Linearized cloudpoint curve correlation for ternary systems consisting of one polymer, one solvent and one non-solvent

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A linear correlation function is found for cloudpoint composition curves of ternary systems consisting of one polymer, one solvent and one non-solvent. The conditions for validity of this correlation function appear to be that the polymer is strongly incompatible with the non-solvent, and that only liquid–liquid demixing occurs. The linearized cloudpoint (LCP) curve is interpreted in terms of the various parameters occurring in the Flory–Huggins theory. The slope of the LCP line appears to be only dependent on the molar volumes of the components. Information about the binary Flory–Huggins interaction parameters and their concentration dependence can be obtained from the intercept of the linearized curve. Cloudpoints induced by crystallization do not follow the correlation. This gives an opportunity to distinguish between crystallization and liquid–liquid demixing without any additional experiments.

INTRODUCTION

Membrane separation as a commercial separation process became practical after the introduction of the phase inversion technique for the preparation of synthetic membranes[1]. Membranes made by phase inversion usually have a very thin, selective top layer and a much thicker porous support.

Phase inversion basically consists of immersing a thin layer of a polymeric solution in a bath which contains a non-solvent for the polymer. This non-solvent should be miscible with the solvent present in the polymer solution. The immersion induces an exchange of solvent and non-solvent between the coagulation bath and the polymer solution[2] by diffusion and convection. Due to these processes, the polymer solution becomes unstable, and phase separation results. In the polymer solution, a polymer lean phase forms droplets in an increasingly concentrating polymer rich matrix. The polymer lean droplets grow out to pores; the surrounding matrix eventually forms the solid membrane structure. The concentration profiles created during the diffusion processes may induce a profile in the pore sizes: near the coagulation bath pores are very small. Deeper inside the polymer solution pores are usually larger.

This process is controlled by diffusion kinetics and thermodynamic properties of the system. Knowledge of the thermodynamics of the system gives absolutely essential insight into the membrane structures possibly obtained by a particular system.

The most straightforward method of characterizing the thermodynamics of a system is by measuring the cloudpoint curve. The cloudpoint curve is the curve that forms the border between the compositions that are completely stable, and the compositions that are meta- or unstable. In a truly ternary system (in which the polymer is monodisperse), the cloudpoint curve coincides with the binodal: the line that represents compositions that can be at equilibrium with one another.

In a quasi-ternary system (in which the polymer is polydisperse), the polymer becomes fractionated at equilibrium between the two phases[3]. The lower molecular weight fractions have preference for the polymer lean phase, while the higher molecular weight fractions are primarily dissolved in the polymer rich phase. This causes the polymer rich phases, in equilibrium with phases leaner in polymer, not to lie exactly on the binodal. The polymer lean phase will also not be located exactly on the binodal.

In a quasi-ternary system the cloudpoint curve represents those compositions which are at the onset of demixing: the demixing has not yet really taken place. The molecular weight distribution of the bulk has therefore not yet changed.

For a thorough theoretical treatment, not only is the theory very complicated, but also the amount of experimental work needed is large. One has to determine all the relevant interaction parameters, eventually also

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as a function of molecular weight. In practice, the differences between the binodal and the cloud point curves are not large, as long as no compositions near the critical point are considered[3]. This comes from the fact that for a membrane forming system, the polymer and the non-solvent are usually very incompatible. The polymer lean phase is therefore very low in polymer concentration. The polymer stays completely in the polymer rich phase, and there is practically no change in the molecular weight distribution. For such a system it is possible to treat a quasi-ternary system as a truly ternary system. This simplifies the theory considerably.

For most ternary systems, the interaction parameters between solvent and non-solvent, and between polymer and solvent, can be easily determined from vapour pressure, osmotic pressure[4], or light scattering measurements[5]. The interaction between polymer and non-solvent is more difficult. The only experimental point one can obtain is the swelling value of the polymer in the non-solvent. This is only one point, and it is not possible to find a concentration dependence of this interaction. Usually, one simply assumes an interaction parameter, after which the binodal is calculated[6]. When this calculated binodal is not too far from the experimental cloudpoints and equilibrium data, this value of the interaction parameter is assumed to be approximately correct.

For efficient scanning of the potentialities of membrane forming systems, it might be useful to have a relation that quickly yields information about the thermodynamics of a membrane forming system. Furthermore, in the fitting procedure mentioned before, one almost forgets the lower concentrations in the phase diagram: the polymer lean phases will be so poor in polymer that in a phase diagram they are effectively situated on the solvent–non-solvent axis. This makes it impossible to discriminate between weight fractions of e.g. 10^{-3} and 10^{-5}. The full potential of experimental data will therefore not be used to obtain the right polymer–non-solvent interaction parameter.

The conclusion is that it might be useful to have a representation of cloudpoints that does not have this disadvantage, and which can be useful in the quick interpretation of cloudpoints.

SIMPLE EXPLICIT RELATIONS FOR CLOUDPOINT CURVES IN TERNARY SYSTEMS

Craubner[7] derived, from perturbation thermodynamics, a relation that described the cloudpoint curve for systems dilute in polymer (less than 1 wt% polymer):

$$\phi_1 = b \ln \phi_3 + a \tag{1}$$

in which ϕ_1 and ϕ_3 are the weight fractions of non-solvent (1) and polymer (3), respectively.

This relation, indeed, holds only for dilute systems. This limits the usefulness of this equation, because for membrane formation also the more concentrated region (up to 40–50 wt% polymer) is important.

