 g_{34}(\upsilon_3) \quad (1)$$

in which φ_i and n_i are respectively the volume fraction and the number of moles of component i. It is assumed that the binary Flory–Huggins interaction parameters g_{ij} are truly binary, i.e., that they are only dependent on the components i and j. The interaction parameters are thus dependent on the following variables:

$$\begin{aligned} &g_{12} \text{ is dependent on } u_2 = \varphi_2(\varphi_2 + \varphi_1) \\ &g_{23} \text{ is dependent on } \upsilon_2 = \varphi_2/(\varphi_2 + \varphi_3) \\ &g_{14} \text{ is dependent on } u_4 = \varphi_4/(\varphi_1 + \varphi_4) \qquad (2) \\ &g_{24} \text{ is dependent on } w_2 = \varphi_2/(\varphi_2 + \varphi_4) \\ &g_{34} \text{ is dependent on } \upsilon_3 = \varphi_3/(\varphi_3 + \varphi_4) \end{aligned}$$

Following Altena,[6] Reuvers,[14,15] Tsay and McHugh,[16–18]

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* To whom correspondence should be addressed. Current address: Unilever Research Laboratory Vlaardingen, P.O. Box 114, 3130 AC Vlaardingen, The Netherlands.

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Tkacik,[20] and Smolders[22] the interaction parameter g_{13} is assumed concentration independent. Other system variables are the ratios of the molar volumes s, r, and t:

$$s = \frac{\bar{v}_1 M_1}{\bar{v}_2 M_2}; \qquad r = \frac{\bar{v}_1 M_1}{\bar{v}_3 M_3}; \qquad t = \frac{\bar{v}_1 M_1}{\bar{v}_4 M_4} \tag{2a}$$

The derivatives of the free enthalpy of mixing with respect to the number of moles of each component yield the chemical potentials of mixing:

$$\partial \Delta G_{\mathrm{m}} / \partial n_i = \Delta \mu_{\mathrm{m},i} \tag{3}$$

Following Altena[6] and Reuvers,[15] the chemical potentials of mixing are expressed per mole of segments of the nonsolvent:

$$\begin{aligned}\Delta\mu_1/RT = {} & \ln \varphi_1 - s\varphi_2 - r\varphi_3 - t\varphi_4 + (1 + g_{12}\varphi_2 + g_{13}\varphi_3 + \\ & g_{14}\varphi_4)(1 - \varphi_1) - sg_{23}\varphi_2\varphi_3 - rg_{34}\varphi_3\varphi_4 - sg_{24}\varphi_2\varphi_4 - \varphi_2 u_2(1 - \\ & u_2)(\partial g_{12}/\partial u_2) - \varphi_4 u_4(\partial g_{14}/\partial u_4)\end{aligned} \tag{4}$$

$$\begin{aligned}s\Delta\mu_2/RT = {} & s \ln \varphi_2 - \varphi_1 - r\varphi_3 - t\varphi_4 + (s + g_{12}\varphi_1 + sg_{23}\varphi_3 + \\ & sg_{24}\varphi_4)(1 - \varphi_2) - g_{13}\varphi_1\varphi_3 - g_{14}\varphi_1\varphi_4 - rg_{34}\varphi_3\varphi_4 + \\ & \varphi_1 u_2(1 - u_2)(\partial g_{12}/\partial u_2) - s\varphi_3 v_2(1 - v_2)(\partial g_{23}/\partial v_2) - \\ & s\varphi_4 w_2(1 - w_2)(\partial g_{24}/\partial w_2)\end{aligned} \tag{5}$$

$$\begin{aligned}r\Delta\mu_3/RT = {} & r \ln \varphi_3 - \varphi_1 - s\varphi_2 - t\varphi_4 + (r + g_{13}\varphi_1 + sg_{23}\varphi_2 + \\ & rg_{34}\varphi_4)(1 - \varphi_3) - g_{12}\varphi_1\varphi_2 - g_{14}\varphi_1\varphi_4 - sg_{24}\varphi_2\varphi_4 - s\varphi_2 v_2(1 - \\ & v_2)(\partial g_{23}/\partial v_2) + r\varphi_4 v_3(1 - v_3)(\partial g_{34}/\partial v_3)\end{aligned} \tag{6}$$

