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Considerations and restrictions on the theoretical validity of the linearized cloudpoint correlation

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The linearized cloudpoint curve correlation presented by Boom et al. [*Polymer*, 1993, **34**, 2348] is revised. Boundaries for the validity of the linearized cloudpoint correlation are given for which an interpretation from the Flory–Huggins theory is possible. The distinction between liquid–liquid and solid–liquid demixing by this correlation must also be subjected to some constraints, although the slope in the correlation still offers a good way to distinguish between solid–liquid and liquid–liquid demixing. The statement, however, that concentration-dependent interaction parameters can be derived from this correlation must be rejected. The empirical rule found by Li et al. [*Desalination*, 1987, **62**, 7955] can be rationalized on the basis of the LCC correlation. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Phase behaviour of ternary polymer solutions can be probed by cloudpoint measurements. Either a certain amount of non-solvent is added to a polymer solution until turbidity sets in or the temperature of a polymer solution is varied until phase separation occurs. These phenomena are detectable by turbidity measurements or a heatflux (e.g. DSC scans).

Cloudpoint curves obtained for polymer solutions were recently rationalized on the basis of linearized cloudpoint curves by Boom et al.[1]. Other correlations were given by Li et al. [2] (for compositions away from the critical point) and Craubner [3] (for very dilute polymer solutions). The potential of the linearized cloudpoint curve (LCC) correlation was that it could be derived directly from the modified Flory–Huggins theory for ternary solutions [4,5]. Such a correlation can also be used to yield quick information about the thermodynamics of ternary systems which can be advantageous in, e.g. scanning potential membrane-forming systems.

In the present paper, three main topics are considered: restrictions of the LCC correlation, comparison with Li's relations and applicability of the LCC correlation to distinguish between liquid–liquid and solid–liquid demixing.

The validity of the linearized cloudpoint correlation is verified by theoretically deriving the phase behaviour for certain input parameters to see if the LCC approach is valid over the entire composition range. It will be shown that the LCC correlation is subjected to some constraints. It is of great importance that users [6] of this powerful correlation know what these constraints are and how this correlation should be used. The influence of polydispersity on the phase behaviour is small for ternary systems consisting of a polymer, solvent and non-solvent, and is therefore not considered here. For systems with two polymers, this effect can be larger. The influence of polarity on the different components is incorporated using concentration-dependent interaction parameters.

The discrimination between solid–liquid demixing and liquid–liquid demixing can still be obtained from the LCC correlation under certain circumstances. Different parameters are discussed which are important for this discrimination.

VERIFICATION OF THE LINEAR CLOUDPOINT CURVE CORRELATION

The linearized cloudpoint curve correlation [equation (1)] [1] expresses a linear relationship between the relative amount of non-solvent (to polymer ratio) needed to give rise to phase separation for a certain relative amount of solvent (to polymer ratio). ϕ_1, ϕ_2 and ϕ_3 denote, respectively, the volume fractions of non-solvent, solvent and polymer.

$$\ln\frac{\phi_1}{\phi_3} = b\ln\frac{\phi_2}{\phi_3} + a \tag{1}$$

The slope b, given in equation (2), depends only on the molar volumes $\bar{\nu}_i$ of the different components. The intercept a, as derived by Boom et al. [1], given in equation (3), is dependent on the interaction parameters g_{ij} between the different components i and j, and the molar volume fractions ϕ_i.

$$b = \frac{\bar{\nu}_1 - \bar{\nu}_3}{\bar{\nu}_2 - \bar{\nu}_3} \tag{2}$$

$$\begin{aligned} a = 0.5((g_{12} + g_{12}{}')(-\bar{\nu}_2 b\phi_1 + \bar{\nu}_1\phi_2) \\ + g_{13}(\bar{\nu}_1\phi_3 - \bar{\nu}_3(1-b)\phi_1) \\ + (g_{12} + g_{12}{}')(-\bar{\nu}_2 b\phi_3 + \bar{\nu}_3(1-b)\phi_2))) \end{aligned} \tag{3}$$

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Equation (3), however, is erroneous. The correct expression [equation (4)] is derived in Appendix A.