Another relation was proposed by Li et al.[8]. He observed that for systems with more than 10 wt% polymer, the ratio between the concentrations of solvent and non-solvent appears to be constant. In formula:

$$\phi_1 = b \phi_2 \tag{2}$$

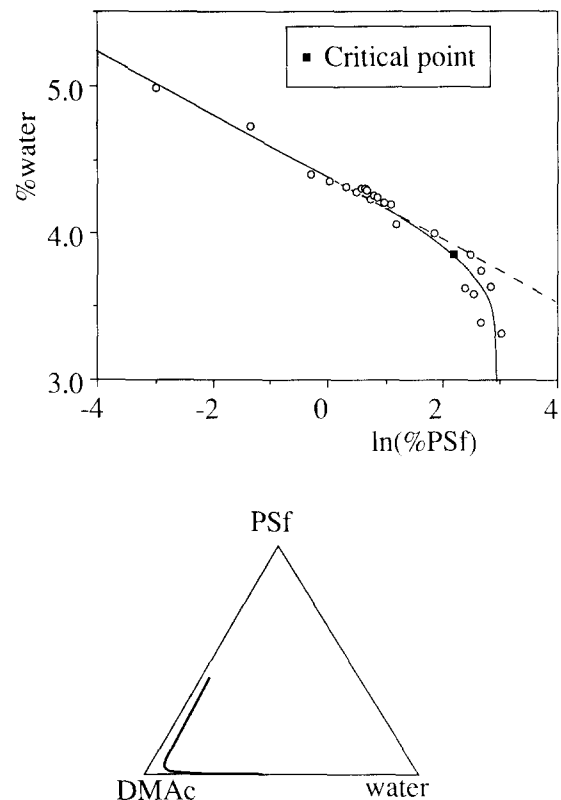As can be seen in *Figure 2*, the relation is approximately

Figure 1 Cloudpoints for the system polysulfone (PSf)–dimethyl acetamide (DMAc)–water, as measured by Li et al.[8], at 20°C, plotted according to the Craubner relation (1). The dotted line is the line expected from this relation; the solid line through the experimental points is only to guide the eye. The critical point is an estimation from calculations according to the Flory–Huggins theory
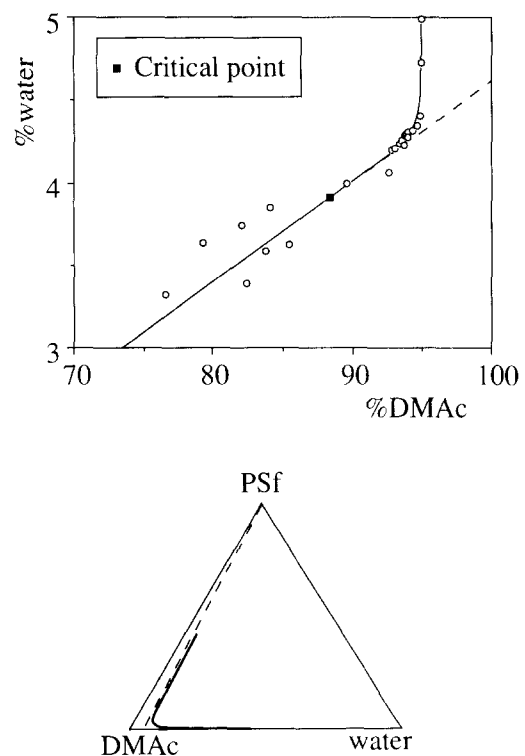

Figure 2 Same cloudpoints as in *Figure 1*, for the system polysulfone (PSf)–dimethyl acetamide (DMAc)–water, as measured by Li et al.[8], at 20°C, plotted according to the Li relation. Explanation of lines as in *Figure 1*. The critical point again is an estimation

valid for high concentrations of polymer, but when the critical point is approached (near 9 wt% polymer), the experimental points deviate sharply from the line.

An early review of relations meant for all types of ternary systems was made by Hand[9]. One of the relations describes the 'dineric distribution', i.e. the distribution of one component, soluble in two phases:

$$\ln\frac{\phi_2'}{\phi_1'}=b\ln\frac{\phi_2''}{\phi_3''}+a \qquad (3)$$

in which ϕ_i signifies the weight fraction of component i. Components 1 and 3 are incompatible; component 2 is miscible with the other two components. The indices ' and " represent the two phases in equilibrium with one another. In fact, this relation can be applied to a demixed, two-phase equilibrium, consisting of a polymer (3), a solvent (2) and a non-solvent (1). For its verification one needs to measure the equilibrium distribution of component 2 over the two phases, containing mainly component 1, and component 3, respectively.

The linearized cloudpoint (LCP) correlation proposed here is closely related to the relation that Hand describes. In our case it correlates the concentrations in any single phase that is on the verge of demixing (the cloudpoints):

$$\ln\frac{\phi_1}{\phi_3}=b\ln\frac{\phi_2}{\phi_3}+a \qquad (4)$$

Here again, ϕ_i is the weight fraction; a and b are constants, to be determined experimentally. This relation does not describe a dineric distribution, but describes the compositions of a single phase at the border between stability and instability, which are more easily determined experimentally. For truly ternary systems, these points give the binodal curve; for quasi-ternary membrane forming systems, the binodal curve is approximated. *Figure 3* shows the relation for a particular system. In this LCP relation, there are two parameters: the slope (b) and the intercept (a). *Figure 4* shows the dependence of the (mathematical) line on these parameters.

VERIFICATION OF THE RELATION

In *Figures 5* and *7* a number of systems which are commonly used as membrane forming system are represented. The cloudpoints represented (from the literature and our laboratory) vary over many decades of polymer concentrations, typically from 10^{-3} to 50 wt% of polymer. Since the critical point is usually between 5 and 10 wt% polymer, the relation holds for both sides of the binodal. The relation is following the experimental data over the full concentration range.

In all cases, the slope of the line is somewhat larger than one, while the intercept of the line varies with the system.

It has to be borne in mind that in the ternary phase diagram, the LCP relation always originates in the point of pure polymer. Since all polymers swell in non-solvents to a certain extent, the relation is only an approximation. *Figure 6* demonstrates this point. The fact that there seems to be no deviation from the line at higher polymer concentrations becomes even more remarkable by this.