$$\begin{aligned}t\Delta\mu_4/RT = {} & t \ln \varphi_4 - \varphi_1 - s\varphi_2 - r\varphi_3 + (t + g_{14}\varphi_1 + sg_{24}\varphi_2 + \\ & rg_{34}\varphi_3)(1 - \varphi_4) - g_{12}\varphi_1\varphi_2 - g_{13}\varphi_1\varphi_3 - sg_{23}\varphi_2\varphi_3 + \\ & \varphi_1 u_4(1 - u_4)(\partial g_{14}/\partial u_4) - s\varphi_2 w_1(1 - w_2)(\partial g_{24}/\partial w_2) - \\ & r\varphi_3 v_3(1 - v_3)(\partial g_{34}/\partial v_3)\end{aligned} \tag{7}$$

To calculate the equilibrium compositions numerically from eqs 4–7, the standard method as used by many other authors is used.[2,6,13–15,19–23] The following objective function is minimized:

$$F = \sum_{i=1}^{4} \left\{ \frac{\Delta\mu_i^{\text{1st phase}}}{RT} - \frac{\Delta\mu_i^{\text{2nd phase}}}{RT} \right\}^2 \tag{8}$$

The polymer concentrations φ_3 and φ_4 were fixed in the first phase. The concentration of component 1 in the first phase and the concentrations in the second phase were varied to find the equilibrium compositions. Convergence in the calculations was assumed when the objective function had a value smaller than 10^{-32}. The calculations were performed using a Newton-type algorithm.

The following basic parameter values valid for this system were used in the calculations:

$$g_{12} = 1.0 \qquad g_{13} = 1.5 \qquad g_{23} = 0.5$$

$$g_{14} = 0.5 \qquad g_{24} = 0.5 \qquad g_{34} = -1.0$$

These values are approximately relevant for a practical system that is extensively used in practice, consisting of (1) water, (2) *N*-methylpyrrolidone (NMP), (3) poly(ether sulfone) (PES), and (4) poly(vinylpyrrolidone) (PVP). The values were from the literature or were measured in our laboratory.[2,10,20,23] For reasons of convenience, constant interaction parameters were used, although in the system mentioned, slightly concentration-dependent parameters were found.

The molecular weight of component 3 was taken as 18 000 g/mol (which is the number-average molecular weight of poly(ether sulfone) Vicrex 5200P from ICI Ltd.[22]).

Results

Results are not shown in a tetrahedron, as would be required for a quaternary phase diagram, but as cross-sections through the phase diagram, in which the ratio of the concentrations of components 3 and 4 is kept constant. This cross-section can then be plotted in two 2-dimensional graphs, which both yield valuable information on the phase behavior.

First, components 3 and 4 are "lumped" together, a (semi)ternary diagram can then be plotted of which the corners represent solvent, nonsolvent, and the "lumped" component (3+4). The cloud point curve in this graph can be plotted. The incipient phases that are connected with the cloud point phases (i.e., the phases that are created by the crossing of the cloud point curve) do not fall into this cross-section: in these phases, different ratios between components 3 and 4 exist. These compositions are *projected* onto the cross-section. The curve that is then obtained is analogous to the "shadow curve" as defined by Koningsveld[21] for the description of phase separation of a polydisperse polymer in a solvent. We will adopt the same terminology.

Second, components 1 and 2 can be "lumped" together; a (semi)ternary diagram results in which the assumed constant ratio of components 3 and 4 lead to a straight line. The shadow curve, at equilibrium with the cloud point curve, can be clearly identified as not having the same ratio of components 3 and 4. The distribution of components 3 and 4 over the two phases can be studied with this type of diagram.

It should be noted that, in practice, components 3 and 4 are polydisperse. This also causes the shadow curve to be different from the cloud point curve. This effect is, however, beyond the scope of this paper and will not be considered further here.

1. Molecular Weight of the Polymeric Additive 4. Figure 1 gives cross-sections through the quaternary phase diagram for different molecular weights of component 4; the ratio between components 3 and 4 is kept at unity.

In all calculations it appears that component 4 always has preference for the phase lean in component 3. At concentrations of components 3+4 higher than the (semi-ternary) critical point, component 4 remains in the original phase. At a concentration that is higher, component 4 accumulates in the incipient phase. This is independent of concentrations and interaction parameters.