$$\begin{aligned} a = &(g_{12} + g_{12}')(-\bar{\nu}_2 b\phi_1 + \bar{\nu}_1\phi_2) \\ &+ g_{13}(\bar{\nu}_1\phi_3 - \bar{\nu}_3(1-b)\phi_1) \\ &+ (g_{23} + g_{23}')(-\bar{\nu}_2 b\phi_3 + \bar{\nu}_3(1-b)\phi_2)) \end{aligned} \qquad (4)$$

with

$$g_{12}' = u_2(1-u_2)\frac{\partial g_{12}}{\partial u_2}$$

$$g_{23}' = \nu_2(1-\nu_2)\frac{\partial g_{23}}{\partial \nu_2}$$

$$u_2 = \frac{\phi_2}{(\phi_1 + \phi_2)}$$

$$\nu_2 = \frac{\phi_2}{(\phi_2 + \phi_3)}$$

The use of equation (3) will lead to a cloudpoint curve which is independent of the interaction between component 2 (solvent) and polymer. Small variations in the interaction parameter between component 2 and the polymer do not indeed influence the position of the cloudpoint curve, but in the case of component 2 being a non-solvent for the polymer, its influence must be taken into account.

The approach of this study is the opposite of that followed by Boom et al. [1]. Based on experiments, they suggested a linear correlation. In our approach, the starting point is a theoretical model. The use of this model will pose some limitations on the applicability of the correlation, but it will have a theoretical basis. As can be seen from equation (4), the intercept a depends on the composition of the two phases.

Assuming that the intercept is equal for both phases and that the intercept is constant for various polymer volume fractions [1], is therefore not straightforward and must be subjected to some constraints, this is vital to translate the Flory–Huggins relation to the LCC correlation. The validity criterium, used in this study, was defined by equation (5) and equation (6). The values in the criterium are arbitrarily chosen and define the deviation in a, which can be tolerated to obtain a linearized curve. The value of a must not only be similar for both equilibrium phases (polymer-poor and polymer-rich), but must not change dramatically for various polymer concentrations (*Figure 1*).

$$|a(\phi_3) - a(\phi_3 + \Delta\phi_3)| \leq 2 \qquad (5)$$

$$|(\phi_3^{\text{poor}}) - a(\phi_3^{\text{rich}})| \leq 2 \qquad (6)$$

The reason why the LCC correlation deviates from the experimentally determined cloudpoints lies in this assumption. These validity boundaries also explain why the LCC correlation is only valid according to Boom et al. [1] for systems with a cloudpoint curve close to the solvent–polymer axis. By considering validity boundaries for the LCC correlation, the concept can be extended to other systems, for which cloudpoint curves lay further away from the solvent–polymer axis.

Different combinations of interaction parameters and molar volumes were used to validate the theoretical intercept-equality for both the dilute and concentrated phase. It can be concluded that the linearized cloudpoint curve is valid around the critical point. For certain combinations of molar volumes and interaction parameters, the Flory–Huggins interpretation of the LCC correlation only holds for a very small polymer concentration region. No clear trends were found for the extent of the validity region as a function of the values of the interaction parameters.

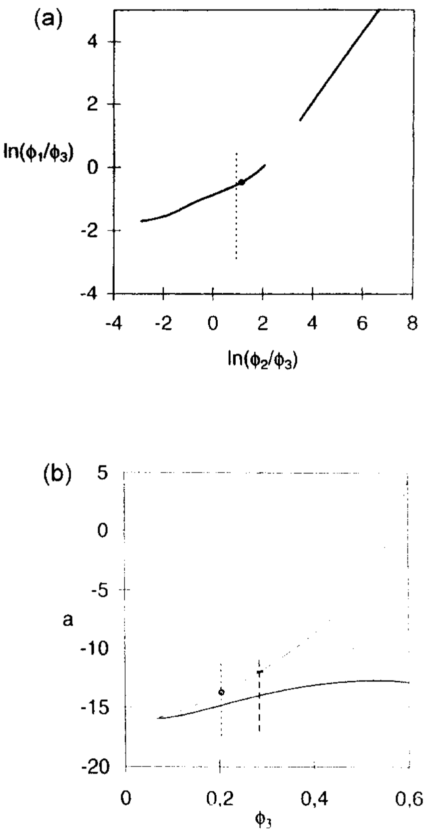

Figure 1 LCC plot (a) and deviations in intercept value a (b) as calculated according to the Flory–Huggins theory; input parameters: g_{12}: 1.0; g_{13}: 1.5; g_{23}: 0.5; $\bar{\nu}_1$: 20; $\bar{\nu}_2$: 100; $\bar{\nu}_3$: 20 000. The dotted line represents the boundary equation (5) and the striped line represents the boundary equation (6)