During membrane formation, not only liquid–liquid demixing is important. Many polymers tend to crystallize more or less slowly in solution. Although the structure of the membrane formed by phase inversion will
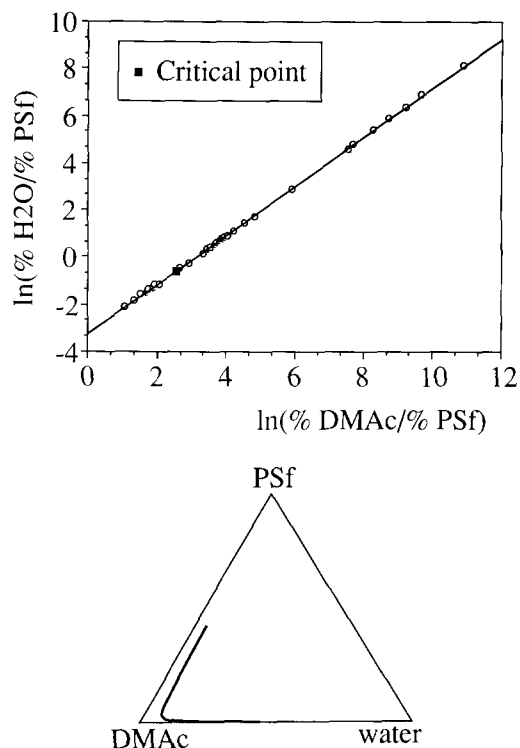

Figure 3 Same cloudpoints as in *Figures 1* and *2*, for the system polysulfone (PSf)–dimethyl acetamide (DMAc)–water, as measured by Li et al.[8], at 20°C, plotted according to the LCP relation (4)
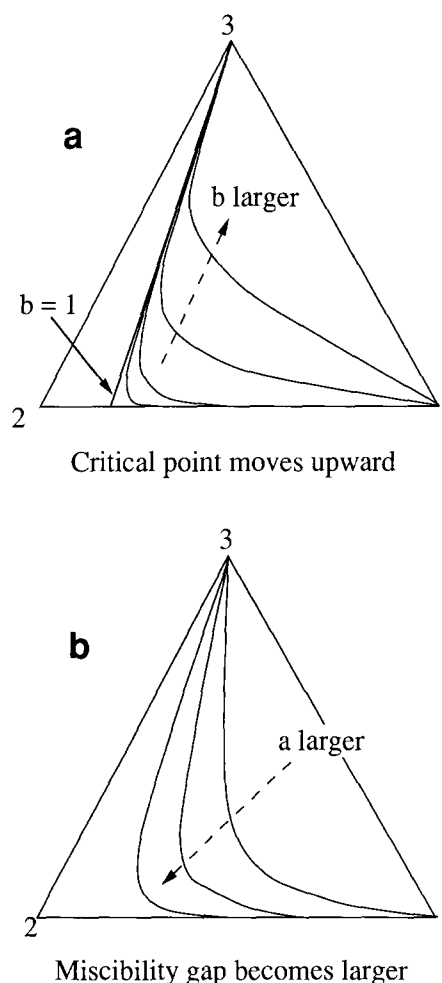

Critical point moves upward

Miscibility gap becomes larger

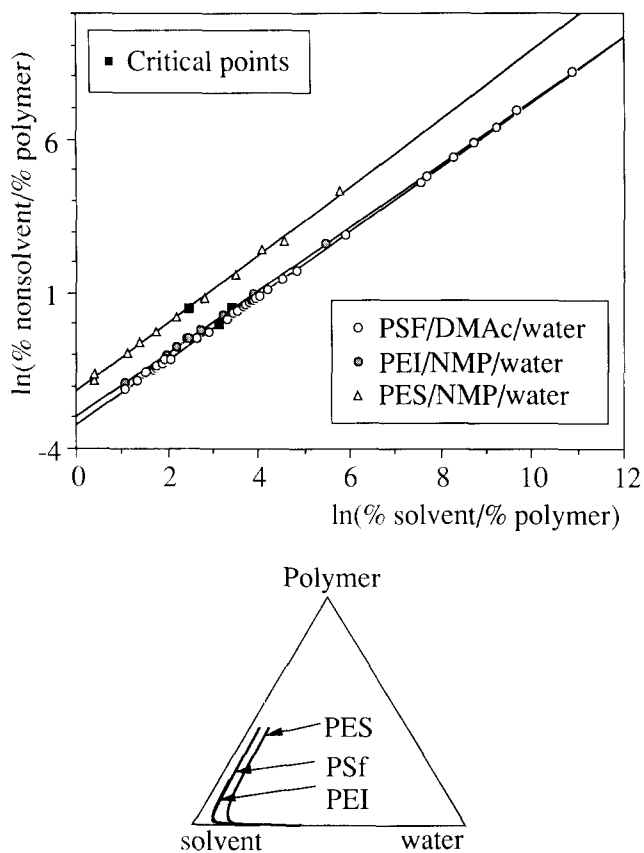**Figure 4** LCP relation, with varying intercept (*a, Figure 4a*) and varying slope (*b, Figure 4b*)

Figure 5 Polysulfone (PSf)–dimethyl acetamide (DMAc)–water (from Li *et al.*[8]), poly(ether sulfone) (PES)–n-methyl pyrrolidone (NMP)–water (from Tkacik and Zeman[10]), and poly(ether imide) (PEI)–n-methyl pyrrolidone (NMP)–water (from Roessink[11]). All cloudpoints were measured at 20°C

cloudpoints, the polymer solutions were slowly cooled, while the light transmittance through the solution was measured. The temperature at which the transmittance starts to decrease is called the cloudpoint. The occurrence of crystallization was controlled by measuring the cooling rate dependence of the cloudpoint temperatures. At a low cooling rate there was a definite cooling rate dependence; at a higher cooling rate the rate dependence disappeared. The 'real' liquid–liquid demixing cloudpoint was defined as that cloudpoint where this dependence disappeared. This is based on the observation that for cellulose acetate, crystallization is much slower than liquid–liquid demixing. *Figure 7* shows that for a crystallizable system, these 'real' liquid–liquid demixing cloudpoints still follow the LCP relation, as observed for completely amorphous systems.

In *Figure 8*, a system is given in which crystallization is fast and plays a more dominant role. The polymer is poly(dimethyl phenylene oxide), the solvent is trichloro ethylene, and the non-solvent is a mixture of a strong solvent (methanol) and a weak non-solvent (octanol). The part with lower polymer concentrations (the right-hand part in the LCP plot) gives a set of straight lines, all with approximately the same slope, but for each methanol/octanol ratio a different intercept is found. For the system with pure methanol as non-solvent, i.e. the strongest non-solvent, the intercept is the smallest. With only octanol as non-solvent, the largest intercept is obtained (i.e. the smallest liquid–liquid demixing gap).