At higher concentrations of polymer the cloud point curve and the shadow curve both extend to higher polymer concentrations: in Figure 1 the cloud point curve and the shadow curve seem to nearly coincide. Note, however, that this is only because the shadow curve is projected onto the diagram. This is illustrated in Figure 2; here the cloud point curve can be seen as a straight line. At low polymer concentrations on the cloud point curve, the shadow curve represents the component 3 rich phase.

At high concentrations 4+3, the miscibility of the polymeric blend with component 1 becomes quite low. The cloud point curves and shadow curves never touch the corner that represents pure 3+4. At a very low concentration of 1+2, the system becomes miscible again. Due to the extremely low concentrations involved, this is not always evident in Figures 1 and 2.

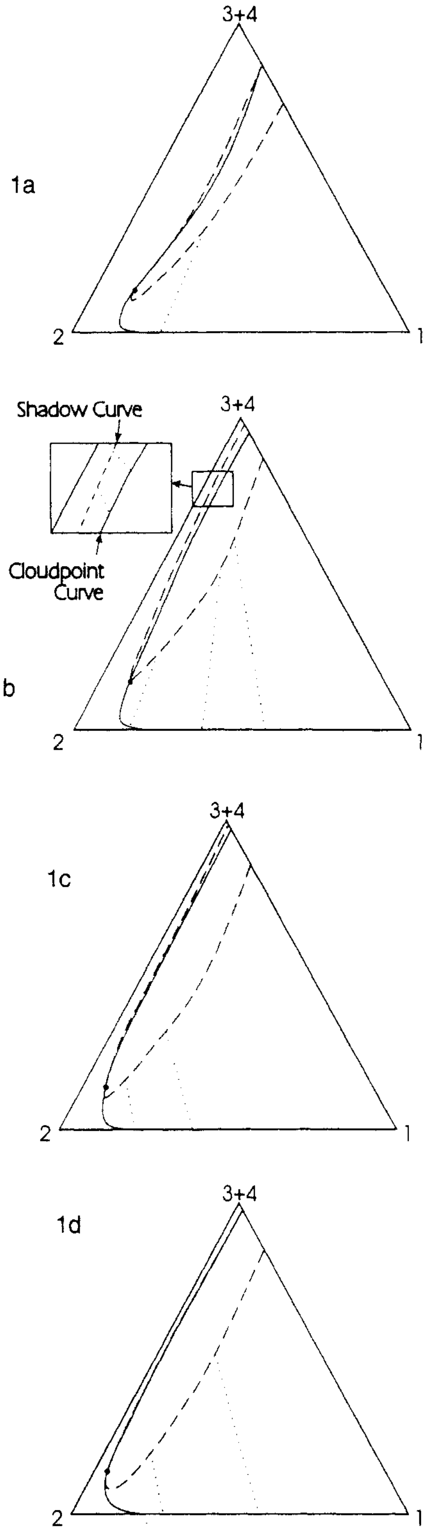

Figure 1. Cross-sections through quaternary phase diagrams at a constant ratio φ_3/φ_4 = 1:1: (a) molecular weight of component 4 is equal to that of component 2 (99.12 g/mol); (b) molecular weight of component 4 is 1000 g/mol; (c) molecular weight of component 4 is 3000 g/mol; (d) molecule weight of component 4 is 10 kg/mol. Uninterrupted lines, cloud point curves; dashed lines, compositions at equilibrium with the cloud point line (shadow curves); dotted lines, tie lines.

It is interesting to note that at higher concentrations of 3 and 4, the sum of the concentrations of 3 and 4 in the two phases is almost equal. The difference between the original phase and the incipient phase is therefore mainly the *ratio* between components 3 and 4. This effect is most strongly present at higher molecular weights of component 4.