In most cases, the LCC correlation holds for the polymer-lean phase. As was shown by Kools et al. [7], the tieline relationship can be described by considering only the chemical potentials variation of solvent and non-solvent. The polymer concentration in the polymer-lean phase is so low that it does not influence the chemical potentials of the other components anymore. This can form the explanation for the linearity of the LCC relationship for the polymer-lean phase.

By changing the molar volumes of the different components in the mixture, the conclusion could be drawn that if the molar volumes of the three components lay more closely together, the validity region becomes smaller. This could explain why the LCC correlation does not hold for low molecular weight components in the mixture water–diethylether–methanol as presented by Boom et al. [1].

When the interaction parameters are known (concentration independent or dependent), calculations of the phase behaviour reveal that the intercept of the LCC relationship is not constant over the entire composition range. Therefore, it can be stated that the conclusion of Boom et al. [1] that interaction parameters 'as well as' their concentration dependence can be obtained from LCC relationships must be questioned. The first is still true, but the latter is not valid. The example given by Boom to extract a constant interaction parameter g_{13} in the system

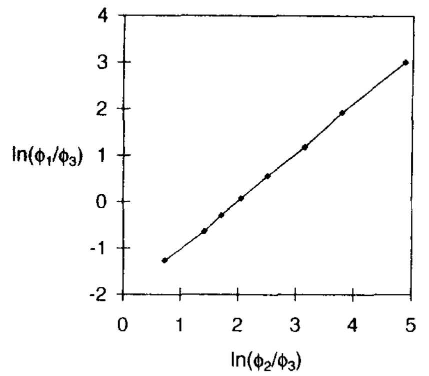

Figure 2 Cloudpoint curve for the system polyethersulfone–*N*-methylpyrrolidone–water: experimental results [8]

water–*N*-methylpyrrolidone–polyethersulfone on the basis of cloudpoint curves as presented by Tkacik and Zeman [8] leads to the value of 2.5 using the corrected intercept relation (*Figure 2*).

COMPARISON BETWEEN THE CORRELATION OF LI AND LCC CORRELATION

In an earlier published paper by Li et al. [2], an empirical rule for cloudpoint curves was given for the membrane-forming system polysulfone–N,N-dimethylacetamide–water [equation (4)]. This correlation is similar to the LCC correlation for b values approaching 1, as elaborated on in Appendix B. As such, Li's equation is a particular case of the LCC correlation. This situation is encountered in many membrane-forming systems.

$$\frac{\phi_1}{\phi_2} = \beta \tag{7}$$

with

$$\beta = \exp(a)$$

The cloudpoint data, as given by Li et al. [2], are represented in a ternary phase diagram (*Figure 3a*), according to both Li's relation (*Figure 3b*) and the LCC correlation (*Figure 3c*). The constant ratio between non-solvent and solvent can thus be derived directly from the Flory–Huggins theory for reasonable polymer concentrations. For the given example, a value of β of 0.042 was found. The value derived from the Flory–Huggins theory also varies around this value.