The part with higher polymer concentrations (the left-hand side of the figure) gives crystallization. For the highest polymer concentrations, which is for low non-solvent concentrations, the cloudpoint curves converge
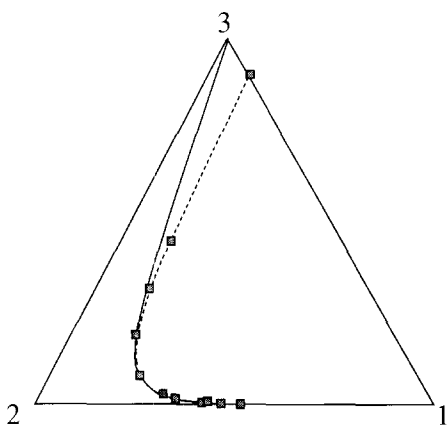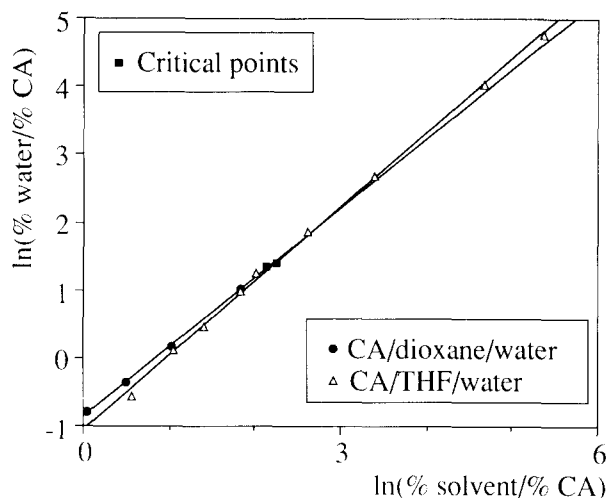

Figure 6 LCP relation always crosses two corners of the ternary phase diagram. Experimental points usually go to a point of a few per cent non-solvent in the polymer. For clarity, the deviations of the experimental points are exaggerated

usually be controlled by fast liquid–liquid demixing, crystallization can be very important for highly crystalline polymers which crystallize rapidly.

Especially in the more concentrated surface region during phase inversion, crystallization may compete with liquid–liquid phase separation, and therefore determine the separation properties of the ultimate membrane.

During cloudpoint measurement, crystallization is usually very difficult to distinguish from liquid–liquid demixing. In *Figure 7*, cloudpoints are given for the crystallizable polymer cellulose acetate. To measure the

Figure 7 Cloudpoint curves for the system cellulose acetate (CA)–tetrahydrofuran (THF)–water[12], in the ternary phase diagram and in the LCP form. The solvents are, respectively, tetrahydrofuran and acetone
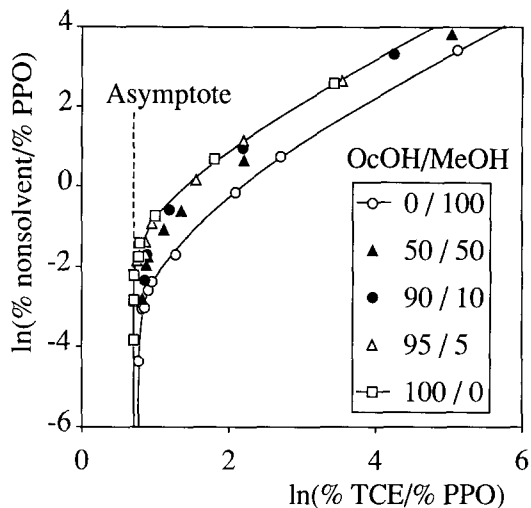
Figure 8 Cloudpoint curves for poly(dimethyl phenylene oxide)–trichloro ethylene–non-solvent, in which the non-solvents are a mixture of methanol and octanol (data from Wijmans *et al.*[12]). The weight ratio of methanol to octanol was varied

to the same vertical line. This line extrapolates to the crystallization point of PPO in trichloro ethylene, which is independent of the non-solvent.

It should be noted that the experimenters[12] observed cooling rate dependence of the cloudpoints for the higher polymer concentrations, which agrees with the assumption that the 'deviating' cloudpoints are crystallization points. The same followed from differential scanning calorimetry measurements, and pulse induced critical scattering (PICS) measurements by the same authors.

In this way, the LCP curve might give a crude but quick way to distinguish between crystallization and liquid–liquid demixing.

For non-polymeric systems, the relation does not seem to hold as nicely as for the systems discussed so far. It appears from *Figure 9*, in which the system water (1)–methanol (2)–diethyl ether (3) is represented, that a not very straight line is obtained. It must be concluded that for non-polymeric systems, the LCP relation is not applicable.

It is interesting to consider a system of two incompatible polymers and a mutual solvent. The non-solvent here is one of the polymers. Of course, in this case the system is no longer 'membrane forming'.

Figure 10 shows the system polyisobutylene (1)–toluene (2)–polystyrene (3), as measured by Van den Esker[13]. It appears that the LCP curve is applying reasonably well, when considering the experimental difficulties in obtaining these cloudpoints. The slope here is much larger than one, which agrees with the fact that the critical point is not in the neighbourhood of the toluene/polystyrene axis in the ternary phase diagram. The LCP relation, therefore, could be useful in gathering information about the interaction between two incompatible polymers. This, however, should be investigated more carefully in future work.