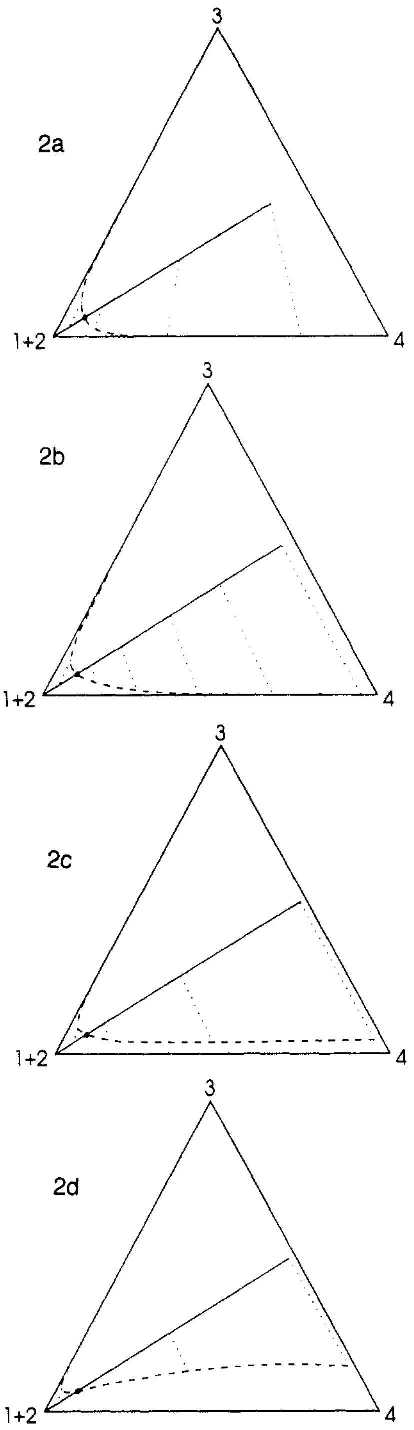

Figure 2. Ternary plots for the same cloud point curves as in Figure 1. Here the components 1 and 2 are taken together. Plots a–d are as in Figure 1. Uninterrupted lines, cloud point curves; dashed lines, compositions at equilibrium with the cloud point line (shadow curves); dotted lines, tie lines.

It appears that with increasing molecular weight of component 4 the miscibility with component 1 is decreasing. Figure 3 shows the amount of component 1 in the solution at the cloud point for solutions containing 10 vol % of component 3 and 10 vol % of component 4.

At increasing molecular weight of component 4, one would expect that component 4 would have more affinity to the component 3 lean phase. In fact, in Figure 4 a different behavior can be seen. Here the calculated amount of component 3 on the shadow curve belonging to a solution at the cloud point containing 35 vol % of component 3 and 35 vol % of component 4 is plotted as a function of the molecular weight of the additive. It appears that the concentration of component 4 in the

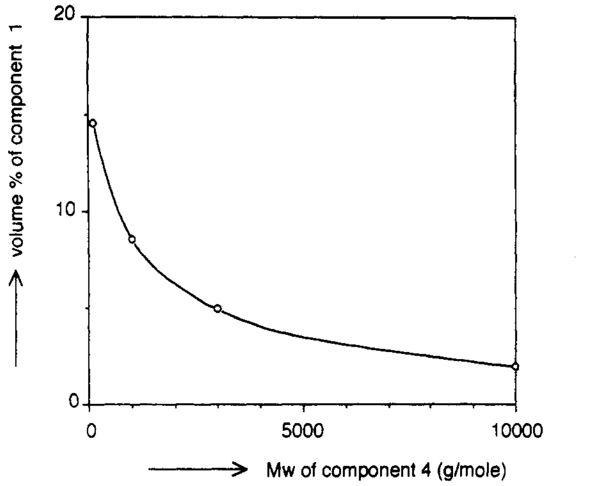

Figure 3. Amount of component 1 that can be dissolved in a solution containing 10 vol % of component 3 and 10 vol % of component 4. The molecular weight of component 4 was varied from 99.12 g/mol to 10 kg/mol.

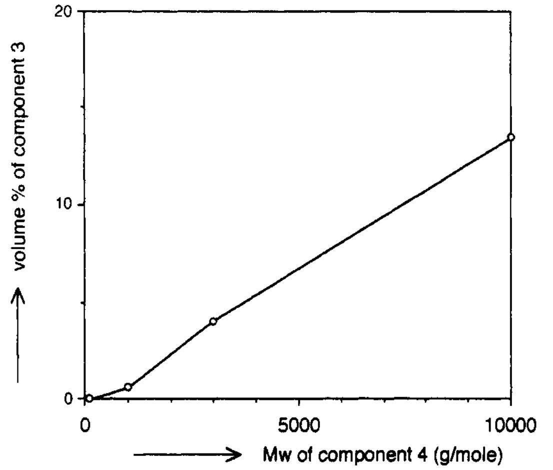

Figure 4. Amount of component 3 present in the incipient phase. The cloud point composition is fixed at 35 vol % of component 3 and 35 vol % of component 4. The molecular weight of component 4 is varied.

component 3 rich phase remains higher at higher molecular weight of component 4. This stems from the fact that the critical curve is shifting to higher polymer concentrations when a high molecular weight component 4 is used.