THE DIFFERENTIATION BETWEEN LIQUID–LIQUID AND SOLID–LIQUID DEMIXING PHENOMENA

The conclusion of Boom et al. [1] that the LCC correlation can be used for the distinction between two types of demixing, i.e. liquid–liquid (l–l) and solid–liquid (s–l) demixing, must be handled with some care. The position of the liquidus line (s–l) strongly depends on the ratio of the molar volumes of the different components involved, the different interaction parameters and the crystallizability of the polymer (melting point as well as the heat of fusion) expressed in parameter A in equation (8). S–l demixing in ternary mixtures can be described [9–11] by equation (8).

$$A = \frac{\bar{v}_1}{\bar{v}_3}\ln\phi_3 + \frac{\bar{v}_1}{\bar{v}_3}(1-\phi_3) - \phi_1 - \frac{\bar{v}_1}{\bar{v}_2}\phi_2 + \left(g_{13}\phi_1 + \frac{\bar{v}_1}{\bar{v}_2}g_{23}\phi_2\right)(1-\phi_3) - g_{12}\phi_1\phi_2 \tag{8}$$

$$A = \left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T^0_{\mathrm{m}}}\right)\frac{\Delta H_{\mathrm{m}}}{R}\frac{\bar{v}_1}{\bar{v}_{\mathrm{u}}} \tag{9}$$

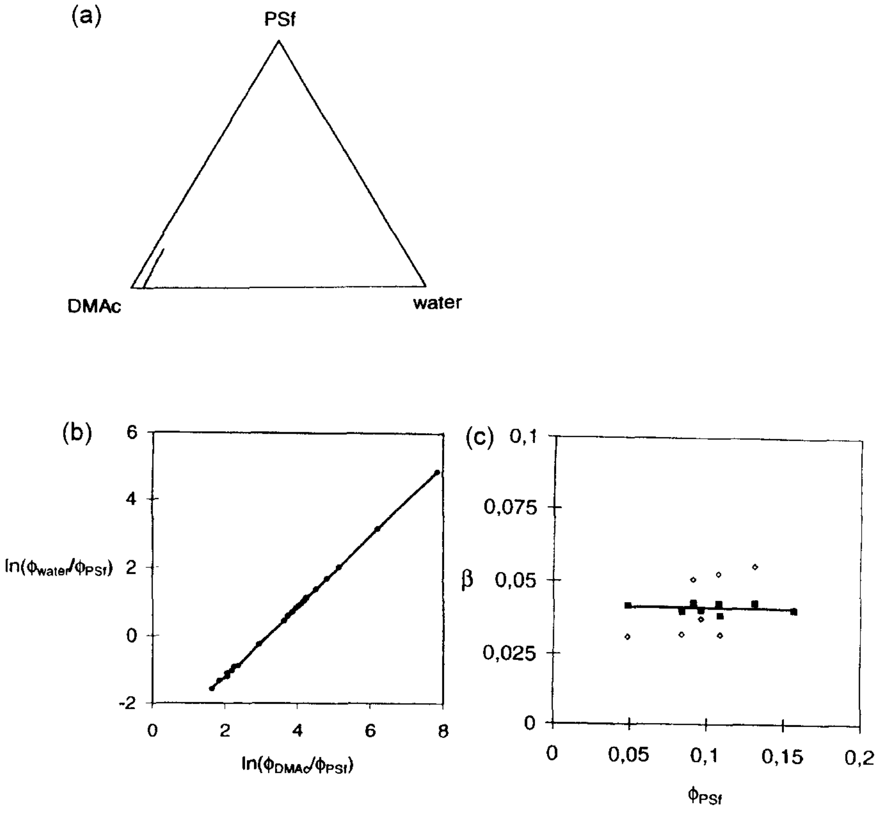

Figure 3 Cloudpoints for the system polysulfone–N,N-dimethylacetamide–water as measured by Li et al. [2], at 20°C, plotted (a) in a ternary phase diagram, according to (b) the LCC correlation and (c) Li's relation (theory and experiment)

with $\bar{\nu}_u$ equal to the molar volume of one monomer unit of the polymer.

The parameters for the phase transitions are the interaction parameters, molar volumes and A. All these parameters have an influence on the phase behaviour of the ternary system. It was derived by Burghardt et al. [12] that the melting point depression depends strongly on the molar volume of the diluent. Equation (9) gives the melting point depression according to Burghardt in a ternary system without considering any interaction parameters, $\bar{\nu}_2$ equal to $\bar{\nu}_u$ and for $\frac{\bar{\nu}_1}{\bar{\nu}_3}$ values approaching zero.