INTERPRETATION OF THE LCP RELATION

The LCP relation, as was proposed:

$$\ln \frac{\phi_1}{\phi_3} = b \ln \frac{\phi_2}{\phi_3} + a \qquad (4)$$
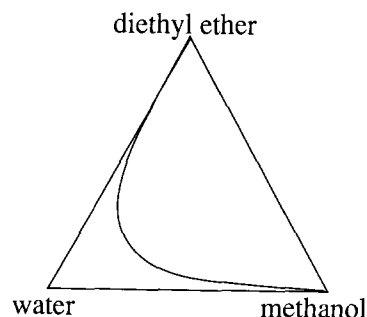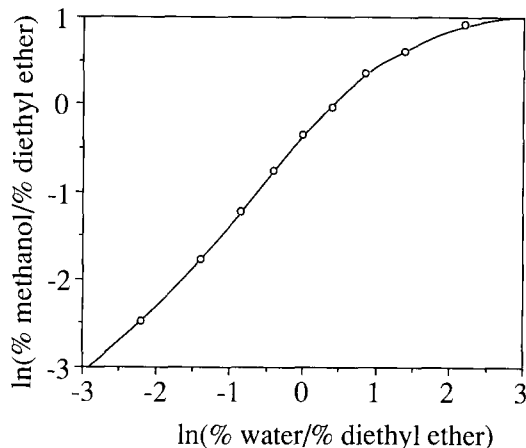

Figure 9 LCP plot for a low molecular weight system. The two immiscible components are here diethyl ether and water, the 'solvent' is methanol. It appears that a not very straight line is obtained. It must be concluded then that the LCP is not applicable to systems without a polymer
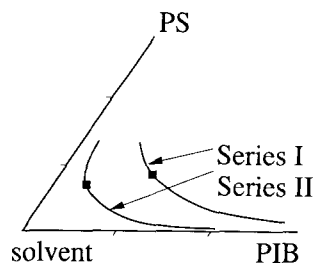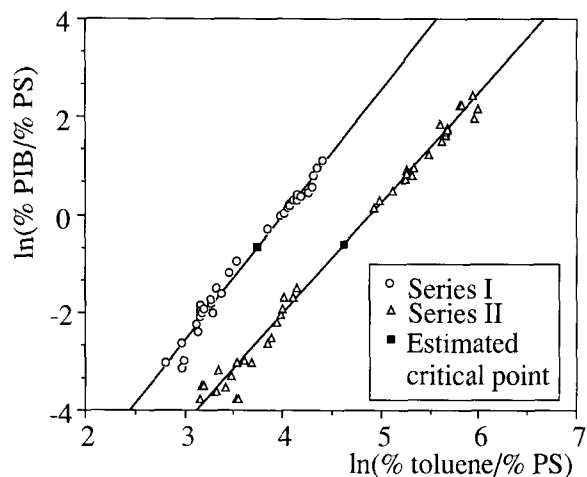

Figure 10 LCP plot for the system polystyrene (3)–toluene (2)–polyisobutylene (1), for two systems with different molecular weights: system one: $MW_{PS} = 194$, $MW_{PIB} = 156 \, kg \, mol^{-1}$, and system two: $MW_{PS} = 526$, $MW_{PIB} = 670 \, kg \, mol^{-1}$

has two parameters, the slope b and the intercept a. From *Figure 3* it is clear that the slope could give information about the situation of the critical point in the phase diagram.

For the slope b, one limiting case is a value of one. This value represents a straight line through the phase diagram. Such a cloudpoint curve would be found for a hypothetical system in which the polymer has infinite molecular weight. In this case, the critical point is situated on the solvent–non-solvent axis. The other extremum, a rather low molecular weight of the polymer, introduces a slope which is larger. A large value of b suggests a critical point near the middle of the binodal curve in the phase diagram.

The intercept a appears to dictate the area covered by the demixing gap (see *Figure 3*), which is mainly governed by enthalpic effects. One would therefore expect that the slope gives only entropic information (the molecular volumes), and that the intercept gives information about enthalpic effects (the g_{ij}s). The interesting fact about the LCP relation seems to be a decoupling of enthalpic and entropic effects.

To investigate this further, we try to interpret the LCP relation according to the Flory–Huggins theory.

The Flory–Huggins equation gives the free enthalpy of mixing as a function of the concentration of the components. From this equation, the slope and the intercept of the LCP line can be obtained, under the assumption that the line is applicable. This does not follow from the Flory–Huggins interpretation, as should be expected: the relation should not be valid for all ternary systems (see *Figure 9*).

The slope is a function of the molar volumes:

$$b = \frac{v_1 - v_3}{v_2 - v_3} \qquad (5)$$

while the intercept a contains the Flory–Huggins interaction parameters:

$$a = \tfrac{1}{2}\{(g_{12} + g'_{12})(-v_2 b \phi_1 + v_1 \phi_2)$$
$$+ g_{13}(v_1 \phi_3 - v_3(1 - b)\phi_1)$$
$$+ (g_{12} + g'_{12})(-v_2 b \phi_3 + v_3(1 - b)\phi_2)\} \qquad (6)$$

In these relations, the following symbols occur:

ϕ_i volume fraction of component i

v_i molar volume of component i (m^3 mol^{-1})

b $\dfrac{v_1 - v_3}{v_2 - v_3}$

g_{ij} Flory–Huggins interaction parameter between components i and j, usually concentration dependent (no unit)

g'_{12} derivative of the interaction parameter g_{12}:

$u_2(1 - u_2)\dfrac{\partial g_{12}}{\partial u_2}$

g'_{23} derivative of the interaction parameter g_{23}:

$v_2(1 - v_2)\dfrac{\partial g_{23}}{\partial v_2}$

u_2 $\phi_2/(\phi_2 + \phi_1)$

v_2 $\phi_2/(\phi_2 + \phi_3)$ \qquad (7)

The intercept is a simple relation in the volume fractions and the interaction parameters. Interestingly, the interaction parameters themselves, g_{ij}, and their derivatives, g'_{ij}, are taken together as one parameter.

The slope b only contains entropic parameters. Systems with a polymer with a high molecular weight have a slope just larger than one. Systems in which the polymer molecular weight is lower have a larger slope.

Interestingly, the low molecular weight system shown in *Figure 9* exhibits a slope of around 0.7. Relation (4) implies that only for ternary systems consisting of polymer, solvent and non-solvent (i.e. a membrane forming system) should the slope be around one. Therefore, the slope in *Figure 9* confirms relation (4). In *Figure 10*, a system with *two* polymers, the slopes are 2.3 to 2.7: again this confirms relation (4).