2. Varying Ratios of Components 3 and 4. Figures 5 and 6 give cloud point curves of the systems with molecular weights of component 4 of 99.12 g/mol, 1000 g/mol, and 10 kg/mol. Three ratios φ_3/φ_4 are given: 2, 1, and 0.5.

The largest influence is seen on the location of the critical point. With decreasing ratio φ_3/φ_4, the critical point in these cross-sections shifts to higher (total) polymer concentrations (3+4). From Figure 6a it appears that the critical point is practically remaining at the same φ_3, since component 4 here has a molecular weight that is equal to that of the solvent. This remains so for up to 1000 g/mol for component 4 (Figure 6b). For higher molecular weights of component 4 the critical point shifts upward. At a ratio φ_3/φ_4 of 0.5, with a molecular weight of component 4 of 10 kg/mol, the critical point is situated at $\sim$24 vol % of component 3 or 73 vol % of components 3+4 (see Figure 6c).

In Figure 7 the phase diagrams of the ternary subsystems 1–3–4 corresponding to situations a, b, and c in Figures 5 and 6 are shown. The critical points in these ternary subsystems shift upward with increasing molecular weight of component 4. This results in the shifting upward of the critical curve already at lower polymer contents.

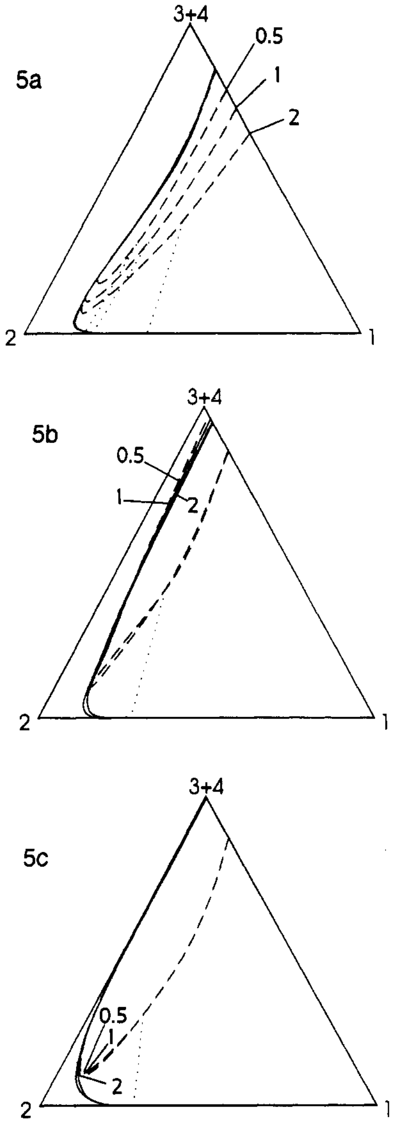

Figure 5. Semiternary cross-sections through phase diagrams; components 3 and 4 are plotted as one component. In each plot three ratios φ_3/φ_4 are drawn. The molecular weight of component 4 is (a) 99.12 g/mol, (b) 1000 g/mol, and (c) 10 kg/mol. The meanings of the uninterrupted, dashed, and dotted lines are as in Figures 1 and 2.

The critical curves for systems with component 4 of varying molecular weight are shown in Figure 8. These critical curves are the collection of critical points from the semiternary cross-sections (see Figure 6). It appears to be always possible to have a cross-section through the quaternary phase diagram that does not contain a critical point by using a low enough ratio φ_3/φ_4. Such a cross-section must always exhibit nucleation of a component 3 rich phase, regardless of the total concentration of components 3 and 4 together. An example of such a situation is shown in Figure 9. Membrane formation must be impossible, since forming a porous membrane structure is closely connected with nucleation of a phase lean in component 3. The situation as depicted in Figure 9 must lead to the formation of a dispersion of component 3 rich droplets in a mixture of the other three components (see Discussion).