$$\phi_3 = 1 - \left(\frac{1}{T_m} - \frac{1}{T_m^0}\right)\frac{\Delta H_m}{R}\frac{\left(1 - \frac{\phi_1}{\phi_2}\right)}{\left(1 + \frac{\bar{\nu}_2\phi_1}{\bar{\nu}_1\phi_2}\right)} \qquad (10)$$

It is clear that when the ratio between non-solvent and solvent becomes smaller, s–l demixing will occur at lower polymer concentrations when the non-solvent concentration increases. In most membrane formation systems, the molar volume of the non-solvent is smaller than the solvent. (This is, however, not always as claimed by Boom et al. [1].) Especially for similar molar volumes of solvent and non-solvent, the liquidus line can resemble the polymer-rich side of the binodal. Looking at the triangular phase diagram, erroneous conclusions can be drawn. If the LCC correlation is used, the distinction between the two mechanisms is improved.

The influence of the various interaction parameters was given by van de Witte [11]. When the interaction parameter between non-solvent and polymer increases, the liquidus will move towards the solvent–polymer axis. The decrease of the solvent–polymer interaction parameter will have a similar effect. This change is more pronounced when compared to its effect on l–l demixing.

Several liquidus lines were calculated for various molar volume ratios and different crystallizabilities. Expressing these liquidi in a LCC plot, the curves are in most cases non-linear and the LCC approach can be used to reveal the demixing mechanism. From calculations to determine the l–l miscibility gap, the shape of the deviation from the linearized cloudpoint curve always turned out to be positive [e.g. the calculated curve has a higher value of $\ln(\phi_1/\phi_3)$ compared to a linear relationship], as represented in *Figure 1a*. For a large number of input parameters, although not always, the deviation of the s–l demixing behaviour from a linear correlation is negative [lower values of $\ln(\phi_1/\phi_3)$ compared to a linear relationship] (*Figure 4*). Therefore, the authors state that the LCC approach can still be used to determine whether solid–liquid or liquid–liquid demixing prevails in cloudpoint experiments, even if the constraints posed by theory are not met.

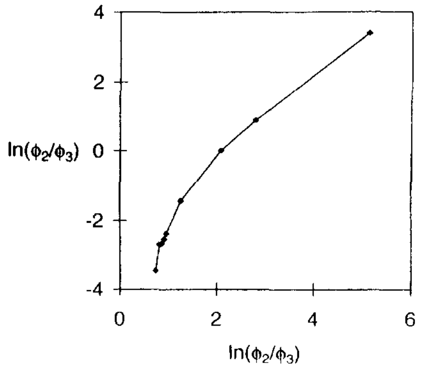

Figure 4 Schematic representation of LCC curve deviations for solid–liquid demixing systems

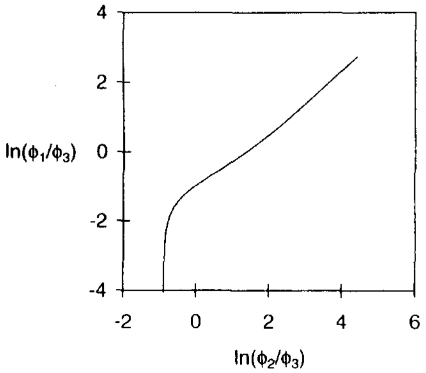

Figure 5 Cloudpoint curves for poly(dimethylphenylene oxide)–trichloroethylene–methanol (data from Ref. [13])

For the system poly-(dimethyl phenylene oxide)–trichloroethylene–methanol–octanol mixtures [13], it is assumed, although not explicitly, that no solid–liquid demixing occurs at low concentrations (*Figure 5*). However, the liquidus represented in an LCC plot is identical to that given by Boom et al. [1]. In such cases, care must be taken in interpreting the LCC correlations. Not only must the correlation be linear, but also the slope must correspond to the theoretical value of b, especially at low polymer concentrations. From the slope of the curves, 1.21 compared to 1.00, it can be derived that in the mentioned example, and also in the case of low polymer concentrations, solid–liquid demixing is responsible for phase separation.

If on the basis of the appearance of the curve (linearity and slope) no distinction can be made between solid and liquid–liquid demixing, and when all parameters are roughly known, these two phenomena can still be distinguished. However, for some cases, the distinction between l–l and s–l cannot be made by the correlation. In these cases, the time dependence of the demixing process can still reveal the nature of the demixing process as well as DSC measurements of the polymer solution.