The intercept a contains the interaction parameters, together with molar volumes. Apparently, the enthalpic interactions are completely taken into account by the intercept.

Information about the interaction parameters can be obtained directly from the value of the intercept a, via relation (6). The LCP is an explicit relation for a cloudpoint (binodal) curve in a ternary membrane forming system. From the Flory–Huggins theory, it is not possible to obtain an explicit relation for the binodal. It appears now that such a relation does exist for certain systems. This relation holds only when the LCP plot holds, i.e. when the interaction parameter between the polymer and the non-solvent is high, and when only liquid–liquid demixing occurs.

We can draw the cloudpoint curve as interpreted from the Flory–Huggins theory in the LCP plot. An example of this is given in *Figure 11*.

RESULTS AND DISCUSSION ON SLOPES AND INTERCEPTS

Amorphous systems with low polymer–non-solvent interaction

For membrane forming systems, the LCP curve always gives a slope slightly larger than one. It is possible to express the cloudpoint curve as a simple function of the interaction parameters (see *Figure 11*). The slope is independent of the interaction parameters, and is only
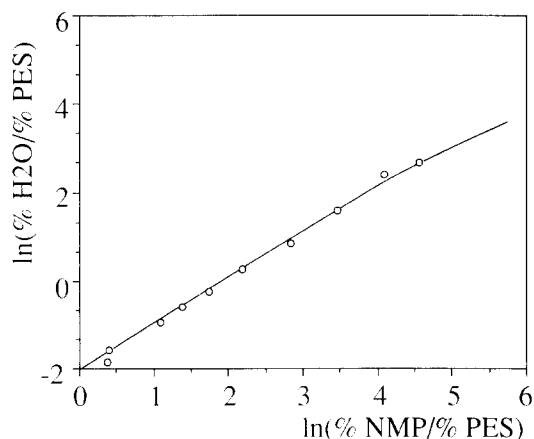

Figure 11 LCP plot for the system poly(ether sulfone)-n-methyl pyrrolidone–water, and the line as given by the derived slope b and intercept a. The interaction parameters used here are: $g_{12} = 0.718 + 0.669u_2$; $g_{23} = 0.290 + 0.501v_2$ (values taken from Tkacik and Zeman[10]). The polymer–non-solvent interaction parameter g_{13} is used as a fitting parameter. The optimal value found was 3.6. The variables u_2 and v_2 are defined in the Appendix. O: experimental points; ——: calculated on the basis of Flory–Huggins interpretation

Table 1 Slopes of the LCP plots shown in *Figure 5*. Although deviations between experiments and theory are significant, the slopes agree reasonably well, when considering that in theory the polydispersity of the polymers is neglected

System	Experimental slope	Theoretical slope
PSf	1.04 ± 0.0025	1.002
PEI	1.02 ± 0.0068	1.003
PES	1.10 ± 0.018	1.04

dependent on the molar volumes. *Table 1* gives some of the slopes of the systems shown in *Figure 5*.

The errors in the values of the slope are quite small (0.24–1.6%), due to the large range of experimental points for which the relation applies. There is a significant difference between the experimental results and theory. In the theory the polydispersity of the polymer is neglected; since the polymers are quite polydisperse, this might explain the difference.

In principle, for these types of systems it should be possible to determine a whole cloudpoint curve by simply measuring two points (when the theoretical slope is assumed, even one cloudpoint would suffice). In practice, a few cloudpoints should be enough to check the validity of the relation. From these few measurements, immediate information is then found for the interaction parameters. From *Figure 11*, it appears that the experimental cloudpoints can be approached using independently measured interaction parameters g_{12} and g_{23}. In this figure, the polymer–non-solvent interaction parameter g_{13} is used as 'fitting parameter'. Tkacik and Zeman[10] assumed a value of 1.5 for this parameter by fitting their binodal on their experimental points. In *Figure 11* we find a value of 3.6, which is in better agreement with swelling data for the polymer in the non-solvent. This example shows that the LCP plot offers a better basis for such fitting procedures, simply because each experimental cloudpoint obtains the same weight in the fitting procedure.

Systems with crystallizable polymers

It appears that even for systems with crystallizable polymers, the liquid–liquid demixing points follow the LCP relation. When crystallization occurs predominantly, the cloudpoints deviate from the LCP line. The deviating points converge to a vertical asymptote (the crystallization point of the polymer in the solvent). This deviation might offer a quick method to see whether a certain system exhibits crystallization phenomena.

The proposed relation is only applicable under certain conditions. These conditions should always be considered before starting any interpretation. It appears that for applicability of the LCP relation, the swelling value of the polymer in the non-solvent must not be too large. For systems which exhibit crystallization, the crystallization phenomena might influence measurement of that swelling value of the polymer in the non-solvent that is due solely to liquid–liquid demixing.

The crystallization process is usually several orders of magnitude slower than liquid–liquid demixing. Investigation of the dependence of the cloudpoint curve on the cooling rate of the samples (when thermal demixing is used) is therefore a suitable tool after deviation from the LCP line showed that crystallization might be present.

CONCLUSIONS

A linearized cloudpoint correlation is proposed, which gives very good experimental results in membrane forming systems:

$$\ln \frac{\phi_1}{\phi_3} = b \ln \frac{\phi_2}{\phi_3} + a \qquad (4)$$

The correlation appears only valid for systems with one polymer. The plot gives straight experimental lines as long as two conditions are satisfied:

1. The polymer and the non-solvents should have poor interaction (high g_{13} interaction parameter, low swelling value of the polymer in the non-solvent).
2. The polymer should be completely miscible in the solvent in all possible concentrations; the same should apply to the solvent and the non-solvent.

The LCP relation only describes a cloudpoint curve caused by liquid–liquid demixing. Whenever other demixing (crystallization) effects play a role, a more or less sharp deviation of the LCP line is found.

The simplicity of the relation makes it useful for the quick evaluation of a ternary membrane forming system. Only two parameters have to be determined: the intercept of the line, and the slope. The slope is not completely unknown, because for membrane forming systems the slope of the line is always slightly larger than one. It should therefore be enough to determine a few cloudpoints (ideally only one, because the slope could be calculated) for characterization of the complete cloudpoint curve.