3. Variation of the Compatibility of the Additive with Nonsolvent and Polymer 3. In Figure 10 the interaction parameter g_{14} has been varied. The cloud point curve with $g_{14} = 0$ is shifted to lower content of component

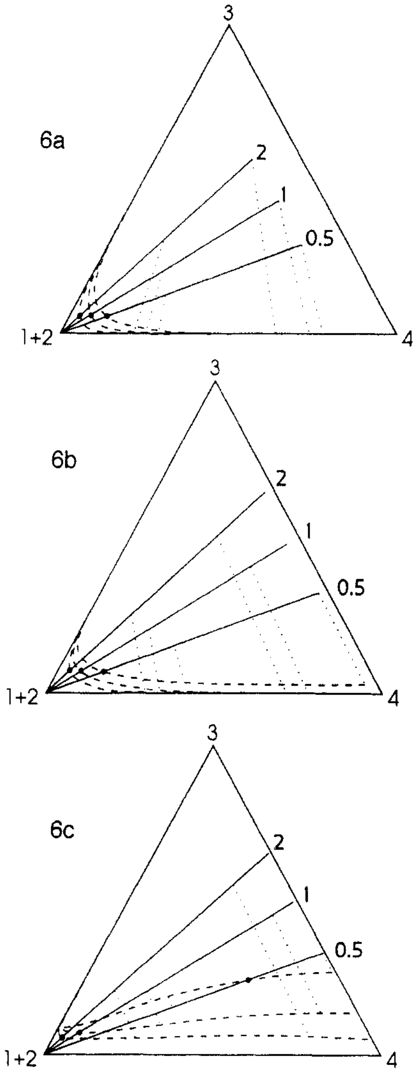

Figure 6. Plots for the cloud point curves shown in Figure 5. Components 1 and 2 are plotted as one component. In each plot three ratios φ_3/φ_4 are drawn. Plots a–c are as in Figure 5. The meanings of the uninterrupted, dashed, and dotted lines are as in previous figures.

1. At higher polymer concentrations (>30 vol %) the cloud point curve remains the same. The critical point of the cross-section appears to shift to lower concentration of 3+4. An appreciably higher interaction parameter than 0.5 gives demixing between the additive 4 and the nonsolvent 1 and is therefore not considered here.

Poly(ether sulfone) and poly(vinylpyrrolidone) have a strong mutual interaction. In fact, PVP shows a strong interaction with many polymers (e.g., with poly(ether imide)[10] or poly(ether amide)[24]). This is thought to stem from hydrogen-bonding effects. Figure 11 shows that for the phase behavior the precise strength of the interaction is not very important as long as the two polymers remain miscible ($g_{34} < 0.5$).

Discussion

It appeared from Figure 8 that by using a certain minimum amount of component 4 and a certain minimum molecular weight of component 4, it is always possible to obtain a situation where nucleation of a component 3 rich phase results. The implications of this phenomenon on membrane formation are important. A solution containing components 2, 3, and 4 (e.g., NMP, PES, and PVP) is contacted with a coagulation bath containing component 1 (e.g., water). The composition in the solution that enters the demixing gap is situated at lower concentrations of components 3+4 than the critical point: nuclei are formed that are richer in component 3 than the original solution. The solution dissolves, creating a dispersion of component 3 in the bath. In practice indeed there is a certain upper limit in the concentration of component 4 that can be used for membrane formation. The authors found it impossible to prepare membranes from a solution containing 15 wt % poly(ether sulfone) and 20 wt % or greater poly(vinylpyrrolidone) (of molecular weight ~100 kg/mol) in *N*-methylpyrrolidone. It led to dissolution of the polymer solution while the coagulation bath became turbid (see also ref 23).