CONCLUSIONS

Close to the critical point, the LCC correlation was directly derived from the Flory–Huggins theory. Further away from the critical point, this relation does not hold anymore. The theoretical validity region for the LCC approach becomes smaller for molar volumes closer together. The example used by Boom et al. [1] for the low molecular weight components can therefore still be analysed by the LCC approach, but in a smaller composition range around the critical point. However, based on the experimental cloudpoint curves, a remarkable linear relationship is found which cannot be rationalized directly by the Flory–Huggins theory. For most systems, concentration-dependent interaction parameters must be used to describe the thermodynamics of ternary systems. When the interaction parameters are known (concentration dependent and concentration independent), calculations of the phase behaviour reveal that the intercept of the LCC relationship is not a constant over the entire composition range. Therefore, it can be stated that the conclusion of Boom et al. [1], that interaction parameters 'as well as' their concentration dependence can be obtained from LCC relationships, must be rejected.

Li's empirical relation can be regarded as a particular case of the LCC correlation.

From the thermodynamics of semi-crystalline polymer solutions, it can be derived that the distinction between liquid–liquid and solid–liquid demixing can still often be made by the LCC approach on the basis of the appearance of the correleation. Some ratios between the molar volumes, however, can give rise to a position of the liquidus line resembling 1–1 demixing. In these cases, the LCC concept must be rejected. A rough idea about the interaction parameters can exclude the possibility of such case.

APPENDIX A: DERIVATION OF THE LCC CORRELATION

The Flory–Huggins theory describes the free enthalpy of mixing ΔG_m for a ternary system as a function of the volume fractions ϕ_i and mole fractions n_i of the different components i. Component 1 represents the non-solvent, 2 the solvent and 3 the polymer.

$$\frac{\Delta G_m}{RT}=n_1\ln\phi_1+n_2\ln\phi_2+n_3\ln\phi_3+\bar{\nu}_1g_{12}n_1\phi_2 + \bar{\nu}_1g_{13}n_1\phi_3+\bar{\nu}_2g_{23}n_2\phi_3 \qquad \text{(A1)}$$

The chemical potentials of mixing $\Delta\mu_i$ of the individual components i are derived by differentiating with respect to the number of moles of those components.

$$\frac{\Delta\mu_1}{\bar{\nu}_1RT}=\frac{\ln\phi_1}{\bar{\nu}_1}-\frac{\phi_1}{\bar{\nu}_1}-\frac{\phi_2}{\bar{\nu}_2}-\frac{\phi_3}{\bar{\nu}_3}+\frac{1}{\bar{\nu}_1} + (g_{12}\phi_2+g_{13}\phi_3)(1-\phi_1)-g_{23}\phi_2\phi_3-g_{12}'\phi_2 \qquad \text{(A2)}$$

$$\frac{\Delta\mu_2}{\bar{\nu}_2RT}=\frac{\ln\phi_2}{\bar{\nu}_2}-\frac{\phi_1}{\bar{\nu}_1}-\frac{\phi_2}{\bar{\nu}_2}-\frac{\phi_3}{\bar{\nu}_3}+\frac{1}{\bar{\nu}_2} + (g_{12}\phi_1+g_{23}\phi_3)(1-\phi_2)-g_{13}\phi_1\phi_3+g_{12}'\phi_1 + g_{23}'\phi_3 \qquad \text{(A3)}$$

$$\frac{\Delta\mu_3}{\bar{\nu}_3RT}=\frac{\ln\phi_3}{\bar{\nu}_3}-\frac{\phi_1}{\bar{\nu}_1}-\frac{\phi_2}{\bar{\nu}_2}-\frac{\phi_3}{\bar{\nu}_3}+\frac{1}{\bar{\nu}_3} + (g_{13}\phi_1+g_{23}\phi_2)(1-\phi_3)-g_{12}\phi_1\phi_2-g_{23}'\phi_2 \qquad \text{(A4)}$$