The relation has advantages for the estimation of the polymer–non-solvent interaction parameter from the cloudpoint curve itself: all experimental cloudpoints are weighed in the same way, therefore giving a better estimate of this interaction parameter. The relation could also be useful when investigating blends of immiscible polymers with a common solvent. The relation could, after measurement of a few cloudpoints in the dilute region, give fast information for these systems, over a broader concentration range.

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APPENDIX

Derivation of the slope (b) *and the intercept* (a)

The Flory–Huggins theory gives the free enthalpy of mixing for a ternary system as a function of the

concentrations:

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3$$

$$+ (v_1 g_{12} n_1 \phi_2 + v_1 g_{13} n_1 \phi_3 + v_2 g_{23} n_2 \phi_3)$$

(A1)

in which n_i and ϕ_i are, respectively, the number of moles and the volume fraction of component i. Component number 1 is the non-solvent, 2 is the solvent, and 3 is the polymer. The quantity v_i is the molar volume (m^3 mol^{-1}) of component i. The g_{ij}s are the Flory–Huggins interaction parameters which are a measure of the enthalpic interaction between components i and j. They are not usually constant, but functions of the concentrations of all the components present. In most cases, it is possible to assume that g_{ij} is only dependent on the concentrations of i and j, and not of the other component present. This means formally:

$$g_{12} = g_{12}(u_2); \quad u_2 = \frac{\phi_2}{\phi_1 + \phi_2}$$

$$g_{23} = g_{23}(v_2); \quad v_2 = \frac{\phi_2}{\phi_2 + \phi_3} \qquad \text{(A2)}$$

The interaction parameter g_{13} is assumed to be independent of the concentrations. The chemical potentials of mixing $\Delta \mu_i$ can now be derived by differentiating with respect to the number of moles of each component:

$$\frac{\Delta \mu_1}{v_1 RT} = \frac{\ln \phi_1}{v_1} - \frac{\phi_1}{v_1} - \frac{\phi_2}{v_2} - \frac{\phi_3}{v_3} + \frac{1}{v_1}$$

$$+ (g_{12}\phi_2 + g_{13}\phi_3)(1 - \phi_1)$$

$$- g_{23}\phi_2\phi_3 - \phi_2 g'_{12}$$

$$\frac{\Delta \mu_2}{v_2 RT} = \frac{\ln \phi_2}{v_2} - \frac{\phi_1}{v_1} - \frac{\phi_2}{v_2} - \frac{\phi_3}{v_3} + \frac{1}{v_2} \qquad \text{(A3)}$$

$$+ (g_{12}\phi_1 + g_{23}\phi_3)(1 - \phi_2)$$

$$- g_{13}\phi_1\phi_3 + \phi_1 g'_{12} + \phi_3 g'_{23}$$

$$\frac{\Delta \mu_3}{v_3 RT} = \frac{\ln \phi_3}{v_3} - \frac{\phi_1}{v_1} - \frac{\phi_2}{v_2} - \frac{\phi_3}{v_3} + \frac{1}{v_3}$$

$$+ (g_{23}\phi_2 + g_{13}\phi_1)(1 - \phi_3)$$
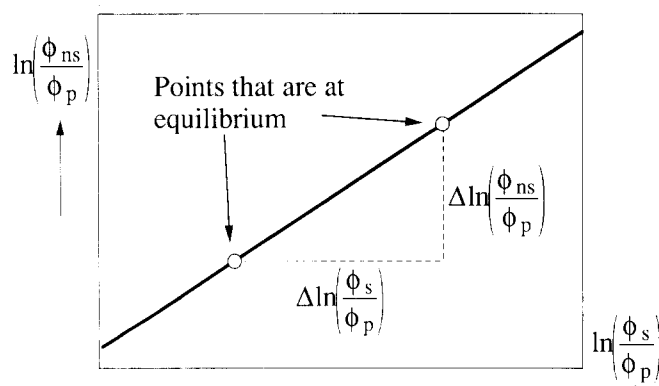
$$- g_{12}\phi_1\phi_2 - \phi_2 g'_{23}$$

Figure A1 LCP line on which two points are located which are in equilibrium with one another. The chemical potentials of all components in the two phases must be equal

The derivatives of the composition dependent interaction parameters g'_{ij} are defined as:

$$g'_{12} = u_2(1 - u_2)\left(\frac{\partial g_{12}}{\partial u_2}\right); \quad g'_{23} = v_2(1 - v_2)\left(\frac{\partial g_{23}}{\partial v_2}\right) \quad \text{(A4)}$$

Two linear combinations of the chemical potentials are calculated. The following two relations result when the logarithmic terms are isolated at the left-hand sides of the equal signs:

$$\frac{\ln\left(\dfrac{\phi_1}{\phi_2}\right)}{v_1 - v_2} = \left\{\frac{\Delta\mu_1 - \Delta\mu_2}{(v_1 - v_2)RT}\right\} + \sum_1^3 \frac{\phi_i}{v_i}$$

$$- \frac{1}{v_1 - v_2}\{g_{12}(v_1\phi_2(1 - \phi_1) - v_2\phi_1(1 - \phi_2))$$

$$- g'_{12}(v_1\phi_2 + v_2\phi_1)$$

$$+ g_{13}(v_1\phi_3(1 - \phi_1) + v_2\phi_1\phi_3)$$

$$+ g_{23}(-v_1\phi_2\phi_3 - v_2\phi_3(1 - \phi_2)) - g'_{23}v_2\phi_3\}$$

(A5)

$$\frac{\ln\left(\dfrac{\phi_3}{\phi_2}\right)}{v_3 - v_2} = \left\{\frac{\Delta\mu_3 - \Delta\mu_2}{(v_3 - v_2)RT}\right\} + \sum_1^3 \frac{\phi_i}{v_i}$$

$$- \frac{1}{v_3 - v_2}\{g_{23}(v_3\phi_2(1 - \phi_3) - v_2\phi_3(1 - \phi_2))$$

$$- g'_{23}(v_3\phi_2 + v_2\phi_3)$$

$$+ g_{13}(v_1\phi_3(1 - \phi_1) + v_2\phi_1\phi_3)$$

$$+ g_{12}(-v_3\phi_2\phi_1 - v_2\phi_1(1 - \phi_2)) - g'_{12}v_2\phi_1\}$$

(A6)