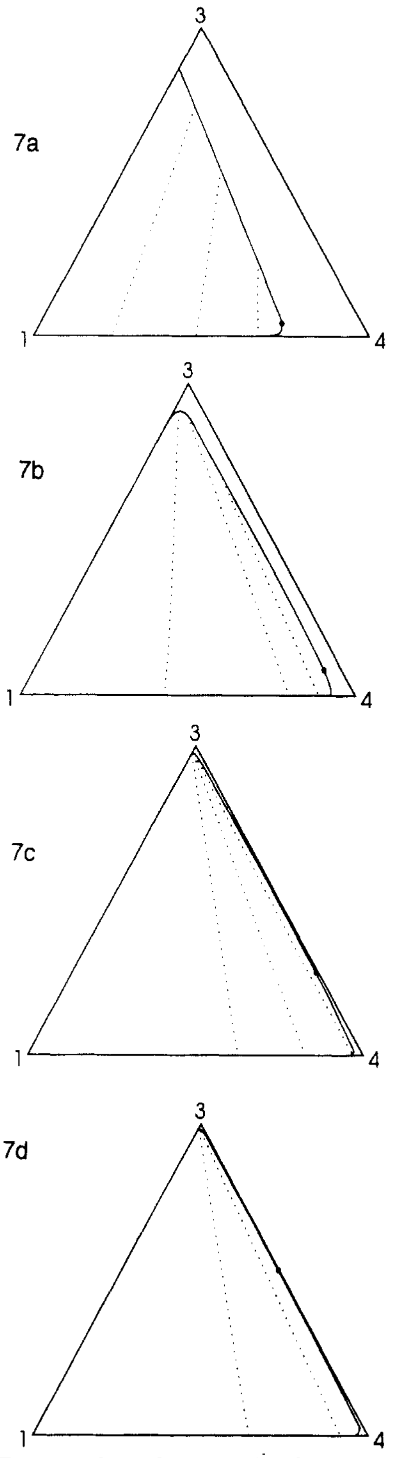

Figure 7. Ternary phase diagrams for the ternary subsystem 1–3–4. The molecular weight of component 4 is varied: (a) 99.12 g/mol; (b) 1000 g/mol; (c) 10 kg/mol; (d) 100 kg/mol. The critical points are indicated by black dots. The meanings of the uninterrupted and dotted lines are as in previous figures; shadow curves are identical to the cloud point curves.

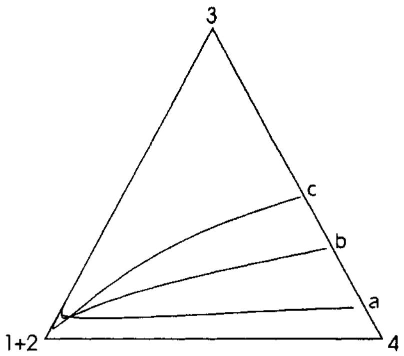

Figure 8. Semiternary representation of the critical curves in three systems with different molecular weights of component 4: (a) 1000 g/mol; (b) 10 kg/mol; (c) 100 kg/mol. The meanings of the uninterrupted, dashed, and dotted lines are as in previous figures.

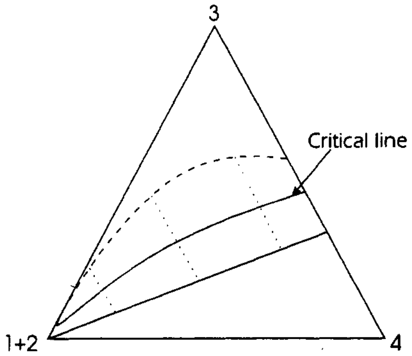

Figure 9. Situation for $\varphi_3/\varphi_4 = 0.5$ and molecular weight of component 4 = 100 kg/mol. The critical curve remains at higher values of φ_3/φ_4 than 0.5. Uninterrupted line, cloud point curve; dashed line, compositions at equilibrium with the cloud point line (shadow curves); dotted lines, tie lines.

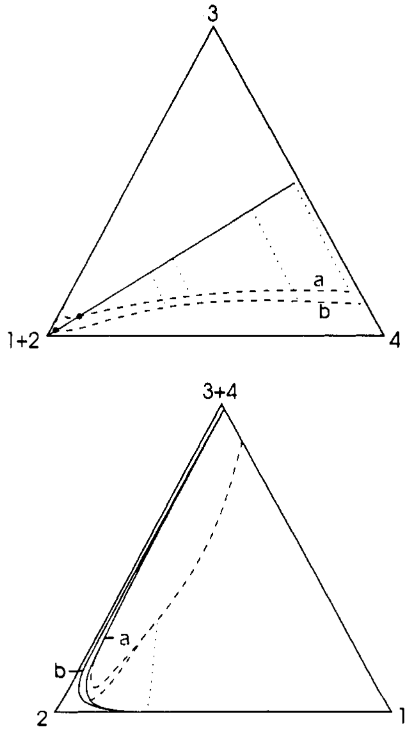

Figure 10. Variation of g_{14}. The value was varied from 0.5 (a) to 0.0 (b). The meanings of the uninterrupted, dashed, and dotted lines are as in previous figures.