To extract~ln $\left(\frac{\phi_1}{\phi_3}\right)$ and~ln $\left(\frac{\phi_3}{\phi_2}\right)$ from this set of equations (A2–A4), two linear combinations, $\frac{\Delta\mu_1-\Delta\mu_3}{RT}$ and $\frac{\Delta\mu_3-\Delta\mu_2}{RT}$ can be calculated. The logarithmic terms are grouped at the left side of the equality sign. Unlike Boom, no large rearrangemnets are needed.

$$\frac{\ln\frac{\phi_1}{\phi_3}}{\bar{\nu}_1-\bar{\nu}_3}=\{\frac{\Delta\mu_1-\Delta\mu_3}{(\bar{\nu}_1-\bar{\nu}_3)RT}\}+\sum_{i=1}^{3}\frac{\phi_i}{\bar{\nu}_i}-\frac{1}{(\bar{\nu}_1-\bar{\nu}_3)} \times\{g_{12}(\bar{\nu}_1\phi_2(1-\phi_1)+\bar{\nu}_3\phi_1\phi_2) + g_{13}(\nu_1\phi_3(1-\phi_1)-\bar{\nu}_3\phi_1(1-\phi_3)) + g_{23}(-\bar{\nu}_1\phi_2\phi_3)-\bar{\nu}_3\phi_2(1-\phi_3)) - g_{12}'\bar{\nu}_1\phi_2-g_{23}'\phi_2\} \qquad \text{(A5)}$$

$$\frac{\ln\frac{\phi_3}{\phi_2}}{\bar{\nu}_3-\bar{\nu}_2}=\{\frac{\Delta\mu_3-\Delta\mu_2}{(\bar{\nu}_3-\bar{\nu}_2)RT}\}+\sum_{i=1}^{3}\frac{\phi_i}{\bar{\nu}_i}-\frac{1}{(\bar{\nu}_3-\bar{\nu}_2)} \times\{g_{23}(\bar{\nu}_3\phi_2(1-\phi_3)-\bar{\nu}_2\phi_3(1-\phi_2)) - g_{23}'(\bar{\nu}_3\phi_2+\bar{\nu}_2\phi_3)+g_{13}(\bar{\nu}_1\phi_3(1-\phi_1) + \bar{\nu}_2\phi_1\phi_3)+g_{12}(-\bar{\nu}_3\phi_2\phi_1-\bar{\nu}_2\phi_1(1-\phi_2)) - g_{12}'\bar{\nu}_2\phi_1\} \qquad \text{(A6)}$$

Substracting these two equations and multiplying by $(v_1 - v_3)$ gives the following relation:

$$\ln\frac{\phi_1}{\phi_3}-\frac{\bar{\nu}_1-\bar{\nu}_3}{\bar{\nu}_2-\bar{\nu}_3}\ln\frac{\phi_2}{\phi_3}=\bar{\nu}_1-\bar{\nu}_3\{\frac{\Delta\mu_1-\Delta\mu_3}{(\bar{\nu}_1-\bar{\nu}_3)RT}-\frac{\Delta\mu_3-\Delta\mu_2}{(\bar{\nu}_3-\bar{\nu}_2)RT}\} + (g_{12}+g_{12}')\left(-\bar{\nu}_2\frac{\bar{\nu}_1-\bar{\nu}_3}{\bar{\nu}_2-\bar{\nu}_3}\phi_1+\bar{\nu}_1\phi_1\right) + g_{13}\left(\bar{\nu}_1\phi_3-\bar{\nu}_3\left(1-\frac{\bar{\nu}_1-\bar{\nu}_3}{\bar{\nu}_2-\bar{\nu}_3}\right)\phi_1\right) + (g_{23}+g_{23}')\left(-\bar{\nu}_2\frac{\bar{\nu}_1-\bar{\nu}_3}{\bar{\nu}_2-\bar{\nu}_3}\phi_3+\bar{\nu}_3\left(1-\frac{\bar{\nu}_1-\bar{\nu}_3}{\bar{\nu}_2-\bar{\nu}_3}\right)\phi_2\right) \qquad \text{(A7)}$$

Two variables can be defined to transform equation (A7) into equation (A8).