From these expressions, it follows by subtracting the equations that:

$$\frac{1}{v_1 - v_2}\ln\frac{\phi_1}{\phi_2} - \frac{1}{v_3 - v_2}\ln\frac{\phi_3}{\phi_2} = \left\{\frac{\Delta\mu_1 - \Delta\mu_2}{(v_1 - v_2)RT} - \frac{\Delta\mu_3 - \Delta\mu_2}{(v_3 - v_2)RT}\right\}$$

$$+ (g_{12} + g'_{12})(\alpha\phi_1 + \beta_1\phi_2)$$

$$+ g_{13}(\beta_1\phi_3 - \beta_3\phi_1)$$

$$+ (g_{23} + g'_{23})(\alpha\phi_3 + \beta_3\phi_2)$$

(A7)

in which:

$$b = \frac{v_3 - v_1}{v_3 - v_2}; \quad \alpha = \frac{v_2}{v_3 - v_2}\left(\frac{b}{b - 1}\right); \quad \beta_1 = \frac{v_1}{v_1 - v_2}; \quad \beta_3 = \frac{v_3}{v_3 - v_2}$$

(A8)

For two compositions in equilibrium with each other, the chemical potential of each component in one phase must be equal to the chemical potential in the other phase:

$$\Delta\mu_i^{\text{one phase}} = \Delta\mu_i^{\text{other phase}} \quad \text{for all } i\text{s} \qquad \text{(A9)}$$

This, then, also applies to a linear combination of these chemical potentials. When the difference over the two phases is considered, the difference of a linear combination of the chemical potentials over the two phases is zero:

$$\left\{\frac{\Delta\mu_1 - \Delta\mu_2}{(v_1 - v_2)RT} - \frac{\Delta\mu_3 - \Delta\mu_2}{(v_3 - v_2)RT}\right\}^{\text{one phase}} = \left\{\frac{\Delta\mu_1 - \Delta\mu_2}{(v_1 - v_2)RT} - \frac{\Delta\mu_3 - \Delta\mu_2}{(v_3 - v_2)RT}\right\}^{\text{other phase}}$$

(A10)

From equation (A7) we obtain with this:

$$\Delta\left\{\frac{1}{v_1-v_2}\ln\frac{\phi_1}{\phi_2}-\frac{1}{v_3-v_2}\ln\frac{\phi_3}{\phi_2}\right\}=\Delta\{(g_{12}+g'_{12})(\alpha\phi_1+\beta_1\phi_2)$$
$$+g_{13}(\beta_1\phi_3-\beta_3\phi_1)$$
$$+(g_{12}+g'_{12})(\alpha\phi_3+\beta_3\phi_2)\}$$

$$(A11)$$

in which Δ indicates the difference of the quantity between brackets over the two phases in equilibrium. Multiplication with a factor v_1-v_2, and rearrangement of both sides of the equation, gives:

$$\Delta\left\{\ln\frac{\phi_1}{\phi_3}-b\ln\frac{\phi_2}{\phi_3}\right\}=\Delta\{(g_{12}+g'_{12})(-v_2b\phi_1+v_1\phi_2)$$
$$+g_{13}(v_1\phi_3-v_3(1-b)\phi_1)$$
$$+(g_{12}+g'_{12})(-v_2b\phi_3+v_3(1-b)\phi_2)\}$$

$$(A12)$$

in which:

$$b=\frac{v_1-v_3}{v_2-v_3}\qquad(A13)$$

As we can see in practice that the LCP plot gives a straight line, apparently the difference term at the right-hand side of the equal sign is zero. If this difference were not zero, we would not obtain a straight LCP line.

The difference over the two phases in equilibrium of the quantity in equation (A11):

$$(g_{12}+g'_{12})(-v_2b\phi_1+v_1\phi_2)+g_{13}(v_1\phi_3-v_3(1-b)\phi_1)$$
$$+(g_{12}+g'_{12})(-v_2b\phi_3+v_3(1-b)\phi_2)$$

$$(A14)$$

must be zero. This indicates that the quantity itself must be constant over the LCP line.

This can be clarified by considering some line, described by:

$$y=bx+a\qquad(A15)$$

Rewriting this to:

$$y-bx=a\qquad(A16)$$

gives a formula comparable to (A11):

$$\Delta(y-bx)=\Delta a\qquad(A17)$$

For each point, it follows now that the parameter a must be constant. Its value can be evaluated by not taking the difference, but the sum over the two phases:

$$\overset{\text{two phases}}{\sum}(y-bx)=\overset{\text{two phases}}{\sum}a\qquad(A18)$$

The value of a is the part of equation (A17) on the right-hand side of the equal sign, divided by 2. This is then also applied to equation (A11):

$$\overset{\text{two phases}}{\sum}\left\{\ln\frac{\phi_1}{\phi_3}-b\ln\frac{\phi_2}{\phi_3}\right\}=\overset{\text{two phases}}{\sum}\{(g_{12}+g'_{12})(-v_2b\phi_1+v_1\phi_2)$$
$$+g_{13}(v_1\phi_3-v_3(1-b)\phi_1)$$
$$+(g_{12}+g'_{12})(-v_2b\phi_3+v_3(1-b)\phi_2)\}$$

$$(A19)$$

It appears that the intercept a can be written out as:

$$a=\tfrac{1}{2}\{(g_{12}+g'_{12})(-v_2b\phi_1+v_1\phi_2)$$
$$+g_{13}(v_1\phi_3-v_3(1-b)\phi_1)$$
$$+(g_{12}+g'_{12})(-v_2b\phi_3+v_3(1-b)\phi_2)\}\quad(A20)$$

which is an explicit relation for the intercept a in the interaction parameters and the molar volumes.

It should be noted that if the enthalpic parts (the terms with the g_{ij}s) of the chemical potentials [equations (A3)] were replaced by one single constant for each chemical potential, the LCP line would immediately follow from this Flory–Huggins interpretation.