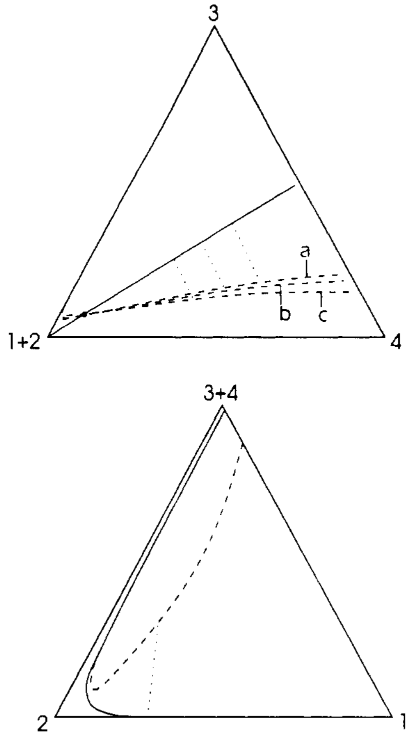

Figure 11. Variation of g_{34} from −1.0 (a), to 0.0 (b), to 0.5 (c). The ratio between the volume fractions of the components 3 and 4 was kept at unity. The meanings of the uninterrupted, dashed, and dotted lines are as in previous figures.

In between the composition region where nucleation of a component 3 lean phase occurs and the region where component 3 rich nuclei are formed, a region is present (near the critical point) where spinodal decomposition is expected. At higher (total) polymer concentrations (e.g., 30 vol % of polymer) the incipient phase appears to have approximately the same concentration of component 1 and component 2 as the original phase from which it is formed.

The strengths of the interactions of component 4 with components 1 and 3 appeared not to be very important. Polymers that do not mix will show a different behavior. A component 4 that is not miscible with component 1 but that is miscible with component 3 will simply remain in the membrane matrix. For membrane formation, the two polymers react as if they were one polymer.

Conclusions

(i) It was shown that addition of a second polymer to a ternary polymer solution has a large influence on the properties of the system relevant to membrane forming. By using a certain minimum concentration of a component 4 with a high molecular weight, spinodal decomposition and even (metastable) dissolution can be induced, independent of the absolute concentration of component 3.

(ii) The phase separation leads to phases that are hardly different in total polymer concentration; the *ratio* of the concentrations of the polymeric components will, however, be greatly different.

(iii) The absolute strengths of the interaction between components 4 and 1 and between components 4 and 3 are not of great importance as long as miscibility is ensured.

List of Symbols

Indices indicate the four components of the system: 1, nonsolvent; 2, solvent; 3, membrane-forming polymer; 4, polymeric additive.

g_{ij}	interaction parameter between components *i* and *j*
M_i	molecular weight of component *i* (kg/mol)
n_i	number of moles of component *i* (mol)

s	$\bar{v}_1M_1/\bar{v}_2M_2$
r	$\bar{v}_1M_1/\bar{v}_3M_3$
R	gas constant ((J/mol)/K)
t	$\bar{v}_1M_1/\bar{v}_4M_4$
T	temperature (K)
u_2	$\varphi_2/(\varphi_2 + \varphi_1)$
u_4	$\varphi_4/(\varphi_1 + \varphi_4)$
v_2	$\varphi_2/(\varphi_2 + \varphi_3)$
v_3	$\varphi_3/(\varphi_3 + \varphi_4)$
$\bar{v}_i$	specific volume of component i (m^3/kg)
w_2	$\varphi_2/(\varphi_2 + \varphi_4)$
ΔG_m	Gibbs energy of mixing (J)
$\Delta\mu_i$	chemical potential of mixing (J/mol)
φ_i	volume fraction of component i

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