$$\ln\frac{\phi_1}{\phi_3}-b\ln\frac{\phi_2}{\phi_3}=\bar{\nu}_1-\bar{\nu}_3\{\frac{\Delta\mu_1-\Delta\mu_3}{(\bar{\nu}_1-\bar{\nu}_3)RT}-\frac{\Delta\mu_3-\Delta\mu_2}{(\bar{\nu}_3-\bar{\nu}_2)RT}\}+a \qquad \text{(A8)}$$

$$a=(g_{12}+g_{12}')(\bar{\nu}_2b\phi_1+\bar{\nu}_1\phi_2)+g_{13}(\bar{\nu}_1\phi_3-\bar{\nu}_3(1-b)\phi_1) + (g_{23}+g_{23}')(-\bar{\nu}_2b\phi_3+\bar{\nu}_3(1-b)\phi_2)) \qquad \text{(A9)}$$

$$b=\frac{\bar{\nu}_1-\bar{\nu}_3}{\bar{\nu}_2-\bar{\nu}_3} \qquad \text{(A10)}$$

At the binodal, two phases are in equilibrium, having similar chemical potentials for every component expressed in the following relationship.

$$\Delta\mu_i^{\text{onephase}}=\Delta\mu_i^{\text{otherphase}} \qquad \text{(A11)}$$

This relationship also holds for linear combinations of these chemical potentials.

$$\{\frac{\Delta\mu_1-\Delta\mu_3}{RT(\bar{\nu}_1-\bar{\nu}_3)}-\frac{\Delta\mu_3-\Delta\mu_2}{RT(\bar{\nu}_3-\bar{\nu}_2)}\}^{\text{onephase}} = \{\frac{\Delta\mu_1-\Delta\mu_3}{RT(\bar{\nu}_1-\bar{\nu}_3)}-\frac{\Delta\mu_3-\Delta\mu_2}{RT(\bar{\nu}_3-\bar{\nu}_2)}\}^{\text{otherphase}} \qquad \text{(A12)}$$

Substituting equation (A8) into equation (A12), and rearranging the terms so that all the logarithmic terms are at the left side of the equality sign, gives equation (A13).

$$\Delta\{\ln\frac{\phi_1}{\phi_3}-b\ln\frac{\phi_2}{\phi_3}\}=\Delta a \qquad \text{(A13)}$$

For a LCC correlation, a linear dependence is needed which is fulfilled if the right hand side of equation (A11) is zero. This constraint will form the boundaries of the applicability of the LLC concept. Unlike as stated by Boom et al. [1], no division by 2 is needed.

Table 1 Molar volumes and interaction parameters for the system water–N,N-dimethylacetamide–polysulfone according to Li et al. [2]

Parameter	
g_{12}	1.0
g_{23}	0.4
g_{13}	2.6
ϕ	18 cm^3
ϕ	93 cm^3
ϕ	21 000 cm^3
β	1.003
a	−3.1
b	0.42

The derived linear cloudpoint curve is thus given by equation (A14).

$$\ln\frac{\phi_1}{\phi_3} - b\ln\frac{\phi_2}{\phi_3} = a \qquad \text{(A14)}$$

APPENDIX B:

The relation of Li et al. [2], given in equation (B1), states that the ratio of the volume fractions of the non-solvent and solvent is a constant, β.

$$\frac{\phi_1}{\phi_2} = \beta \qquad \text{(B1)}$$

For b values approaching 1, the LCC relation [equation (A14)] can be rewritten into equation (B2).

$$a = \ln(\phi_1) - b\ln(\phi_2) - (1-b)\ln\phi_3 = \ln\frac{\phi_1}{(\phi_2)^b}$$
$$-(1-b)\ln\phi_3 \approx \ln\frac{\phi_1}{\phi_2} \qquad \text{(B2)}$$

This simplification can be made if condition (B3) is fulfilled.

$$\phi_3 \gg \exp\left(\frac{a}{1-b}\right) \qquad \text{(B3)}$$

For the system studied by Li et al. [2], the right hand term corresponds to very low values. The molar volumes and interaction parameters are summarized in *Table 1*.

β in the relation of Li et al. [2] can therefore be represented by equation (B4)

$$\beta = \exp(a) \qquad \text{(B4)}$$

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